Computational Micromechanics Analysis of Deformation and Damage Sensing in Carbon Nanotube Based Nanocomposites

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Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy in Engineering Mechanics

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March 29, 2016
Blacksburg, Virginia

Keywords: Carbon Nanotube, Nanocomposite, Piezoresistivity, Electron Hopping, Computational Micromechanics, Strain Sensing, Damage Sensing, Cohesive Zone, Interface Damage, Material Point Method

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ABSTRACT

The current state of the art in structural health monitoring is primarily reliant on sensing deformation of structures at discrete locations using sensors and detecting damage using techniques such as X-ray, microCT, acoustic emission, impedance methods etc., primarily employed at specified intervals of service life. There is a need to develop materials and structures with self-sensing capabilities such that deformation and damage state can be identified in-situ real time. In the current work, the inherent deformation and damage sensing capabilities of carbon nanotube (CNT) based nanocomposites are explored starting from the nanoscale electron hopping mechanism to effective macroscale piezoresistive response through finite elements based computational micromechanics techniques. The evolution of nanoscale conductive electron hopping pathways which leads to nanocomposite piezoresistivity is studied in detail along with its evolution under applied deformations. The nanoscale piezoresistive response is used to evaluate macroscale nanocomposite response by using analytical micromechanics methods. The effective piezoresistive response, obtained in terms of macroscale effective gauge factors, is shown to predict the experimentally obtained gauge factors published in the literature within reasonable tolerance. In addition, the effect of imperfect interface between the CNTs and the polymer matrix on the mechanical and piezoresistive properties is studied using coupled electromechanical cohesive zone modeling. It is observed that the interfacial separation and damage at the nanoscale leads to a larger nanocomposite irreversible piezoresistive response under monotonic and cyclic loading because of interfacial damage accumulation. As a sample application, the CNT-polymer nanocomposites are used as a binding medium for polycrystalline energetic materials where the nanocomposite binder piezoresistivity is exploited to provide inherent deformation and damage sensing. The nanocomposite binder medium is modeled using electromechanical cohesive zones with properties obtained through the Mori-Tanaka method allowing for different local CNT volume fractions and orientations. Finally, the traditional implementation
of Material Point Method (MPM) is extended for composite problems with large deformation (e.g. large strain nanocomposite sensors with elastomer matrix) allowing for interfacial discontinuities appropriately. Overall, the current work evaluates nanocomposite piezoresistivity using a multiscale modeling framework and emphasizes through a sample application that nanocomposite piezoresistivity can be exploited for inherent sensing in materials.
In memory of
Avi and Naani ji
Acknowledgments

I am grateful to Dr. Gary Seidel who served as my faculty advisor and Chair of my Ph.D. committee for his guidance through the course of my tenure as a doctoral student. It is because of his vision and support with the research presented herein and with my overall professional development that I have reached a point where I can present my work hoping that it will be well received. I am also grateful to my parents, Sangeeta and Vivekanand Chaurasia, and my fiance, Abhilasha Maurya, for bearing with me during this time and standing by me at every turn of the road. It was, in large part, their confidence in me which helped me feel ready for the challenges that I encountered along the way.

I would like to thank my Ph.D. committee members, Drs. Romesh Batra, Rakesh Kapania, Scott Case, Anne Staples and Mayuresh Patil for their valuable insights into the research undertaken and for ensuring I understand the fundamentals of mechanics and that they were followed during the solution process.

I would also like to acknowledge all of the colleagues I have collaborated with over the course of my doctoral research. I have learned a great deal working with Drs. Michael Philen, Eric Freeman, Francis Aviles, Andres Oliva and Xiang Ren. I also had a great time collaborating and working with Dr. Gustavo Dominguez-Rodriguez, Engin Sengezer, Krishna Talamadulpula and Stefan Povolny. In addition, I would like to thank Dr. Yumeng Li and Naveen Prakash for many fruitful conversations about some aspects of the research presented in the current work.

Finally, I would like to acknowledge my grandparents who defied the socio-economic structure of their time and had the vision to propel the family in a direction which enabled me to
pursue my passion. Without their incredible determination and hard work none of this would have been possible for me.
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Chapter 1

Introduction

While a large class of materials have been observed to be inherently multiscale in nature, modeling of such materials, coupling the appropriate scales and the evolution of properties across the scales, is not very well established. As a specific example, the ability to predict when and where damage will occur, and more importantly, how it will evolve from dispersed isolated instances into large cracks that cause discernible degradation in material properties and finally into complete material and structural failure remains an extremely important challenge in the mechanics community, especially in composite materials which are increasingly becoming a part of the civil infrastructure. Phenomenological models for when and where large scale or significant aggregation of damage will occur have been applied in single scale models and have had a profound impact on structural design, but have not been able to answer questions such as which direction a crack a will grow and why, nor can they discern why the crack formed where it did beyond a stochastic answer. This is largely because the answers to these questions are intimately tied to damage initiation and evolution at a number of subscales, and more importantly, how damage transitions from those subscales to larger scales. In the absence of sufficient experimental or computational modeling based description of local deformation, damage initiation and propagation at the subscales, it is difficult to understand the current deformation and damage state of the material. In some cases, the material or structure is inspected for signs of damage at the macroscale using visual inspection or some non-destructive evaluation to assess an effective state of the ma-
terial. However, these inspections are performed offline and disrupt the service cycle of the structure or component. In some other cases, the evaluation of material or structural state may not be possible or may not be cost effective which results in the material or structure being discarded after a preassigned service life.

It is anticipated that the recent push in exploring and developing multifunctional materials may help provide a better description of the strain and damage state of the material through coupled material response. For example, in nanostructured composite materials (e.g. carbon nanotube nanocomposites, fuzzy fiber laminates etc.), the origin of the damage and damage based variation in effective multifunctionality (e.g. piezoresistivity, i.e. the change in macroscale resistivity with applied strains) lies in the complex interactions at the nanoscale. In order to establish the connection between the local deformation and damage state at the subscales and the observed material or structural multifunctional response, a multiscale multiphysics computational modeling framework is needed. The development of multiscale models for multifunctional materials can not only lead to optimum sensor/sensing system designs, but also have the capacity to contribute to a fundamental shift in structural health monitoring (SHM) applications. At present SHM focuses primarily on the sensors and sensing systems for detecting instances and locations of damage through techniques such as X-ray, microCT, acoustic emission, lamb wave, impedance methods, etc., which only detect cracks at relatively large length scales (100\,\mu m and above). In contrast, the Digital Twin paradigm and virtual fleet proposals from NASA and the US Air Force aim at integrating ultra-high fidelity computational models with the vehicle health management system, maintenance history and all available historical and fleet data to mirror the life of its flying twin and enable unprecedented levels of safety and reliability, i.e. moving from detecting to detecting and prognosticating the remaining structural life or updated performance tolerances. It is anticipated that development of such prognosis systems will require the understanding of local deformation, damage initiation and evolution across several length scales down to the scale of smallest microstructural features. In conjunction with the understanding of deformation and damage mechanisms, a detailed understanding of their influence on the coupled multifunctional mechanisms will be key in exploiting material multifunctionalities for sensing applications.
The current modeling of multiscale multifunctional materials is generally developed using single scale models for predicting effective properties, and do not account for induced irreversible path dependent nonlinearities (e.g. damage, plasticity etc.) that may lead to evolution of microstructure, and hence multifunctionality, over time. It is anticipated that in order to achieve transformative developments in this novel class of materials a detailed understanding of upscaling of these properties from the finest scale of influence to the macroscale will be required. This is especially important since experiments for probing multifunctional response at smaller scales (microscale and lower) in-situ as the microstructure and corresponding material properties evolve are currently in development, are expensive, not universally available or do not exist. The need for such modeling tools is highlighted in the recently introduced Materials Genome Initiative [1] aimed at virtually exploring material prototypes for identification of the material system and architecture with application specific effective response. The initiative indicates that "Rapid advances in computational modeling and data exchange and more advanced algorithms for modeling materials behavior must be developed to supplement physical experiments." Such systems are likely to make use of some of the multifunctional capabilities which originate and propagate from subscales and are not readily accessible in current experimental capabilities.

1.1 CNT-Polymer Nanocomposites for SHM Applications

The potential use of carbon nanotube (CNT)-polymer nanocomposites in structural health monitoring (SHM) applications is an area of rapidly growing interest [2–9]. In much of the work to date, SHM capability is provided in the form of strain sensing obtained from changes in electrical resistivity observed at the macroscale under applied deformations (i.e. nanocomposite piezoresistivity) [3,6–8,10–20]. In some cases, nanocomposite strain sensing patches consisting of either single or multi-walled CNTs have been applied to test samples in much the same manner as conventional strain gauges [3, 4, 7, 8, 11, 12] in both quasi-static [3,7,12,13] and cyclic loading tests [4,8,11]. The nanocomposite patches were found
to have performed well, without any significant lag, and yielding gauge factors between 0.9 and 4.2 comparable to the commercially available (metallic) strain gauges with gauge factor of 2 [21]. As opposed to making nanocomposite strain sensing patches, others have tried to develop structural composites with embedded nanocomposite strain sensing [5, 6] e.g., CNTs grown on fibers or dispersed in the matrix of composites with observed gauge factors of around 1.5. In order to ascertain CNT orientation effects on nanocomposite piezoresistivity, Sengezer and Seidel [22, 23] dispersed aligned SWNTs in a blend of two different photopolymerizable monomers which consisted of urethane dimethacrylate (UDMA) and 1,6-hexanediol dimethacrylate (HDDMA). It was observed that the electrical resistance change of as-produced aligned nanocomposites subjected to cyclic tensile loading followed the applied deformation with no lag and the transverse piezoresistive response sensitivity surpassed the axial piezoresistive response.

Several experimental studies have attempted to characterize the piezoresistive response of CNT-polymer nanocomposites [11,12,19,24–28] and CNT doped fiber reinforced composite laminates [9, 29] under cyclic loading conditions. Ku-Herrera and Aviles [19] applied ten cycles of quasi-static cyclic tensile loading with about 1% maximum tensile strain on multi-walled CNT (MWCNT)-vinyl ester nanocomposite samples and observed close correlation between the applied strains and change in macroscale resistance. It was further observed that there is insignificant lag in the piezoresistive response for the small applied tensile strains. Additionally, they performed cyclic compressive tests with up to 10% maximum applied compressive strain and observed that the loading and unloading pathways for the effective piezoresistive response were different especially when subjected to larger compressive strains. Nofar et al. [24] applied up to 500 cycles of applied tensile strain on MWCNT-fiber glass-epoxy nanocomposites and observed that the residual change in nanocomposite resistance in the undeformed state increases with the number of strain cycles, indicating that the nanocomposite damage can be correlated to the change in macroscale resistance for CNT-polymer nanocomposites. Vega et al. [27] applied cyclic strains on single-walled CNT-epoxy nanocomposites with incrementally increasing maximum strain amplitude starting from 0.1% to about 3% tensile strain. They observed that the relative change in resistance increases with increasing strain amplitude in addition to irreversible piezoresistive response i.e. differ-
ences in loading/unloading paths. The authors attributed the observed response to interfacial separation phenomenon at the CNT-polymer interface. Thus, in addition to the studying the effect of evolving electron hopping pathways when subjected to monotonic loading, the current work explores the effect of cyclic loading on effective properties of CNT-polymer nanocomposites using the computational micromechanics framework developed. The study aims to understand the relationship between interfacial damage accumulation and the observed effective piezoresistive response for such nanocomposites.

In addition to strain sensing, CNT-polymer nanocomposites have been shown to be effective in damage detection [6, 9, 14, 27, 30–32]. Thostenson and Chou [31] fabricated [0/90]s carbon fiber epoxy composites with embedded CNTs and observed that the CNT network conductivity was highly sensitive to both damage initiation and accumulation. Gao et al. [9] premixed 0.5 wt% MWCNTs in EPON 862 epoxy resin and used vacuum assisted resin transfer molding (VARTM) to produce [0/90]2 cross-ply E-glass fiber composite laminates. Using quasi-static tension tests, the composite laminates were subjected to quasi static monotonically and cyclic loading to failure while simultaneously monitoring changes in the electrical resistance and taking acoustic emission data. Piezoresistive response outperformed acoustic emission measurements by not only detecting the onset of damage prior to noticeable effects in the stress strain response, i.e. measuring instances of new damage initiation, but also in being able to provide continuous assessment of the damage state between damage initiation events. Ku-Herrera et al. [30] characterized the piezoresistive behavior of MWCNT-vinyl ester polymer nanocomposites in tension and compression from the elastic up through the plastic regime and on to final failure. They observed that the piezoresistive response was able to delineate between the elastic, plastic, and fracture regimes of the nanocomposite sample loading. Such observations confirm the SHM potential of nanocomposites as strain, damage initiation, and damage state indicators. Yet in order to take full advantage of the SHM potential of CNT-polymer nanocomposites, it is necessary to understand the mechanisms behind strain and damage sensing, and therefore to understand the origin of the multifunctional properties of these nanocomposites.
1.2 Nanocomposite Piezoresistivity

The piezoresistive response observed in CNT-polymer nanocomposites is believed to originate due to physical effects at the nanoscale transitioning through the microscale network structure which evolves when the nanocomposite is subjected to applied deformation leading to change in macroscale resistance. At the nanoscale, the key physical effects that influence the observed macroscale piezoresistive response are 1) electron hopping (or quantum tunneling) [25, 32–38] and 2) inherent CNT piezoresistivity [39–44]. At the microscale, formation and disruption of conductive pathways due to the changing nanotube network in the matrix medium can lead to changes in observed macroscale response [32, 40]. Finally, initiation and evolution of damage at the subscales (nano, micro or macro scale) in the matrix, CNT medium or at the interface can lead to significant changes in effective macroscale properties [6,9,14,30–32].

Part of the current work is focused on modeling the effect of electron hopping on the piezoresistive response of single-walled CNT-epoxy nanocomposites. The electrical conductivity of nanocomposites is believed to be strongly influenced by the nanoscale effect of electron hopping or quantum tunneling [33, 38, 45, 46]. This effect allows for the transfer of electrons intra-tube or from one CNT to another, and is noted to be dependent on the separation distance between the tubes (or parts of the same tube) and on the properties of the material in between them [45]. The effective intertube resistivity (tunneling resistance) of CNT-polymer nanocomposites is dependent on 1) intrinsic nanotubes resistivity, 2) the potential barrier at the CNT-polymer interface [47] and 3) the hopping resistivity of the polymer layer in between the nanotubes. Simmon’s model [48] provides an effective theoretical assessment of the intertube resistance with a separating dielectric medium in between. The two key parameters in the model are the intertube distance and the electron hopping potential barrier (i.e. potential needed for the electron to hop) which represents the combination of the three factors mentioned above. Fuhrer et al. [49] reported crossed contact resistance of CNT-CNT (metallic and nonmetallic) to be in the range 100-400 kΩ which is comparable to the intertube resistance due to electron hopping for small intertube separation [25, 32–37] and is several order of magnitudes smaller than polymer resistance (≈ 10^{15}Ω). Other theoreti-
cal studies [50, 51] have predicted that the intertube resistance in direct contact can range from 100kΩ to 3.4MΩ. The electron hopping barrier potential (\( \lambda \)) depends on the type of CNT and the polymer matrix medium, with values typically between 0.05eV and 2.5eV for epoxy and other polymers [12, 25, 33–35, 38, 52, 53] from which the maximum electron hopping range is estimated to be between 1nm and 30nm. From a quantum mechanical point of view, the mechanisms of electron transfer through electron hopping and quantum tunneling are different [54]. Electron hopping refers to when an electron in a sufficiently high energy state, i.e. comparatively small potential barrier, hops over the electron hopping potential barrier. Whereas, quantum tunneling refers to an electron which is not in a high enough state of energy to jump across the potential barrier, but probabilistically tunnels through the potential barrier. For this study, the effective resistance that the electron has to overcome to hop/tunnel across the nanotubes is of interest rather than the actual mechanism of electron transfer. Hence the terms 'electron hopping' and 'quantum tunneling' will be used interchangeably throughout the current text.

The electron hopping effect, in conjunction with a given CNT dispersion, results in conductive paths between CNTs [38, 55, 56] believed to be the source of the extremely low volume fraction percolation (0.12-4.5% by wt) observed in nanocomposite electrical conductivity measurements [38, 57–63]. It is likely a combination of these effects, as well as some inherent piezoresistivity of the CNTs [64], which results in the strain sensing and damage detection capabilities of CNT-polymer nanocomposites needed for SHM applications, and which therefore should be captured in nanocomposite models to allow for optimal nanocomposite sensor design, calibration and interpretation for prognostication. It has been shown in some recent studies that the effect of inherent piezoresistivity of CNTs has a smaller influence on the effective nanocomposite piezoresistive response [65–68]. The findings of these studies further support the idea of electron hopping being the dominant mechanism and provides further reason to study its effect on nanocomposite piezoresistivity.

Some efforts to model the effect of the electron hopping on the piezoresistive response of CNT-polymer nanocomposites [32, 34, 40, 69, 70] are based on idealizing the nanotubes as rigid members dispersed in the polymer medium forming a 2-D or 3D stick network. The
changing intertube resistivities when deformations are applied were then converted into a resistor network model where deforming the network leads to changes of resistance within the network corresponding to an effective piezoresistive response. The electrical and mechanical material response is thus coupled in an indirect manner. Even though these models attempt to study the strain dependent behavior of the nanocomposites, they fail to incorporate the effect of CNT deformation which might cause significant variation in the piezoresistive response, especially at high volume fractions. In addition, these studies fail to represent the detailed description of nanocomposite morphology at different scales because of a single scale representation. Seidel et al. [71,72] proposed a continuum micromechanics model based on Composites Cylinder Method, studying the effect of electron hopping by introducing a continuum interphase layer which results in a distinct electron hopping induced percolation concentration for uniformly dispersed randomly oriented nanotubes inside a polymer matrix. However, the effect of application of strains on the changing conductivity cannot be studied using such an approach. In the current work, a computational continuum micromechanics based method is developed to study the changing CNT-polymer morphology at the nanoscale, the subsequent changing electron hopping pathways in between nanotubes and their effect on the macroscale piezoresistive response of nanocomposites. The effective nanoscale properties of the nanocomposite medium is transitioned into macroscale properties using analytical multiscale homogenization through the Mori-Tanaka method. In doing so, the effect of differences in local volume fractions of the nanocomposite medium and the orientation of CNTs in the nanocomposite is explored.

In addition to strain sensing, CNT-polymer nanocomposites provide damage sensing capabilities because of local changes in electron hopping pathways at the nanoscale due to the initiation/evolution of damage. The current work aims to explore the effect of interfacial separation and damage at the nanoscale CNT-polymer interface on the effective macroscale piezoresistive response. In order to study the effect of nanoscale interface separation/damage on the effective electrostatic and piezoresistive response, the nanoscale CNT-polymer interface is modeled through electromechanical cohesive zones in the current work. Cohesive zones were first introduced by Dugdale [73] and Barenblatt [74] in order to allow for non-zero tractions in the wake of the crack tip. Extending on these ideas, Needleman [75, 76]
developed a constitutive model for a cohesive zone in which the interfacial tractions were described as a function of normal separation across the cohesive interface in the form of a potential function based on experimental observations and the theoretical potentials used to model atomic bonds. Tvergaard [77] further developed a cohesive zone model with decohesion dependent upon both normal and tangential interfacial separation. A number of theories have aimed at improving or extending these ideas for application specific cohesive zone traction displacement laws with linear, non-linear or time dependent problems, typically within a finite element framework [78–81]. In some of the studies [78, 82], attempts have been made to model the cracks at internal interfaces using mechanical cohesive zones for crystalline and composite materials. For CNT-polymer nanocomposites, the mechanical behavior of CNT-polymer interfaces at the nanoscale has been studied through molecular dynamics based simulations generating interfacial traction response [82–85], which can be used to describe nanoscale CNT-polymer interface separation and damage when subjected to applied strains. It has been observed that the interfacial separation and damage results in degradation of effective mechanical properties of CNT-polymer nanocomposites [82,85].

In a part of the current work, interfacial separation and damage are allowed to evolve at the CNT-polymer interface through coupled electromechanical cohesive zones, within a finite element based computational micromechanics framework, resulting in electron hopping based current density across the separated CNT-polymer interface. The macroscale effective material properties and gauge factors are evaluated using micromechanics techniques based on electrostatic energy equivalence. The impact of the electron hopping mechanism and nanoscale interface separation and damage evolution on the effective nanocomposite electrostatic and piezoresistive response is studied in comparison to perfectly bonded interface. It is observed that the macroscale effective gauge factors are highly sensitive to strain induced formation/disruption of electron hopping pathways, interface separation and the initiation/evolution of interfacial damage.
1.3 Polymer Bonded Energetic Materials

As an example application of the in-situ sensing capability provided by CNT-polymer nanocomposites, polycrystalline/granular energetic materials are considered in the current work. Energetic materials, such as polymer bonded explosives (PBXs) [86–94] which are composed of two phases, the explosive crystals/grains and a polymeric binder, are a class of composite materials designed to release high amounts of energy in response to a trigger. PBXs are used in various applications such as rocket propellants and detonators [95]. Typically, these energetic materials are comprised of explosive materials such as HMX (Octahydro -1,3,5,7-tetranitro -1,3,5,7- tetrazocine), RDX (1,3,5- Trinitroperhydro -1,3,5- triazine), PETN (pentaerythritol - tetranitrate), or TATB (triamino - trinitrobenzene) which are present in the composite in the form of small (∼100µm) crystals. Polymer binder materials, e.g. estane, are used in these composites which typically constitute around 10% or less of the volume.

The overall mechanical properties of the composite are largely determined by the polymer binder because of relatively larger compliance when compared to explosive grains. In addition, the polymer binder contributes significantly to the improvement of the toughness and impact tolerance of such composites [96]. The explosive event in PBX is usually divided into various stages: ignition, the growth of deflagration (burning) and deflagration to detonation transition (DDT). Usually, a shock impact event results in adiabatic compression of the material which generates enough heat to trigger the desired chemical reaction which leads to detonation immediately [97]. However, in many situations which involve accidental low velocity impact during transportation and handling or tool drop, inadvertent ignition of the energetic material can occur [98]. In order to assess the structural integrity of the composite in terms of the current deformation and damage state, it is anticipated that the piezoresistive response of carbon nanotube(CNT)-polymer nanocomposites can be exploited by dispersing CNTs in the polymer binder phase which makes the binder medium inherently piezoresistive. Computational modeling of these nanocomposite bonded energetic materials can further provide insights into the key piezoresistive mechanisms and may help with prognostication of remaining life of the composite.

Several experimental studies [86–90] have focused on characterizing the energetics and mock/surrogate
materials to assess the mechanical and thermomechanical properties of these materials. The mock/surrogate materials have similar microstructural features and mechanical properties as the energetic crystals, but they are non-energetic which makes them safer to work with. Peeters [86] et al. performed tensile and compression testing for different strain rates at room temperature on PBX 9501, PBX 9502, and on 900-10 mock materials, as well as creep and cyclic tests for each material to obtain a phenomenological characterization of energetics and applicable mock materials. Liu et al. [87] fabricated PBX 9502 specimens containing a cavity in order to investigate damage initiation, progression and cracking under compression. It was observed that the non-uniform stress distribution around cavity in the energetic material resulted in the development of microcracks under compression. Liu et al. [88] also examined the aging effects in high explosives. Brazilian disk samples made of pristine and artificially aged PBX 9501 materials were subjected to compression testing at different temperatures in conjunction with digital image correlation in order to observe microcrack initiation, propagation and accumulation. Aged PBX 9501 samples were much weaker and much more brittle than pristine ones, leading to easier macroscopic cracking. Liu et al. [89] investigated the fracture process of PBS (polymer bonded sugar) 9501 sugar mock, a PBX 9501 high explosive simulant mock. The most dominating mechanical failure mechanism in high explosives of microcrack initiation and propagation was similarly observed in PBS 9501 sugar mock material. It was also observed that crystal interlocking and friction along with binder stretching contributed to the formation and extension of stress-bridging zones, leading to crack bridging processes. Liu et al. [90] also tested Mock 900-21, a PBX 9501 high explosive simulant which was subjected to monotonic and cyclic loading in order to assess the macroscopic crack formation and crack growth in these materials. It was postulated that the heterogeneity in the microstructure of the energetic material led to macroscopic crack formation under cyclic loading at load levels which were below the failure stresses observed for monotonic strain to failure.

On the modeling side, Seidel et al. [78, 99] developed viscoelastic cohesive zone models for highly filled polymer energetic materials such as LX17, with a phenomenological damage law. They observed that cohesive zone models captured nonlinear material behavior, formation and coalescence of microcracks into macrocracks, and eventual failure which are typically
observed in the experimental results. Barua et al. [100–102] studied the deformation and
damage of PBX materials subjected to dynamic loading conditions using a cohesive zone
finite element formulation. The cohesive interfaces were embedded in the grains, the matrix
and the interface to study the fracture paths in the composite. They concluded that the
main form of deformation is debonding at the grain-binder interface which further leads to
cracking and sliding of the grains. In addition, Panchadhara and Gonthier [103,104] used a
Lagrangian finite and discrete element technique to study compaction of HMX under uniax-
ial deformation waves and concluded that frictional heating was the dominant mechanism in
formation of the hot spots in energetics. Subsequently, Hardin et al. used a finite element
framework to investigate thermomechanical response of polycrystalline $\hat{I}^2$-HMX [105] and
concluded that the local heating due to crystal plasticity leading to hot spot formation. In
the current work, the in-situ sensing in HMX-CNT-epoxy hybrid nanocomposite energetic
material is explored using a finite elements based multiscale micromechanics framework. The
CNT-epoxy nanocomposite binder medium is modeled as an effective interface between the
HMX grains using electromechanical cohesive zones. The electromechanical cohesive zones
are constructed using effective properties of the nanocomposite obtained at the nanoscale
and transitioned though Mori-Tanaka method based multiscale homogenization scheme into
effective nanocomposite binder properties. Several different aspects of the entire material
system e.g. grain properties, CNT volume fractions, CNT orientations, ductile vs brittle
binder failure etc. are studied parametrically to explore the design space for CNT nanocom-
posites based in-situ sensing in energetic materials.

1.4 Material Point Method

Material point method (MPM) was developed as an extension of particle-in-cell method
[106, 107] for solving solid dynamic problems involving large deformations and flow. In
MPM, a collection of material points is overlayed over a traditional finite element (FEM)
computational mesh to account for both Eulerian and Lagrangian description simultaneously.
For materials which have a history dependent constitutive relationship, the Eulerian scheme
might not be suitable. On the other hand, using a Lagrangian scheme (e.g. implicit FEM) might result in severe mesh distortion and ill conditioning resulting in erroneous results. In MPM, the classical nodal force and mass matrix integrals for the background mesh are written in the usual FEM manner, but the MPM then discretizes these FEM integrals through the use of a Dirac delta function to approximate the density field on the overlayed material points. The equilibrium equations are solved over the background computational with information from the discrete material points because of the Dirac-delta function based material density. Once the primary variables are obtained from this analysis, they are mapped back to the material points and the new positions of the material points at a higher time step is calculated.

As an example, Bardenhgen et al [108] modeled the particle flow behavior using Material Point Method and an algorithm to generate the contact tractions. The solution was based on the premise that the deformations of individual particles are small as compared to the bulk deformation. This is because of the dynamics of individual particles throughout the domain which causes large bulk deformation and fluid like behavior. Nairn et al. [109, 110] extended potential application of MPM to dynamic fracture modeling by suppressing the MPM requirement of extrapolating the particle information to a single velocity field on the background grid. This means that the node on the background mesh near the crack can have separate velocity fields for information interpolated from particles on opposite side of the crack. Solutions of illustrative problems were compared to the experimental results and FEM. They postulated that crack propagation can be modeled by adding crack segments based in the crack tip energy release rate.

The applications of MPM have been explored in several engineering problems involving large deformation [111–114], contact mechanics [115, 116], material singularities [109,110,117–120], multiphase flows [121], hypervelocity impact [122] and geomechanics problems [123]. Several authors [124–129] have studied the MPM algorithm examining the implementation choices within the MPM framework and understanding the effect of these implementation choices on the quality of the solutions obtained. In the current work, the focus is on appropriately modeling composite interfaces in MPM with special treatment of the interface since
the traditional form of MPM does not allow for composite interfaces. Composite interfaces in traditional MPM get homogenized over the background mesh losing some key interfacial characteristics critical for micromechanics based composite modeling. A more detailed modeling of composite interfaces will be achieved in the current work using cohesive zone principles. Subsequently, the cohesive zone MPM model is used to model electromechanical composite problems which is needed for problems like elastomeric nanocomposite sensing films [130] where large deformation of the matrix medium needs to be modeled.

1.5 Organization

A mathematical description of of the micromechanics based description of the multiscale problem is provided in Chapter 2 along with details of the Mori-Tanka method for homogenization over phases and orientations. In addition, mathematical description of the electromechanical cohesive zone modeling is provided in Chapter 2. Application of the computational micromechanics framework to find the effective piezoresistive properties of the nanoscale nanocomposite medium is presented in Chapter 3 where nanoscale electron hopping based evolution of conductive intertube pathways is explored. The effective piezoresistive response for the nanoscale is used to construct analytical micromechanics based multiscale analysis in Chapter 4 where orientation effects of microscale CNT bundles on effective macroscale piezoresistivity are explored. Modeling of interfacial separation and damage at the nanoscale CNT-polymer interface is presented in Chapter 5 along with its effect of nanocomposite effective piezoresistive response in comparison to the perfectly bonded results presented in Chapter 3. Exploration of nanocomposite piezoresistivity under cyclic loading is presented in Chapter 6 where connections between interfacial damage accumulation are made to the effective piezoresistive response. The nanocomposite in-situ sensing capabilities are extended to nanocomposite bonded energetic materials in Chapter 7 where a computational exploration of the material design space is presented using several different parametric studies over material properties and microstructural features. The traditional implementation of semi-meshless Material Point Method is extended to allow for interfacial
discontinuities for composite problems in Chapter 8 to allow for electromechanical modeling of nanocomposites with elastomeric polymer matrix undergoing large deformation. Finally, Chapter 9 offers some conclusions and implications of the current work and recommendations for further work.
Chapter 2

Mathematical Preliminaries

2.1 Mathematical Description of Micromechanics Framework

Engineering materials, in general, are heterogeneous such that at scales smaller than the macroscale the different constituents or phases are identifiable. These identifiable material constituents or phases are referred to as material microstructure. As an example, copper is homogeneous at the macroscale but under a microscope one can see the granular structure with the dimensions of each grain of the order of 1\(\mu\)m. The effective macroscale response of these materials is governed by the microstructural features i.e. size, distribution, material properties of the microstructural constituents. However, from an engineering point of view, we are generally interested in the average effects of the microstructure on the effective macroscale properties.

In order to relate the microstructural features to the effective macroscale response, the first step is to identify the separation of scales in the microstructural features on which the macroscale properties are dependent. Unlike copper where one scale of influence was identified to be the microscale where microstructural grain dimensions are of the order of 1\(\mu\)m, other engineering materials can have several scales with identifiable microstructural features.
and scale dependent physical mechanisms (e.g. dislocations in crystals at the microscale).

As an example, CNT-polymer nanocomposites have been observed to have microstructural features at the microscale (CNT bundles) and nanoscale (individual CNTs in polymer matrix). The general procedure in micromechanics is to identify the separation of scales with length scales $L$, $D$ and $d$ ($L > D$ and $D >> d$) on which the macroscale properties at a length scale of $L$ (e.g. stiffness of the effective material) are defined over a representative volume element at $D$ (e.g. distribution of particles) which are dependent on the microstructure and the microscale properties over $d$ (e.g. stiffness of the particles and matrix). The microscale is defined by $d$ and corresponds to the smallest scale of key physical mechanisms or constituent phase whose physical properties, orientation and shape are judged to have direct effects on the macroscale effective properties of the heterogeneous material at a length scale of $D$. The length scale $d$ is selected based on systematic multiscale morphology characterization and is expected to include appropriate microscale microstructural features to be representative of the effective material and is used to construct the microscale representative volume element. Macroscale length scale, $D$, should be large enough such that the perturbations in field variables (e.g. local stress/strain components) due to the local variation in microstructure influence the the effective properties only through the averaged field variables. On the other hand, the variations in field variables at the macroscale $D$ are not significant at the microscale such that the macroscale fields are locally uniform at the microscale. If these conditions hold, the macroscale local field variables can be applied to the microscale as boundary conditions i.e. local macroscale strains can be applied to the microscale RVE as homogeneous strain displacement boundary conditions or the local macroscale stresses can be applied to the microscale RVE as homogeneous stress traction boundary tractions as

$$\begin{align*}
\hat{u}_i(x^b) &= \varepsilon_{ij}^0(X)\hat{x}_{j}^b \\
\hat{t}_i(x^b) &= \sigma_{ij}^0(X)\hat{x}_{j}^b
\end{align*}$$

(2.1)

where $\hat{u}_i(x^b)$ and $\hat{t}_i(x^b)$ are the boundary displacement or tractions applied at the boundary coordinates $x^b$, $\varepsilon_{ij}^0(X)$ and $\sigma_{ij}^0(X)$ are the local strain and stress components at the macroscale point $X$ which the microscale RVE represents and $\hat{x}_{j}^b$ are the local microscale coordinates of the material points where the boundary conditions are applied. The repeating
indices imply summation of components over the three spatial coordinates.

### 2.1.1 Micromechanics Based Effective Properties

In general, we can define the volume averaged stress or strain components over a domain occupying a volume $V$ as

\[
\langle \varepsilon_{ij} \rangle = \frac{1}{V} \int_V \varepsilon_{ij}(\vec{x})dV \quad \langle \sigma_{ij} \rangle = \frac{1}{V} \int_V \sigma_{ij}(\vec{x})dV
\]

(2.2)

where $\langle \varepsilon_{ij} \rangle$ and $\langle \sigma_{ij} \rangle$ are the averaged local strain ($\varepsilon_{ij}$) and stress components ($\sigma_{ij}$), and $\vec{x}$ is the vector pointing to a general material point in the domain. If the material is heterogeneous, it can be shown that the integral over the volume $V$ can be broken into a summation of integrals over the subvolumes corresponding to each phase as

\[
\langle \varepsilon_{ij} \rangle = \sum_{r=1}^{N} c_r \langle \varepsilon_{ij} \rangle^r \quad \langle \sigma_{ij} \rangle = \sum_{r=1}^{N} c_r \langle \sigma_{ij} \rangle^r
\]

(2.3)

where $\langle \varepsilon_{ij} \rangle^r$ and $\langle \sigma_{ij} \rangle^r$ are the averaged strain and stress components over the $r$th phase in the domain with $N$ total number of phases and $c_r$ is the volume fraction of each phase such that they satisfy the consistency condition $\sum_{r=1}^{N} c_r = 1$. It is to be noted that a void is also counted as a phase since it has non-zero strains because the boundaries of the void are free to deform even though the local stresses are identically zero. The average strain and stress theorems state that the averaged strains and stresses over a microscale RVE are equal to the local strain and stress at the macroscale material point $X$ when the macroscale field variables are applied to the microscale as boundary conditions (as shown in Eqn. 2.1) such that

\[
\langle \varepsilon_{ij} \rangle = \varepsilon_{ij}^0 \quad \langle \sigma_{ij} \rangle = \sigma_{ij}^0
\]

(2.4)

where $x^b$, $\varepsilon_{ij}^0(X)$ and $\sigma_{ij}^0(X)$ are the local strain and stress components at the macroscale
point which the microscale RVE is representative of. Following from the averaged strain ans stress theorems, the Hill-Mandel theorem states that the averaged strain energy density over the domain is equal to the averaged strain multiplied by the averaged stress such that

\[
\langle \varepsilon_{ij} \sigma_{ij} \rangle = \langle \varepsilon_{ij} \rangle \langle \sigma_{ij} \rangle \tag{2.5}
\]

if the boundary fields are uniform as shown in Eqn. 2.1. Using the Hill-Mandel theorem, the linear elastic constitutive equations and the strain energy equivalence between the heterogeneous microscale RVE and the homogeneous effective medium, it can be shown that the averaged stress is related to averaged strain as

\[
\langle \varepsilon_{ij} \rangle = M_{ijkl}^{Eff} \langle \sigma_{ij} \rangle \quad \langle \sigma_{ij} \rangle = L_{ijkl}^{Eff} \langle \varepsilon_{ij} \rangle \tag{2.6}
\]

where \( L_{ijkl}^{Eff} \) and \( M_{ijkl}^{Eff} \) are the effective linear elastic stiffness and compliance components and \( L_{ijkl}^{Eff} = \left( M_{ijkl}^{Eff} \right)^{-1} \). Thus, the effective stiffness of heterogeneous material can be defined in terms of volume averaged strain and stress over a heterogeneous microscale RVE which is energetically equivalent to a microscale statistically homogeneous material with uniform effective material properties.

Substituting the result in Eqn. 2.6 into the definitions of averaged strain and averaged stress shown in Eqn. 2.3, we get

\[
\langle \varepsilon_{ij} \rangle = \sum_{r=1}^{N} c_r M_{ijkl}^{r} \langle \varepsilon_{ij}^{r} \rangle \quad \langle \sigma_{ij} \rangle = \sum_{r=1}^{N} c_r L_{ijkl}^{r} \langle \varepsilon_{ij}^{r} \rangle \tag{2.7}
\]

Let us introduce the concept of concentration tensors which transform the average stress or strain over the entire volume into a phase averaged quantity such that

\[
\langle \varepsilon_{ij}^{r} \rangle = A_{ijkl} \langle \varepsilon_{ij} \rangle \quad \langle \sigma_{ij}^{r} \rangle = B_{ijkl} \langle \sigma_{ij} \rangle \tag{2.8}
\]

where \( A_{ijkl} \) and \( B_{ijkl} \) are the \( r \)th phase strain and stress concentration tensors, respectively,
which define the concentration of averaged local stress or strain in a phase as compared to the total averaged stress or strain in the composite. Thus, for a highly stiff inhomogeneity in a matrix, the strain concentrations are close to zero and the stress concentration tensors are close to 1. These concentration tensors are dependent on the shape, orientation, material properties, material symmetry properties and material symmetry orientation. Substituting the definitions of the strain and stress concentration tensors into Eqn. 2.7 and then comparing to Eqn. 2.6 it can be shown that

\[
L_{ijmn}^{Eff} = \sum_{r=1}^{N} c_r L_{ijkl}^{r} A_{klmn}^{r} \quad M_{ijmn}^{Eff} = \sum_{r=1}^{N} c_r M_{ijkl}^{r} B_{klmn}^{r}
\]  

(2.9)

For composite materials, where fillers are introduced in a matrix medium, calculation of concentration tensors for the matrix phase may be difficult because of the shape of the matrix phase. In order to avoid calculating the concentration tensors for the matrix phase we use the consistency condition, \( \sum_{r=1}^{N} c_r = 1 \), and the averaged strain definitions in Eqn. 2.3 and compare them to the definition of the concentration tensors in Eqn. 2.8 to show that

\[
I_{ijkl} = \sum_{r=1}^{N} c_r A_{ijkl}^{r} \quad I_{ijkl} = \sum_{r=1}^{N} c_r B_{ijkl}^{r}
\]

(2.10)

where \( I_{ijkl} \) is the fourth order identity tensor. From Eqn. 2.10 we can separate out the matrix phase contribution, say phase \( N \), as

\[
c_N A_{ijkl}^{N} = I_{ijkl}^{Eff} - \sum_{r=1}^{N-1} c_r A_{ijkl}^{r} \quad c_N B_{ijkl}^{N} = I_{ijkl}^{Eff} - \sum_{r=1}^{N-1} c_r B_{ijkl}^{r}
\]

(2.11)

Substituting this definition back into Eqn. 2.9, we get

\[
L_{ijmn}^{Eff} = L_{ijmn}^{N} + \sum_{r=1}^{N-1} c_r (L_{ijkl}^{r} - L_{ijkl}^{N}) A_{klmn}^{r}
\]

(2.12)

\[
M_{ijmn}^{Eff} = M_{ijmn}^{N} + \sum_{r=1}^{N-1} c_r (M_{ijkl}^{r} - M_{ijkl}^{N}) B_{klmn}^{r}
\]

(2.13)
2.1.2 Mori-Tanka Method for Multiphase Composites

The micromechanics based Mori-Tanka method provides for a way to evaluate the strain and stress concentrations tensors required to calculate the effective properties for composite materials. The Mori-Tanka approximates the displacement field at the boundary of a phase in an infinite matrix medium by including a perturbation term in the boundary strains to account for the presence of other phases in the vicinity. This enables applicability of Mori-Tanka method to larger volume fractions of fillers as compared to other methods for concentration tensor approximation e.g. dilute method. A summary of important results obtained from the Mori-Tanka method are outlined here but a detailed derivation may be found in [131]. The Mori-Tanka strain concentration tensor for the \( r \)th phase can be written as

\[
A_{ijmn}^r = T_{ijkl}^r \left[ c_N I_{mnkl} + \sum_{s=1}^{N-1} c_s T_{mnkl}^s \right]^{-1}
\] (2.14)

where \( T_{klmn} \) is the dilute strain concentration tensor which is given by

\[
T_{klmn}^r = \left[ I_{mnkl} + S_{mnopq}^r M_{pqr}^N \left( L_{mnkl}^r - L_{mnkl}^N \right) \right]^{-1}
\] (2.15)

where \( S_{mnopq}^r \) is the Eshelby’s tensor for the \( r \)th phase which is dependent on the shape of the inhomogeneity and the properties of the matrix phase, \( M_{pqr}^N \) and \( L_{pqr}^N \) are the compliance and stiffness tensors of the matrix phase and \( L_{pqr}^r \) is the stiffness tensor of the \( r \)th phase.

It is to be noted that the assumptions on the shape of the inhomogeneity can be lifted by using computational techniques to evaluate \( S_{mnopq}^r \) instead of the analytical Eshelby’s methods which restrict the shapes to some general definition of ellipsoids. The Mori-Tanka stress concentration tensor can be shown to be

\[
B_{ijmn}^r = P_{ijkl}^r \left[ c_N I_{mnkl} + \sum_{s=1}^{N-1} c_s P_{mnkl}^s \right]^{-1}
\] (2.16)
where $P_{ijkl}^r$ is the Hill’s polarization tensor for the $r$th phase which can be evaluated as

$$P_{ijpq}^r = L_{ijkl}^r T_{klmn}^r M_{mnpg}^N$$ (2.17)

where $L_{ijkl}^r$ is the stiffness of the $r$th phase and $M_{mnpg}^N$ is the compliance of the matrix phase.

In general, the volume fraction and the material properties of the matrix and fillers needs to be known to evaluate the effective properties using micromechanics based techniques. In addition, the shape and orientation of the fillers needs to be either specified or approximated to evaluate the Eshelby’s tensor in Eqn. 2.15. The derivation of Eshelby’s tensor follows through a Green’s function solution of an eigenstrain in a matrix medium. For a general anisotropic linear elastic matrix medium and for arbitrary shapes of the fillers, a numerical solution for the Eshelby’s tensor needs to be evaluated. In some other cases, the dilute strain concentration tensor in Eqn. 2.15 can be directly evaluated using numerical techniques by-passing the need for Eshelby’s solutions. However, for linear elastic or transversely isotropic matrix material and for ellipsoidal filler geometries, the components of the Eshelby’s tensor can be evaluated analytically. As an example, for a spheroidal inclusion (i.e. subset of a general ellipsoidal inhomogeneity) where the three radii $(a_1, a_2, a_3)$ follow $a_1 = a_2 \neq a_3$ the components of the Eshelby’s tensor are given by

$$S_{4141} = S_{4242} = \begin{cases} \frac{\alpha}{2(a^2-1)^{\frac{3}{2}}} \left[ \text{arccosh}(\alpha) - \alpha(1 - \alpha^2)^{\frac{3}{2}} \right] & \alpha < 1 \\ \frac{\alpha}{2(a^2-1)^{\frac{3}{2}}} \left[ \alpha(1 - \alpha^2)^{\frac{3}{2}} - \text{arccosh}(\alpha) \right] & \alpha > 1 \\ \frac{1}{3} & \alpha = 1 \end{cases}$$

$S_{4343} = 1 - 2S_{4141}$

$S_{4n4b} = 0 \quad \forall \ n \neq b$ (2.18)

where $\alpha$ is the aspect ratio of the spheroid calculated as $\alpha = a_3/a_1 = a_3/a_2$ and the Eshelby’s tensor follows the following symmetry properties in general

$$S_{ijkl} = S_{jikl} = S_{ijlk}$$ (2.19)

It is to be noted that for a spherical inhomogeneity or inclusion $\alpha = 1$ and for an infinite
aspect ratio cylindrical fiber $\alpha \to \infty$.

### 2.1.3 Orientation Averaging Using Mori-Tanka method

In cases where the filler has an aspect ratio different from unity (i.e. $\alpha \neq 1$, not spherical) and the dispersion of the fillers in the matrix medium cannot be controlled precisely, the orientation of the fillers may follow a distribution. If no attempts are made to control the dispersion of the filler the resulting composite has statistically randomly oriented fillers in the matrix. If attempts have been made to control the orientation of the fillers, e.g. using electric (dielectrophoresis) or magnetic (magnetophoresis) fields, the orientations would most likely follow a distribution about a mean orientation. The effective macroscale properties of the composite depend significantly on the orientation distribution of the fillers especially for cases where the filler properties are non-isotropic, e.g. carbon nanotubes have an order of magnitude larger axial stiffness as compared to their transverse stiffness. Even for cases with spherical (i.e. $\alpha = 1$) inhomogeneities, if the material is not isotropic the orientation of the axis of symmetry of the fillers needs to be considered. In such cases, it becomes important to account for the orientation distribution within the micromechanics framework to evaluate the effective properties.

The key in determining the effective properties with orientation distribution is to incorporate each representative orientation as a separate phase in the Mori-Tanka method (or dilute or self-consistent methods). Let us say that the volume fraction of inhomogeneities with the $J$th discrete orientation is given by $c_J$ such that the sum of volume fractions of all different orientation is the total volume fraction of the inhomogeneity, i.e. $\sum_{J=1}^{P} c_J = v_f$. Lets consider a case with 2D orientation distribution of the inhomogeneities such that the orientation can be described by two variable Euler angles $\psi$ and $\varphi$ with the third angle $\theta$ being a constant, the probability distribution function of the orientations can be expressed as $p(\psi_k, \varphi_m)$ for the $k$th and $m$th orientation in the two Euler angles. The effective stiffness of the composite can be expressed as
\[ I_{ijkl}^{\text{Eff}} = L_{ijkl}^N + \frac{v_f}{4\pi} \sum_{k=1}^{P_1} \sum_{m=1}^{P_2} p^r(\psi_k, \varphi_m) \left( L_{ijmn}^r(\psi_k, \varphi_m) - L_{ijmn}^N \right) A_{mnkl}^B(\psi_k, \varphi_m) \sin(\varphi_m) \Delta \varphi \Delta \psi \]

(2.20)

The components of the strain concentration tensors, \( A_{mnkl}^r(\psi_k, \varphi_m) \) can be evaluated using the Mori-Tanaka method and are expressed as

\[ A_{ijkl}^r(\psi_k, \varphi_m) = Q_{im}Q_{nj}(\psi_k, \varphi_m)T_{mnpq}^r Q_{ps} Q_{rq}(\psi_k, \varphi_m) \left[ (1 - v_f^B)I_{rskl} + \frac{v_f}{4\pi} \sin(\varphi_m) \right] \left( \sum_{a=1}^{P_1} \sum_{b=1}^{P_2} (Q_{rq} Q_{ps}(\psi_a, \varphi_b)T_{pquv}^r Q_{ul} Q_{kv}(\psi_a, \varphi_b)) \sin(\varphi_m) \Delta \varphi \Delta \psi \right]^{-1} \]

(2.21)

where the dilute strain concentration tensor \( T_{mnpq}^r \) is given by

\[ T_{mnpq}^{(B)} = \left[ I_{mnrs} + S_{mnuv} \left( \tilde{L}^{(N)}_{avij} \right)^{-1} \left( \tilde{L}_{ijpq}^r - L_{ijpq}^N \right) \right]^{-1} \]

(2.22)

where \( Q_{ij}(\psi_r, \varphi_s) \) are the components of the second order rotation matrix used to transform the local inhomogeneity coordinate system to the effective macroscale medium coordinate system.

### 2.1.4 Effective Properties Through Averaged Field Variables

Eshelby’s solution based micromechanics techniques, like the Mori-Tanaka method, are powerful tools to evaluate effective material properties without having to solve boundary value problems at any scale. However, their application is typically limited to cases with homogeneous fillers with weak interactions (only through perturbations in stress/strain fields) between the fillers. In cases where the fillers are non-homogeneous, e.g. hollow fiber, coated fiber etc., and in cases where there is a larger interaction amongst the fillers, e.g. direct contact between the fillers at large volume fractions, the applicability of Eshelby’s solutions becomes questionable. In the current work, the carbon nanotubes are hollow isotropic fibers.
when represented as an effective continuum and have large electrostatic interactions in terms of electron hopping. In such cases, computational solutions of boundary value problems at the subscales may be required at scales where there are large interactions between the fillers and which can then be upscaled into effective macroscale properties using a Mori-Tanaka based method. As an example, the effective properties for CNT bundles which form at the microscale can be computationally evaluated and thereafter the effective CNT bundle properties may be used as the filler properties in the orientation averaging procedure using Mori-Tanaka method described earlier.

The evaluation of effective properties through computational solutions of boundary value problems makes use of uniform boundary conditions (Eqn. 2.1), the Hill-Mandel theorem (Eqn. 2.5) and energy equivalence principles, from which an averaged representation of the constitutive equations (Eqn. 2.6) is derived, with effective properties relating the averaged strains and stresses over the representative volume element. As an example, the effective properties of a hollow fiber (e.g. CNTs) in a matrix medium is known to result in transversely isotropic properties with the axis of symmetry in the axial fiber direction (say \( x_1 \)). Let us say the five independent properties to be evaluated for a transversely isotropic material are the axial modulus \( E_{11}^{\text{Eff}} \), axial stiffness \( C_{11}^{\text{Eff}} \), in-plane bulk modulus \( \kappa_{23}^{\text{Eff}} \), axial shear modulus \( \mu_{12}^{\text{Eff}} \) and in-plane shear modulus \( \mu_{23}^{\text{Eff}} \). The other properties, like the in-plane (\( \nu_{23}^{\text{Eff}} \)) and axial (\( \nu_{12}^{\text{Eff}} \)) Poisson’s ratios, can be calculated using one or more of the five independent properties. In order to simplify the choice of boundary conditions let us choose the RVE to be concentric cylinders with a hollow region enveloped within a fiber (say CNT) layer. The axial modulus \( E_{11}^{\text{Eff}} \) can then be calculated using energy equivalence in terms of averaged field variables with appropriate boundary conditions as

\[
E_{11}^{\text{Eff}} = \frac{\langle \sigma_{11} \rangle}{\langle \varepsilon_{11} \rangle}
\]

\[
u_2 = \frac{u_z(r, \theta, L)}{\varepsilon_0 L} = \frac{u_z(r, \theta, -L)}{\varepsilon_0 L}
\]

\[
\sigma_{rr}(r_0, \theta, z) = 0 \quad \sigma_{rr}(r_N, \theta, z) = 0
\]

where \( L \) is the length of the RVE in the \( x_1 \) direction, \( \varepsilon_0 \) is the applied strain in the axial direction, \( r_0 \) is the radius of the hollow region and \( r_N \) is the outermost radius of the hollow
fiber assembly. The axial stiffness component, $C_{11}^{Eff}$, can be found using a similar expression, however, instead of specifying $\sigma_{rr}(r_N, \theta, z) = 0$, the outer boundary needs to be left free such that $u_r(r_N, \theta, z) = 0$. The in-plane bulk modulus ($\kappa_{23}^{Eff}$) can be evaluated as

$$\kappa_{23}^{Eff} = \frac{\langle \sigma_{22} \rangle}{\langle \varepsilon_{22} \rangle}$$

subject to

$$u_z(r, \theta, L) = 0 \quad u_z(r, \theta, -L) = 0$$

$$\sigma_{rr}(r_0, \theta, z) = 0 \quad u_r(r_N, \theta, z) = \varepsilon_0 r_N$$

where $\varepsilon_0$ is a constant applied strain. The axial Poisson’s ratio, which is a derived property, can then be evaluated as

$$\nu_{12}^{Eff} = \sqrt{\frac{C_{11}^{Eff} - E_{11}^{Eff}}{\kappa_{23}^{Eff}} / \kappa_{23}^{Eff}}$$

The axial shear modulus can be evaluated as

$$\mu_{12}^{Eff} = \frac{\langle \sigma_{12} \rangle}{\langle \varepsilon_{12} \rangle}$$

subject to

$$\sigma_{zz}(r, \theta, L) = 0 \quad \sigma_{zz}(r, \theta, -L) = 0$$

$$\sigma_{rz}(r_0, \theta, z) = 0 \quad u_z(r_N, \theta, z) = 2\varepsilon_0 r_N \cos(\theta)$$

Finally, the in-plane shear modulus ($\mu_{23}^{Eff}$) can be evaluated as

$$\mu_{23}^{Eff} = \frac{\langle \sigma_{23} \rangle}{\langle \varepsilon_{23} \rangle}$$

subject to

$$u_z(r, \theta, L) = 0 \quad u_z(r, \theta, -L) = 0$$

$$\sigma_{rr}(r_0, \theta, z) = 0 \quad \sigma_{r\theta}(r_0, \theta, z) = 0$$

$$u_r(r_N, \theta, z) = \varepsilon_0 r_N \sin(\theta) / 2 \quad u_\theta(r_N, \theta, z) = \varepsilon_0 r_N \cos(\theta) / 2$$

For the case of in-plane shear modulus, applying displacement boundary conditions and traction boundary conditions leads to the bounds for the property which are non-coincident. In order to overcome this, a generalized self-consistent approach is followed where another layer of phase with effective material property is added and the solution is achieved by updating the guess solution iteratively until the desired tolerance is achieved for the bounds.
Some other dependent variables of interest, transverse shear modulus ($E_{22}^{Eff}$) and in-plane Poisson’s ratio ($\nu_{12}^{Eff}$), can then be evaluated using the five independent properties calculated as

$$E_{22}^{Eff} = \frac{4\mu_{23}^{Eff}E_{23}^{Eff}}{\kappa_{23}^{Eff} + \mu_{23}^{Eff} + 4(\nu_{12}^{Eff})^2 \mu_{23}^{Eff} \kappa_{23}^{Eff} / E_{11}^{Eff}}$$

$$\nu_{23}^{Eff} = \frac{\kappa_{23}^{Eff} - \mu_{23}^{Eff} - 4(\nu_{12}^{Eff})^2 \mu_{23}^{Eff} \kappa_{23}^{Eff} / E_{11}^{Eff}}{\kappa_{23}^{Eff} + \mu_{23}^{Eff} + 4(\nu_{12}^{Eff})^2 \mu_{23}^{Eff} \kappa_{23}^{Eff} / E_{11}^{Eff}}$$

(2.28)

For the concentric cylinder RVE chosen here for demonstration, the strain and stress fields can be evaluated using the composites cylinder method [132] where the functional form of analytical displacement fields is known a priori using energy equivalence methods. The related constants can be evaluated by satisfying boundary conditions at the boundaries and interfaces. The composite cylinder method, however, generally assumes perfect bonding between the cylinders and does not account for direct interactions between fillers e.g. direct contact. In such a case, an appropriate RVE needs to be chosen which is statistically representative of the material phases and the interactions between them. On a general RVE, the uniform boundary conditions that need to be applied may take a more complex form but the relations between the effective properties and averaged fields variables remain the same. Hence, the same general structure may be used to evaluate properties using averaged field variables. In the discussion of micromechanics based methods so far only evaluation of mechanical properties has been presented. Calculation of effective properties for the electrostatic problem follows identically with analogous properties and field variables.
2.2 Mathematical Description of the Multiscale Electromechanical Problem

2.2.1 Mechanical Governing Equations at the Macroscale

The conservation of linear momentum for quasi static conditions neglecting the body forces can be written as

$$\sigma_{ij,j} = 0 \quad (2.29)$$

where $\sigma_{ij}$ is the macroscale stress tensor and i,j are indices that vary from 1 to 3, where repeated indices imply summation over that index and commas denote differentiation with respect to a cartesian coordinate system. The infinitesimal strain displacement relations at the macroscale are given by

$$\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}) \quad (2.30)$$

The macroscale constitutive relation using the effective macroscale medium definition can be expressed as

$$\sigma_{ij} = C_{ijkl}^{\text{Eff}} \varepsilon_{kl} \quad (2.31)$$

where $C_{ijkl}^{\text{Eff}}$ are the effective stiffness components which are obtained from the volume averaging of the stress-strain response at the nanoscale using the Hill-Mandel theorem and the equivalence of strain energy between the heterogeneous nanoscale RVE and an effective homogeneous medium. Thus, $C_{ijkl}^{\text{Eff}}$ can be evaluated using

$$\langle \hat{\sigma}_{ij} \rangle = C_{ijkl}^{\text{Eff}} \langle \hat{\varepsilon}_{kl} \rangle \quad (2.32)$$
where $\langle \cdot \rangle$ denotes volume averaging over the nanoscale RVE and the hat symbol denotes nanoscale variables through the remainder of the text. The mechanical boundary value problem at the macroscale becomes well posed when the governing differential equations are supplemented with the displacement and traction boundary conditions.

### 2.2.2 Electrostatic Governing Equations at the Macroscale

The electrostatic problem at the macroscale is constructed by using the steady state conservation of charge

$$J_{i,i} = 0 \quad (2.33)$$

where the macroscale electrostatic current density, $J_i$, at each point is related to the macroscale electric field, $E_i$, according to Ohms law given by

$$J_i = \Sigma_{ij}^{Eff} E_j \quad (2.34)$$

where $\Sigma_{ij}^{Eff}$ are the effective macroscale conductivity components and $E_i$ are the macroscale electric field components. The electric field vector in Eqn. 2.34 can be expressed using electrostatic potential ($\phi$) as

$$E_i = -\phi_{,i} \quad (2.35)$$

such that the effective macroscale conductivity components are obtained from the volume averaged current density-electric field response at the nanoscale as

$$\langle \hat{J}_i \rangle = \Sigma_{ij}^{eff} \langle \hat{E}_j \rangle \quad (2.36)$$

Again, the electrostatic BVP at the macroscale becomes well-posed when supplemented with
the electrostatic potential or current density boundary conditions. In general, the effective electrostatic properties, like the effective elastic properties, are independent of the boundary conditions imposed at the macroscale and subsequently transferred to the nanoscale. However, due to electron hopping at the nanoscale, the effective electrostatic properties depend on the macroscale mechanical boundary conditions in producing the macroscale observed piezoresistive response of nanocomposites. The result is a one-way electromechanical coupling where the effective electrostatic properties are dependent on the mechanical boundary conditions while the effective mechanical properties remain independent of the electrostatic boundary conditions.

2.2.3 Mechanical Governing Equations at the Nanoscale

The conservation of linear momentum at the nanoscale, in absence of body forces, can be written as

\[ \hat{\sigma}_{ij,j} = 0 \] (2.37)

where \( \hat{\sigma}_{ij} \) denotes the nanoscale stress tensor. The infinitesimal strain displacement relations at the nanoscale can be written as

\[ \hat{\varepsilon}_{ij} = \frac{1}{2}(\hat{u}_{i,j} + \hat{u}_{j,i}) \] (2.38)

where \( \hat{\varepsilon}_{ij} \) denotes the nanoscale strain tensor and \( \hat{u}_i \) is the nanoscale displacement vector. At the nanoscale, the CNT annulus and polymer matrix can be assumed to be isotropic linear elastic materials such that their constitutive relationships can be denoted with the Lame’s constants as

\[ \hat{\sigma}_{ij} = 2\mu^{(r)}\hat{\varepsilon}_{ij} + \lambda^{(r)}\hat{\varepsilon}_{kk}\delta_{ij} \] (2.39)

where the superscript \( (r) \) on the material properties denote CNT or polymer matrix medium,
and the standard relationships $\mu = \frac{E}{2(1+\nu)}$ and $\lambda = \frac{E\nu}{(1+\nu)(1-2\nu)}$ for isotropic linear elastic materials hold. The boundary conditions on the nanoscale RVE can be expressed as either traction or displacement boundary conditions by

$$\hat{t}_i = \hat{n}_j \sigma_{ij}(X_k)$$
$$\hat{u}_i = \hat{x}_j \varepsilon_{ij}(X_k)$$

(2.40)

where $\sigma_{ij}(X_k)$ and $\varepsilon_{ij}(X_k)$ are the macroscale stress and strain at a macroscale material point, $X_k$, which the nanoscale RVE represents. The local macroscale stress and strain states can then be represented in terms of the nanoscale strain and stress states as

$$\sigma_{ij}(X_k) = \langle \hat{\sigma}_{ij} \rangle$$
$$\varepsilon_{ij}(X_k) = \langle \hat{\varepsilon}_{ij} \rangle$$

(2.41)

### 2.2.4 Electrostatic Governing Differential Equations at the Nanoscale

The electrostatic problem is constructed by using the steady state conservation of charge as shown in Eqn. 2.42.

$$\hat{J}_{i,i} = 0$$

(2.42)

where the nanoscale electrostatic current density, $\hat{J}$, at each point in the bundle is assumed to be obtained from the local electric field, $\hat{E}$, according to the Ohm’s law given by

$$\hat{J}_i = \hat{\Sigma}_{ij}^{(r)} \hat{E}_j$$

(2.43)

where the superscript (r) denotes the electrostatic conductivity tensor corresponding to the SWCNT annulus, matrix or the varying intertube/electron hopping region, all of which are isotropic. The nanoscale electric field vector in Eqn. 2.43 can be related to the nanoscale potential field as
\[
\hat{E}_i = -\hat{\phi}_{ji}
\] (2.44)

The electrostatic boundary conditions on the nanoscale RVE can be expressed as either current density or potential conditions as

\[
\hat{n}_i \hat{J}_i = \hat{n}_j J_j(X_k)
\]

\[
\hat{\phi} = \hat{x}_j E_j(X_k)
\] (2.45)

such that in general the macroscale and nanoscale RVE current densities and electric fields can be related to one another through nanoscale volume averages as

\[
J_i(X_k) = \langle \hat{J}_i \rangle
\]

\[
E_i(X_k) = \langle \hat{E}_i \rangle
\] (2.46)

where \(J_i(X_k)\) and \(E_i(X_k)\) are the macroscale current density and electric field at a macroscale material point, \(X_k\), which the nanoscale RVE represents. The macroscale applied strains can be envisioned to affect the nanoscale conductivities through electron hopping because of changing CNT-polymer morphology at the nanoscale.

### 2.3 Effective Piezoresistive Properties

The general relationship for a piezoresistive material relates the strain tensor to the relative change in resistivity, i.e. current strain resistivity minus unstrained resistivity \((\Delta \rho)\) normalized by the unstrained resistivity \((\rho_0)\), as

\[
\frac{\Delta \rho_{(i)(j)}}{\rho_{0_{(i)(j)}}} = \Pi_{ijkl} \varepsilon_{kl}
\] (2.47)

where () indicates no sum on the enclosed index. In the current study, it will be assumed that both the nanotube and the polymer are not inherently piezoresistive, i.e. all components of
the piezoresistive strain tensor at the nanoscale ($\hat{\Pi}_{ijkl}$) are zero. However, due to the electron hopping effect, the effective macroscale material demonstrates an effective piezoresistive response, i.e. $\Pi_{ijkl}^{Eff}$ has non-zero components. Recalling that the Hill-Mendel theorem was used with the energy equivalence to find the effective stiffness ($C_{ijkl}^{Eff}$) and conductivity ($\Sigma_{ij}^{Eff}$) tensor components, the effective macroscale piezoresistive strain coefficients are similarly related through the volume averaged normalized change in resistivity and strain fields at the nanoscale as

$$\left\langle \frac{\Delta \hat{\rho}_{(i)(j)}}{\hat{\rho}^0_{(i)(j)}} \right\rangle = \Pi_{ijkl}^{Eff} \left\langle \hat{\varepsilon}_{kl} \right\rangle$$ (2.48)

where $\Pi_{ijkl}^{Eff}$ is the effective macroscale fourth order piezoresistive strain co-efficient tensor and $\hat{\varepsilon}_{kl}$ is the second order strain tensor at the nanoscale. The changes in volume averaged resistivities needed to determine the components of the piezoresistive strain tensor are obtained from the averaged representation of Ohm’s law (Eqn 2.36) which is expanded using the plane strain assumptions (i.e. plane electric field in this case, $\hat{E}_1 = 0$) as

$$\left\langle \hat{J}_1 \right\rangle = \Sigma_{11}^{Eff} \left\langle \hat{E}_1 \right\rangle + \Sigma_{12}^{Eff} \left\langle \hat{E}_2 \right\rangle$$
$$\left\langle \hat{J}_2 \right\rangle = \Sigma_{21}^{Eff} \left\langle \hat{E}_1 \right\rangle + \Sigma_{22}^{Eff} \left\langle \hat{E}_2 \right\rangle$$ (2.49)

The components of the effective conductivity tensor are obtained by systematically allowing only one component of the applied electric field to be non-zero, e.g. when $E_1$ is non-zero, the conductivity components $\Sigma_{11}^{Eff}$ and $\Sigma_{21}^{Eff}$ are obtained from Eqn. 2.49. The conductivity component $\Sigma_{11}^{Eff}$ relates the applied electric field in the $x_1$ direction to the current density in the $x_1$ direction. The conductivity component $\Sigma_{21}^{Eff}$ related the applied electric field in the $x_1$ direction to current density in the $x_2$ direction. For most engineering materials (e.g. monolithic materials) an applied electric field does not result in a significant current density in the $x_2$ direction leading to zero $\Sigma_{21}^{Eff}$, however, for composites this may not be true. The effective conductivity in the CNT alignment direction ($\hat{x}_3$) is dominated by CNT conductivity for the 2D plane strain problem with infinitely long CNTs studied here [133]. The effective axial gauge factor, thus, is less significantly effected by electron hopping and
interfacial separation/damage mechanisms considered herein. The piezoresistive strain coefficient tensor has been observed to have the following internal symmetry properties [68].

\[ \Pi_{ijkl}^{Eff} = \Pi_{ijlk}^{Eff} = \Pi_{jikl}^{Eff} = \Pi_{jilk}^{Eff} \]  

(2.50)

The symmetry properties enable representation in Voigt’s notation as the number of independent components for the fourth order \( \Pi_{ijkl} \) reduce from 81 to 36. The piezoresistive equation expressed in terms of volume averages for composite materials (Eqn. 2.48) can then be expanded in Voigt’s notation using plain strain assumptions as

\[
\begin{align*}
\langle \Delta \rho_1 / \rho_0 \rangle &= \Pi_{111}^{eff} \langle \hat{\varepsilon}_1 \rangle + \Pi_{122}^{eff} \langle \hat{\varepsilon}_2 \rangle + \Pi_{166}^{eff} \langle \hat{\varepsilon}_6 \rangle \\
\langle \Delta \rho_2 / \rho_0 \rangle &= \Pi_{211}^{eff} \langle \hat{\varepsilon}_1 \rangle + \Pi_{222}^{eff} \langle \hat{\varepsilon}_2 \rangle + \Pi_{266}^{eff} \langle \hat{\varepsilon}_6 \rangle \\
\langle \Delta \rho_6 / \rho_0 \rangle &= \Pi_{611}^{eff} \langle \hat{\varepsilon}_1 \rangle + \Pi_{622}^{eff} \langle \hat{\varepsilon}_2 \rangle + \Pi_{666}^{eff} \langle \hat{\varepsilon}_6 \rangle
\end{align*}
\]  

(2.51)

Figure 2.1: Schematic representation of the experimental setup analogous to the current model for uniaxial transverse tension test corresponding to the definition of \( G_{22}^{Eff} \) in Eqn. 2.64.

As opposed to reporting piezoresistive coefficients, many of the nanocomposite characterization efforts in the literature report gauge factors. Based on the effective resistivities reported
here, gauge factors are determined for comparison with characterization efforts. The gauge factor for a uniaxial tension/compression or a uniform shear test can be expressed, in general, as

\[ G = \frac{\Delta R}{R} = \frac{\rho^f L_f - \rho^0 L_0}{\rho^0 L_0 \varepsilon_0} \]  

(2.52)

where \( G \) is the macroscale gauge factor, \( \varepsilon \) is the absolute applied uniaxial strain and \( R \) is the resistance measured in between the electrodes across the gauge section as shown in Fig 2.1. For the case of plane strain uniaxial test (with strains applied in the 2-direction) in the transverse nanoscale RVE, the general form of Eqn. 2.52 can be further modified using correlations between the initial and final resistivities (\( \rho_0, \rho_f \)), cross sectional areas (\( A_0, A_f \)) and lengths (\( L_0, L_f \)) of the specimen. For an effective orthotropic macroscale medium undergoing plane-strain uniaxial unconstrained tension/compression test with 1 and 2 being the in-plane directions and 3 being the out-of-plane direction (Fig. 2.1), if \( \varepsilon_0 \) is applied in the 2-direction, we can write,

\[ \varepsilon_{22} = \varepsilon_0 \]  

(2.53)

\[ \sigma_{11} = 0 \]  

(2.54)

Therefore, using the constitutive relationship for the effective homogeneous material under in plane strain assumption (\( \hat{\varepsilon}_{33} = \hat{\varepsilon}_{23} = \hat{\varepsilon}_{13} = 0 \)), we have

\[ \varepsilon_{11} = -\frac{\nu_{21}}{E_{22}}\sigma_{22} - \frac{\nu_{31}}{E_{33}}\sigma_{33} \]  

(2.55)

\[ \varepsilon_0 = -\frac{1}{E_{22}}\sigma_{22} - \frac{\nu_{32}}{E_{33}}\sigma_{33} \]  

(2.56)
\[ 0 = -\frac{\nu_{23}}{E_{22}} \sigma_{22} - \frac{1}{E_{33}} \sigma_{33} \quad (2.57) \]

Substituting Eqn. 2.56 and 2.57 in Eqn. 2.55,

\[ \varepsilon_{11} = -\frac{\nu_{21} + \nu_{31} \nu_{23}}{1 - \nu_{32} \nu_{23}} \varepsilon_0 \quad (2.58) \]

Now, for a plane strain unconstrained tension test,

\[ L^f = L^0 (1 + \varepsilon_{22}) = L^0 (1 + \varepsilon_0) \quad (2.59) \]

For the plane strain constrained tension test \( \varepsilon_{11} = 0 \).

\[ A^f = A^0 (1 + \varepsilon_{11})(1 + \varepsilon_{33}) = A^0 (1 - \frac{\nu_{21} + \nu_{31} \nu_{23}}{1 - \nu_{32} \nu_{23}} \varepsilon_0) \quad (2.60) \]

\[ \rho^0 = \rho_{22}(0) \quad (2.61) \]

\[ \rho^f = \rho_{22}(\varepsilon_0) \quad (2.62) \]

Substituting Eqn. 2.59 to 2.62 in Eqn. 2.52, we get,

\[ G_{22}^{Eff} = \frac{1}{\varepsilon_0} \left[ \frac{\rho_{22}(\varepsilon_0)}{\rho_{22}(0)} \frac{1 + \varepsilon_0}{1 - \frac{(\nu_{21} + \nu_{31} \nu_{23}) \varepsilon_0}{1 - \nu_{32} \nu_{23}}} - 1 \right] \quad (2.63) \]

For composite materials, the local resistivities \( \rho_{ij} \) and Poisson’s ratios \( \nu_{ij} \) in Eqn. 2.63 are replaced by effective macroscale resistivities \( \rho_{ij}^{Eff} \) and Poisson’s ratios \( \nu_{ij}^{Eff} \).
$$G_{22}^{\text{Eff}} = \frac{1}{\varepsilon_0} \left[ \frac{\rho_{22}^{\text{Eff}}(\varepsilon_0)}{\rho_{22}^{\text{Eff}}(0)} \left( \frac{1 + \varepsilon_0}{1 - \frac{\nu_{22}^{\text{Eff}} + \nu_{33}^{\text{Eff}} \nu_{23}^{\text{Eff}}}{1 - \nu_{22}^{\text{Eff}} \nu_{23}^{\text{Eff}}} \varepsilon_0} - 1 \right) \right] \quad (2.64)$$

where $\nu_{ij}^{\text{Eff}}$ are the effective Poisson’s ratios in the specified direction which can be determined using established analytical techniques such as the Composite Cylinder method [134] or Mori-Tanaka method [131]. The effective Poisson’s ratios can also be obtained from the finite element solutions for the mechanical BVP using a 3D nanoscale RVE. It has been shown [135] that the three methods listed above yield acceptably similar results. For this study, Mori-Tanaka method is used to find the effective Poisson’s ratio components.

In addition, the cross coupled gauge factors, i.e. transverse to the direction of applied strain ($\hat{x}_2$) and transverse to CNT alignment direction ($\hat{x}_3$), were calculated using [136]

$$G_{12}^{\text{Eff}} = \frac{1}{\varepsilon_0} \left[ \frac{\rho_{11}^{\text{Eff}}(\varepsilon_0)}{\rho_{11}^{\text{Eff}}(0)} \frac{1}{1 + \varepsilon_0} - 1 \right] \quad (2.65)$$

### 2.4 Cohesive Zone Modeling

In cohesive zone models, the crack propagation plane is idealized as a cohesive zones or interfaces and is assumed to support a nominal traction $T$, unlike in the classical fracture mechanics where the crack surface is assumed to be in a state of zero traction. The surface traction in the crack propagation case has components in directions both normal and tangential to the surface normal vector at the crack surface. The mechanical response of the cohesive zone is described through a cohesive law (sometimes a potential function) relating the surface traction to the separation of the crack surface. The crack tip is assumed to have an infinitesimal damage zone in front of it where the damage has initiated but the surfaces are not completely separated. In the damaged zone there is formation of localized voids and coalescence which leads to material heterogeneity in the form of load bearing strand, or fibrils, connecting the two separating surfaces. These localizes fibrils exert localized closing traction on the crack surface based on the separation distance. Thus, in general the damage
zone has a constitution that is different from the material surrounding it, emphasizing the need for a different constitutive law for the interface separation which is provided by the cohesive traction separation laws.

### 2.4.1 Mechanical Cohesive Zone Modeling

In modeling of cohesive zones within the finite element framework, the total traction across the interface for one set of initially overlapping cohesive zone node pair can be written as

\[ \mathbf{T} = T_n \mathbf{e}_n + T_t \mathbf{e}_t \]  \hspace{1cm} (2.66)

where \( T_n \) and \( T_t \) are the normal and tangential interface traction components, \( \mathbf{e}_n \) and \( \mathbf{e}_t \) are the local interface cartesian base vectors along the normal and tangential direction of the interface, respectively. The traction-separation response of the interface can be represented through a nonlinear stiffness connecting the interface separation to the interfacial traction components. The normal and tangential traction can be expressed in terms of interface stiffness as

\[ T_n = -k_n^r(\Delta u_n)\Delta u_n - T_n^r \]
\[ T_t = -k_t^r(\Delta u_t)\Delta u_t - T_t^r \]  \hspace{1cm} (2.67)

where \( k_n^r(\Delta u_n) \) and \( k_t^r(\Delta u_t) \) are linear or nonlinear normal and tangential interface stiffnesses at the \( r \)th time step, receptively, \( T_n^r \) and \( T_t^r \) are the externally applied traction at the interface in the normal and tangential directions, respectively, and \( \Delta u_n \) and \( \Delta u_t \) are the interface separations in the normal and tangential directions, respectively, which can be expressed as

\[ \Delta u_n = u_n^+ - u_n^- \quad \Delta u_t = u_t^+ - u_t^- \]  \hspace{1cm} (2.68)

where \( u_n^+ \) and \( u_n^- \) are the normal displacements of the two initially coincident cohesive zone node pairs, \( u_t^+ \) and \( u_t^- \) are the tangential displacements of the cohesive zone node pairs. Once the coordinate transformation are performed going from interface local base vectors to
the global coordinate system, the interaction of nodes connected through cohesive zones can be represented in terms of finite element formulation for one pair of cohesive zone nodes as

\[
\begin{bmatrix}
\tilde{K}^{11} & \tilde{K}^{12} & \tilde{K}^{13} & \tilde{K}^{14} \\
\tilde{K}^{21} & \tilde{K}^{22} & \tilde{K}^{23} & \tilde{K}^{24} \\
\tilde{K}^{31} & \tilde{K}^{32} & \tilde{K}^{33} & \tilde{K}^{34} \\
\tilde{K}^{41} & \tilde{K}^{42} & \tilde{K}^{43} & \tilde{K}^{44}
\end{bmatrix}
\begin{bmatrix}
\tilde{u}_x^+ \\
\tilde{u}_y^+ \\
\tilde{u}_x^- \\
\tilde{u}_y^-
\end{bmatrix}
= 
\begin{bmatrix}
\tilde{T}_x^+ \\
\tilde{T}_y^+ \\
\tilde{T}_x^- \\
\tilde{T}_y^-
\end{bmatrix}
\] (2.69)

It should be noted that the tractions on the upper and lower cohesive zone nodes is equal and opposite in signs such that \( T_n^+ = -T_n^- \) and \( T_i^+ = -T_i^- \). The details of assembly of the stiffness matrix and the force vector for a node pair is provided in the work by Seidel [137]. However, here the major results of the derivation are presented. Once the global-local coordinate transformations are performed in order to represent the upper and lower tractions in terms of displacements of the cohesive zone nodes in the global coordinate system, the equations for the nodal tractions in the normal and tangential direction can be used to calculate the stiffness matrix and force vector components as

\[
\tilde{K} = 
\begin{bmatrix}
K^{11} - \frac{w}{2} (k^{11}_{i} + k^{11}_{n}) & K^{12} - \frac{w}{2} (k^{12}_{i} + k^{12}_{n}) \\
K^{21} - \frac{w}{2} (k^{21}_{i} + k^{21}_{n}) & K^{22} - \frac{w}{2} (k^{22}_{i} + k^{22}_{n})
\end{bmatrix}
\]

\[
\tilde{T} = 
\begin{bmatrix}
\frac{w}{2} (t^1_{i} + t^1_{n}) \\
\frac{w}{2} (t^2_{i} + t^2_{n})
\end{bmatrix}
\] (2.70)

where \( K^{ij} \) are the components of the stiffness matrix for the cohesive zone node pairs without contributions from cohesive interface stiffness, \( k^{ij}_{n} \) and \( k^{ij}_{i} \) are the components for the normal and tangential cohesive zone stiffness evaluated after spatial transformation at the current time step, \( t^i_{n} \) and \( t^i_{i} \) are the normal and tangential cohesive zone force evaluated after spatial transformation at the current time step vectors, \( w \) is the width of the cohesive zone which is approximated using the averaged distance between adjacent node pairs along a cohesive edge and \( \theta \) is the angle between the local cohesive edge and the global coordinate system measured from \(+x_1\) axis to the orientation of the local cohesive edge. The cohesive zone
stiffness \((k_{ij}^n, k_{ij}^t)\) and force vector \((j_i^n, j_i^t)\) components after transformation can be evaluated for each cohesive zone node pair in 2D using

\[
\begin{align*}
    k_{11}^n &= \begin{bmatrix} -k_n\sin^2\theta & k_n\sin\theta\cos\theta \\ k_n\sin\theta\cos\theta & -k_n\cos^2\theta \end{bmatrix} \\
    k_{11}^t &= \begin{bmatrix} -k_t\cos^2\theta & -k_t\sin\theta\cos\theta \\ -k_t\sin\theta\cos\theta & -k_t\sin^2\theta \end{bmatrix} \\
    k_{12}^n &= -k_{11}^n = k_{21}^n = -k_{22}^n \\
    k_{12}^t &= -k_{11}^t = k_{21}^t = -k_{22}^t \\
    t_1^n &= \begin{bmatrix} T_n^r\sin\theta \\ -T_n^r\cos\theta \end{bmatrix} \\
    t_1^t &= \begin{bmatrix} -T_t^r\sin\theta \\ -T_t^r\cos\theta \end{bmatrix} \\
    t_2^n &= -t_1^n \\
    t_2^t &= -t_1^t
\end{align*}
\]

In the finite element framework, the stiffness matrix components and the force vector components shown in Eqn. 2.69 get added to the assembly of the global stiffness matrix and the global force vector directly corresponding to the appropriate degree of freedoms. It is to be noted that the negative signs on the leading diagonals for the definitions of \(k_{ij}^n\) and \(k_{ij}^t\) are acceptable since a negative of these matrices is added to the overall stiffness matrix in Eqn. 2.70.

### 2.4.2 Electrostatic Cohesive Zone Modeling

For the electrostatic cohesive zone modeling, the mathematical formulation is derived analogous to the mechanical cohesive zones where the interface current density-separation laws are specified which are analogous to the traction-separation laws. The electrostatic potential difference across the interface can be expressed as \(\Delta \phi = \phi^+ - \phi^-\). For the current work, only normal electrostatic current density is allowed at the interface i.e the tangential interface resistance is assumed to be infinite leading to zero tangential current density. The normal current density across the interface can then be expressed as
\[ J^+ = -\frac{\Delta \phi}{w t R^r} - J^r_n \]
\[ J^- = \frac{\Delta \phi}{w t R^r} + J^r_n = -J^+_n \]  

(2.72)

where \( R^r \) is the interface resistance per unit area of the interface at the \( r \)th time step, \( J^r_n \) is the current density applied to the cohesive zone node pair at the \( r \)th time step, \( w \) is the width of the cohesive zones and \( t \) is the plane elasticity thickness for the problem. The current density across the interface after appropriate coordinate transformations can be written as

\[ J^+_x = -\frac{1}{w t R^r}\sin\theta(\phi^+ - \phi^-) - J^r_n\sin\theta \]
\[ J^-_x = \frac{1}{w t R^r}\sin\theta(\phi^+ - \phi^-) + J^r_n\sin\theta \]
\[ J^+_y = \frac{1}{w t R^r}\cos\theta(\phi^+ - \phi^-) + J^r_n\cos\theta \]
\[ J^-_y = -\frac{1}{w t R^r}\cos\theta(\phi^+ - \phi^-) - J^r_n\cos\theta \]  

(2.73)

where \( J^+_x, J^-_x, J^+_y \) and \( J^-_y \) are the current densities at the cohesive zone node pairs in the \( x \) and \( y \) directions. The electrostatic cohesive zone interaction across the interface is represented in terms of components of the conductivity matrix and the current density vector as

\[
\begin{pmatrix}
\tilde{B}^{11} & \tilde{B}^{12} \\
\tilde{B}^{21} & \tilde{B}^{22}
\end{pmatrix}
\begin{pmatrix}
\tilde{\phi}^+ \\
\tilde{\phi}^-
\end{pmatrix} =
\begin{pmatrix}
\tilde{j}^+ \\
\tilde{j}^-
\end{pmatrix}
\]

(2.74)

where \( \tilde{B}^{ij} \) are the equivalents of conductivity components and \( \tilde{j}^+_i \) are the current density vector components obtained from electrostatic cohesive zones. Comparing the conductivity components in Eqn. 2.74 and the transformed expressions for current density components in Eqn. 2.73, the conductivity matrix and current density vector components can be expressed as
\[
\tilde{B} = \begin{bmatrix}
B^{11} - \frac{w}{2} b^{11}_n & B^{12} - \frac{w}{2} b^{12}_n \\
B^{21} - \frac{w}{2} b^{21}_n & B^{22} - \frac{w}{2} b^{22}_n
\end{bmatrix}
\]
\[
\tilde{J} = \begin{bmatrix}
w (j^1_n) \\
w (j^2_n)
\end{bmatrix}
\]

(2.75)

where \(B_{ij}\) are the components of the electrostatic conductivity matrix for the cohesive zone node pairs without contributions from cohesive interface stiffness, \(b_{ij}^{ij}\) are the components for the normal cohesive zone conductivity evaluated after spatial transformation at the current time step, \(j^i_n\) and \(j^j_t\) are the normal and tangential cohesive zone current density evaluated after spatial transformation at the current time step vectors and \(w\) is the width of the cohesive zone which is approximated using the distance between different node pairs. The cohesive zone conductivity components \((b_{i}^{ij}, b_{t}^{ij})\) and current density vector \((t_{i}^i, t_{i}^t)\) components after transformation can be evaluated for each cohesive zone node pair using

\[
\begin{align*}
b_n^{11} &= -\frac{1}{w R} \sin \theta \\
b_n^{12} &= \frac{1}{w R} \sin \theta \\
b_n^{21} &= \frac{1}{w R} \cos \theta \\
b_n^{22} &= -\frac{1}{w R} \cos \theta \\
j_n^1 &= -J_n^i \sin \theta \\
j_n^2 &= J_n^t \cos \theta
\end{align*}
\]

(2.76)

In the finite element framework, the conductivity matrix components and the current density vector components shown in Eqn. 2.75 get added to the assembly of the global conductivity matrix and global current density vector directly corresponding to the appropriate degree of freedoms.

## 2.5 Material Point Method

The description of the micromechanics framework and the cohesive zone modeling so far relies on computational modeling at a subscale using the finite element method. However, the finite element method has its limitations when the composite RVE undergoes large
deformation and damage. In such cases, modeling using finite elements may result in severe distortion of elements under complex local rearrangements resulting in singular matrices. In addition, the connectivity of the elements remains fixed which forces material species to follow certain contact conditions and inhibits material flow. All of these aspects may be critical in modeling nanocomposites especially when process-structure-property relationships needs to explored instead of the structure-property relationships studied herein. As an example, some experimental work in the literature has focused on highly stretchable nanocomposite strain sensors with CNTs dispersed in an elastomeric matrix [130]. For such nanocomposite systems up to 500% applied strains can be applied. Thus, there is a need to move to meshless methods which allow for convection of material through large deformation and flow. The Material Point Method (MPM) is a solution technique for initial boundary value problems which allows for materials particles to kinematically undergo large deformation and flow behavior through an Eulerian-Lagrangian solution scheme.

The MPM algorithm is broadly divided into three phases: Initialization Phase, Lagrangian Phase, and Convective Phase. During the Initialization Phase, the information such as the position of the particles, corresponding mass and velocity are transferred from the material points to the background mesh. In the Lagrangian Phase the equations of motion are solved in an updated Lagrangian framework on the computational mesh. Thereafter, the displacements of the background mesh nodes are calculated by solving the discretized equations of motion. Finally, in the Convective Phase, the momentum of the grid nodes are updated, the particle positions and velocities are hence found by mapping these to the material points and using explicit time integration. The new positions of these material points would, in effect, cause the body to move over the background mesh. These three phases are repeated for each time step, transporting material points and hence material properties assigned to them, over the background mesh. During the course of simulation, the material points can cross over between elements of the background mesh and start contributing to different mesh nodes.

As an example, Fig. 2.2 shows a generalized body at position $X$ in the reference configuration at time $t_0$ as a collection of material points over a rectangular background mesh. On
Figure 2.2: Schematic description of progressive solution scheme in MPM and convection of material points over the background mesh over solution time.

application of initial and boundary conditions to the undeformed body at \( \mathbf{X} \), it deforms to a new position given by \( \mathbf{X} + \mathbf{u}_1 \) at time \( t_1 \). In going from time \( t_0 \) to \( t_1 \), the material points associated with the continuum body have convected over the background mesh, which remains fixed in the space. Similarly, the body undergoes several incremental displacements over time to point \( t_n \) where the final configuration \( \mathbf{x} \) of the body is given by \( \mathbf{x} = \mathbf{X} + \sum_{r=1}^{n} \mathbf{u}_r \).

Since the background spatial mesh is independent of the translation and deformation of the body, the issues relating to mesh entanglement for large displacement and flow problems which are observed in conventional finite element methods can be avoided.

In the Material Point Method (MPM), a continuum body is discretized into \( N_p \) material points, with each point assigned a mass \( M_p \), consistent with the material density. The continuum body composed of discrete material points is overlaid over a background computational Finite Element mesh with \( N_n \) nodes. In general, the number of material points \( (N_p) \) is significantly larger than the number of nodes in the background mesh \( (N_n) \) such that every active background mesh element consists of a finite number of material points. During the course of MPM solution scheme, several key material parameters need to be mapped between the material points and the background mesh. This mapping and its inverse is typically achieved using conventional FEM basis functions, having compact support over the background mesh nodes.

For the two dimensional plane elasticity quasi-static mechanical boundary value problem, the weak form of the conservation of linear momentum in the \( x \) direction without dynamic
terms can be written as

\[ h_e \int_{\Omega} \frac{\partial w_1}{\partial x} \left( C_{11} \frac{\partial u}{\partial x} + C_{12} \frac{\partial v}{\partial y} \right) + \frac{\partial w_1}{\partial y} \left( C_{16} \frac{\partial u}{\partial y} + C_{16} \frac{\partial v}{\partial x} \right) \, d\Omega - h_e \int_{\Omega} w_1 F_x \, d\Omega - h_e \int_{\Gamma_s} w_1 T_x \, d\Gamma_s = 0 \]  

(2.77)

where \( w_1 \) is the test function which needs to be at least once differentiable in \( x \) and \( y \), \( u \) and \( v \) are the displacements in the \( x \) and \( y \) direction, respectively, \( C_{11}, C_{12} \) and \( C_{16} \) are the material constants for plane elasticity, \( \Omega \) is the domain of the body, \( \Gamma_s \) is the part of the boundary where secondary boundary conditions are applied, \( F_x \) is the body force in the \( x \) direction applied over \( \Omega \) and \( T_x \) is the applied traction in the \( x \) direction on \( \Gamma_s \). The traction over the boundary can be written in terms of the displacement components and the normals to the surface as

\[ T_x = \left( C_{11} \frac{\partial u}{\partial x} + C_{12} \frac{\partial v}{\partial y} \right) n_x + C_{16} \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) n_y \]  

(2.78)

where \( n_x \) and \( n_y \) are the components of the normal vector to the boundary, \( \Gamma_s \). In Eqn 2.77, substituting the finite element approximations

\[ w_1 = \psi_i, \quad u = \sum_{j=1}^{N} u_j \psi_j, \quad v = \sum_{j=1}^{N} v_j \psi_j \]  

(2.79)

where \( \psi_i(x, y) \) are the finite element basis function with compact support over the background mesh elements which are at least once differentiable in \( x \) and \( y \), so that Eqn 2.77 can be rewritten as

\[ h_e \int_{\Omega} \frac{\partial \psi_i}{\partial x} \left( C_{11} \sum_{j=1}^{N} u_j \frac{\partial \psi_j}{\partial x} + C_{12} \sum_{j=1}^{N} v_j \frac{\partial \psi_j}{\partial y} \right) + \frac{\partial \psi_i}{\partial y} \left( C_{16} \sum_{j=1}^{N} u_j \frac{\partial \psi_j}{\partial y} + C_{16} \sum_{j=1}^{N} v_j \frac{\partial \psi_j}{\partial x} \right) \, d\Omega - h_e \int_{\Omega} \psi_i F_x \, d\Omega - h_e \int_{\Gamma_s} \psi_i T_x \, d\Gamma_s = 0 \]  

(2.80)

Eqn. 2.80 can be further written in a simplified form as

\[ h_e \int_{\Omega} \sum_{j=1}^{N} K_{ij}^{11} u_j \, d\Omega + h_e \int_{\Omega} \sum_{j=1}^{N} K_{ij}^{12} v_j \, d\Omega - h_e \int_{\Omega} \psi_i F_x \, d\Omega - h_e \int_{\Gamma_s} \psi_i T_x \, d\Gamma_s = 0 \]  

(2.81)
where $K_{ij}^{11}$ and $K_{ij}^{12}$ are expressed as

\[
K_{ij}^{11} = C_{11} \frac{\partial \psi_i}{\partial x} \frac{\partial \psi_j}{\partial x} + C_{66} \frac{\partial \psi_i}{\partial y} \frac{\partial \psi_j}{\partial y} \\
K_{ij}^{12} = C_{12} \frac{\partial \psi_i}{\partial x} \frac{\partial \psi_j}{\partial y} + C_{66} \frac{\partial \psi_i}{\partial y} \frac{\partial \psi_j}{\partial x}
\]  
(2.82)

Similar to Eqn. 2.77, the weak form of the conservation of linear momentum in the $y$ direction can be subjected to the same procedure resulting in a discretized equation similar to Eqn. 2.81. The conservation of linear momentum in the $y$ direction with the finite element approximation can be written as

\[
h_e \sum_{j=1}^{N} K_{ij}^{21} u_j d\Omega + h_e \sum_{j=1}^{N} K_{ij}^{22} v_j d\Omega - h_e \int_{\Omega} \psi_i F_y d\Omega - h_e \int_{\Gamma_s} \psi_i T_y d\Gamma_s = 0 
\]  
(2.83)

where $K_{ij}^{21}$ and $K_{ij}^{22}$ can be expressed as

\[
K_{ij}^{21} = K_{ij}^{12} = C_{12} \frac{\partial \psi_i}{\partial x} \frac{\partial \psi_j}{\partial y} + C_{66} \frac{\partial \psi_i}{\partial y} \frac{\partial \psi_j}{\partial x} \\
K_{ij}^{22} = C_{66} \frac{\partial \psi_i}{\partial x} \frac{\partial \psi_j}{\partial x} + C_{22} \frac{\partial \psi_i}{\partial y} \frac{\partial \psi_j}{\partial y}
\]  
(2.84)

The integrals in Eqn. 2.81 and Eqn. 2.83 are evaluated over the background mesh elements using numerical integration over a set of material points distributed over the domain. These material points carry all of the constitutive information between every time/load step in an updated Lagrangian fashion, resulting in convection of the body comprised by these material points, over the background computational mesh. In other words, the material points in MPM serve as the numerical Gauss points when compared to the tradition finite element framework. The entire volume of the background mesh elements is represented in the calculation of the effective stiffness matrix for each active element since a large number (say 50 or larger) of the material particles are expected to occupy each background mesh element. This form of numerical gauss integration is an artifact of approximating the material density in MPM using a Dirac delta function which can be expressed as
\[ \rho(x, t) = \sum_{k=1}^{M} M_k \delta(x - x_k^t) \] (2.85)

where \( M_k \) is the specific mass of each material particle and \( x_k \) are the locations of each of the \( M \) material points. For quasi-static simulations, assuming that the density of material is uniform since the material points are uniformly/randomly seeded with more or less similar interparticle distances and there is no time dependence, the density \( \rho(x, t) \) can be eliminated from the equations but the Dirac delta function remains leading to Gauss integration over the material points. The numerical integration of the integral, then, follows a general definition which is written as

\[ \int_{\Omega} F(x, y) d\Omega = \sum_{k=1}^{M} F(x_k, y_k) w_k \] (2.86)

where \( F(x, y) \) is any continuous and differentiable function, \((x_k, y_k)\) are the positions of \( M \) material points over the domain \( \Omega \). Unlike the numerical integration in finite element method, the numerical integration is performed over the actual element instead of an associated isoparametric element which eliminates the need of a Jacobian matrix in the formulation as would be expected for finite element solutions. The weights for the material particles, \( w_k \), are the specific masses of the material points for a full 3D transient model. However, for 2D quasi-static analysis with no inertial forces, \( w_k \) becomes the area associated with each material point. In the current work, the material particles are seeded using a uniform triangular random element mesh with statistically similar element sizes. The areas associated with a material point are calculated in the current work as an average of one-third of the adjoining elements to each material point. These weights can be initially assigned depending on the seeding method for the material particles, and can be updated during the solution process which is especially needed for large deformation problems where the initial material point seeding evolves significantly with time.

Using the numerical integration described in Eqn. 2.86, the conservation of linear momentum
with finite element approximation, as shown in Eqn. 2.81 and 2.83, can be written as

\[
\begin{bmatrix}
    K^{11}_{ij}(x_k, y_k) & K^{12}_{ij}(x_k, y_k) \\
    K^{21}_{ij}(x_k, y_k) & K^{22}_{ij}(x_k, y_k)
\end{bmatrix}
\begin{bmatrix}
    u_j \\
    v_j
\end{bmatrix}
-
\begin{bmatrix}
    h_e \sum_{k=1}^{M} \sum_{j=1}^{N} \psi_i(x_l, y_l) T_x(x_k, y_k) w_l \\
    h_e \sum_{k=1}^{M} \sum_{j=1}^{N} \psi_i(x_l, y_l) T_y(x_k, y_k) w_l
\end{bmatrix} = 0
\]

(2.87)

where \( K_{ij}^{AB}(x_k, y_k) \) components with \((A, B) \in [1, 2]\) are defined using the expression defined in Eqn. 2.82 and Eqn. 2.84 and evaluated at the location of the material points \((x_k, y_k)\). Similarly, the body force, traction and basis functions are evaluated at the material point locations, \((x_k, y_k)\). The last term in each of Eqn. 2.87 is summed over \( M_s \) which are the set of material points on the boundary where the secondary boundary conditions are prescribed. The system of equations described in Eqn. 2.87 can be simplified into a matrix form for computations as

\[
\begin{bmatrix}
    K^{11} & K^{12} \\
    K^{21} & K^{22}
\end{bmatrix}
\begin{bmatrix}
    u \\
    v
\end{bmatrix}
=
\begin{bmatrix}
    f_x \\
    f_y
\end{bmatrix}
\]

(2.88)

which can be solved using conventional banded symmetric solvers. Once the displacement components at the nodes of the background mesh are obtained by solving the set of equations described in Eqn. 2.88, these displacement components are used to update the positions of the material particles in the domain using standard finite element basis functions. One of the options is to use the same basis functions which were used for the test and trial functions such that

\[
u^t_i(x^t_k) = \sum_{k=1}^{M} u^t_k \psi_k(x^t_i)
\]

(2.89)

where \( t \) is the quasi-static solution time for the incremental Lagrangian problem. \( x^t_i \) are
the coordinates of the background mesh nodes and $x_k^t$ are the coordinates of the material points. Similarly, the other field variables (strains and electric fields in an electromechanical BVP) which are dependent on the derivatives of the displacements are updated using the derivatives of the basis functions (and a constitutive law for the case of stress and current density) to increment the prior value of these field variables as

$$
\begin{align*}
  x &= X + \sum_{r=1}^{n} u_r \\
  \varepsilon &= \varepsilon^0 + \sum_{r=1}^{n} \varepsilon_r \\
  \sigma &= \sigma^0 + \sum_{r=1}^{n} \sigma_r 
\end{align*}
$$

(2.90)

where $\varepsilon^0$ and $\sigma^0$ are the initial strain and stress in the underformed configuration, if any. Once the positions of the material particles have been updated, the background mesh is reset to the original configuration and the process is repeated akin to defining a new reference configuration for the next increment for the next quasi-static time step. When repeated over a number of steps, this algorithm leads to convection of material particles over the background mesh. In the process, the background mesh elements may change from inactive to active or vice-versa which needs to be evaluated at every increment. For the inactive background mesh, the stiffness matrices are modified to result in a trivial solution with zero displacements of the nodes.

Specifying the primary boundary conditions in MPM is non-trivial, as is the case for most meshless methods [138]. This is because the local values of the primary variables at the boundary are dependent on a set of particles in the region of influence, which for MPM is the background mesh element in which the material particle lies. In MPM, there are two possible options to apply the primary boundary conditions, e.g. displacement components. The first alternative is to apply the primary boundary conditions on the background mesh nodes instead of the foreground material particles. For the boundary condition to be satisfied well, the material particles where the boundary condition was to be specified should lie
on the edges the elements. This would require a mesh which conforms to the geometry of the body, which is undesirable. The second alternative is to use a penalty function method or a Lagrange multiplier method, where the primary boundary conditions are specified as constraints in the weak form of the problem through an effective penalty or Lagrange multipliers. The discretization of these terms in the weak form results in components which modify the stiffness matrix and the force vector appropriately, such that the primary boundary conditions are satisfied at least in a weak sense. Using either of these methods leads to application of the boundary conditions on the material particles at the boundaries such that a conforming mesh is not needed. However, the penalty parameter or the Lagrange multipliers need to be either specified or evaluated, which may be non-trivial for some cases. For the current work, a penalty function [138] based method is used for application of primary boundary conditions.
Chapter 3

Nanocomposite Nanoscale Effective Piezoresistive Response

The micromechanics based 2-scale modeling scheme introduced in Chapter 2 based on energy equivalence methods is used to evaluate the effective nanocomposite properties at the nanoscale. The nanoscale boundary value problem (BVP) is solved using finite element method to evaluate the nanoscale local electromechanical field variables which are averaged and further used to evaluate the effective nanoscale properties for CNT-polymer nanocomposites. The nanoscale computational domain is chosen to have a periodic hexagonal arrangement of CNTs in the polymer matrix assuming that the CNTs are infinitely long. The infinite aspect ratio of CNTs allows for plane strain approximations such that only a 2D BVP is solved at the nanoscale. In addition, non-continuum electron hopping phenomenon is included in the nanoscale finite element modeling by modifying the electrostatic properties of the intertube polymer medium based on the intertube separation distance between corresponding pairs of CNTs. A parametric study is conducted by varying the electron hopping range and nanoscale CNT volume fraction to assess their effect on the effective nanoscale electromechanical properties. This is done for several different cases of applied boundary conditions to identify unique components of the piezoresistive strain tensor components and the corresponding effective nanoscale gauge factors for CNT-polymer nanocomposites. The results presented in this chapter are published in [139].
3.1 Nanocomposite Morphology

In order to study the piezoresistive effect which originates from several length scale dependent mechanisms, a multiscale model accounting for these mechanisms at appropriate length scales is needed. An important question for multiscale nanocomposite modeling is the identification of the key scales and the corresponding scale dependent phenomena. The multiscale modeling idealization for the general SWCNT-polymer nanocomposites composed of randomly oriented SWCNT bundles considered here is shown in Fig. 3.1.

![Multiscale modeling idealization for the nanocomposites composed of randomly oriented SWCNT bundles consisting of locally aligned high aspect ratio SWCNTs.](image)

Figure 3.1: Multiscale modeling idealization for the nanocomposites composed of randomly oriented SWCNT bundles consisting of locally aligned high aspect ratio SWCNTs.

The scale of particular interest for the current work is the nanoscale ($\approx 10^{-9}m$), where electron hopping between nanotubes is expected to be one of the dominant phenomenon governing the electrical properties of the nanocomposite. While CNT polymer nanocomposites can be idealized as a homogeneous material domain at the macroscale, at the microscale one can start to differentiate between bundles of nanotubes and the polymer matrix. In an actual microstructure, these bundles might have significant variation in the distribution and orientation of nanotubes along the length. However, for the current study, the key assumption is that the microscale bundles are composed of several, identical, aligned SWC-
NTs arranged in a regular periodic hexagonal arrangement and bound together by polymer matrix. The dimensions of the computational domain are determined based on the volume fraction of SWCNTs inside the bundles. For this study, we will assume that all microscale bundles are identical and are composed of same volume fraction of aligned SWCNTs, implying that there is only need for one nanoscale RVE that is representative of all of the nanotube bundles in the nanocomposite. The local volume fraction of SWCNTs inside the bundles can be identified as,

\[ v_f^{CB} = \frac{N^{CNT}Vol_{CNT}}{Vol_B} \]  

(3.1)

where \( N^{CNT} \) is the number of CNTs inside the bundles with \( Vol_{CNT} \) and \( Vol_B \) as the volumes of an individual CNT and the nanotube bundles, respectively. The volume fraction of the SWCNTs within the nanocomposite can therefore be written as \( v_f^{CNT} = v_f^{CB}v_f^B \), where \( v_f^B \) is the volume fraction of the bundles in the microstructure. It can be recognized that the volume fraction of CNTs in the polymer matrix can be deduced to a certain degree of confidence, but finding the volume fraction of CNTs inside the CNT bundles is a non trivial task. However, it is expected that \( v_f^{CB} \) will be much higher (0.1 – 0.8) than \( v_f^{CNT} \) which is typically less than 0.01 for fully percolated systems. Some work in the literature has suggested based on scanning electron microscope (SEM) imaging that the bundle volume fraction is 0.48 [140]. Other studies have found the local bundle volume fraction to be less than 0.48 for all cases [141]. Some others have reported that the local intertube distances between the CNTs in the CNT bundle (also called CNT ropes) are between 0.3-0.4nm i.e. a bundle volume fraction of about 0.7 [142, 143]. In this study, RVEs at several different volume fractions (\( v_f^{CB} \)) in the range 0.15-0.6 are constructed to demonstrate key features of the electron hopping mechanism. Fig. 3.1 shows the aligned SWCNTs inside the bundles at the nanoscale, which when looking in the direction of CNT alignment are arranged in a regular periodic hexagonal array. Identifying the periodicity of the microstructure, a 2D plane strain nanoscale RVE is used in this study as shown in Fig. 3.1, shown there at what corresponds to a volume fraction of 0.58 which is contoured according to the conductivity in the unstrained state with no electron hopping. The red region, of high conductivity,
corresponds to the nanotubes while the blue corresponds to the polymer matrix.

Table 3.1: Material parameters for continuum representation of the nanotube and polymer as an isotropic homogeneous material [72,135,144]. (E: Young’s Modulus, ν: Poisson’s ratio, Σ_{ij}: Electrostatic conductivity components)

<table>
<thead>
<tr>
<th>Material Description</th>
<th>E</th>
<th>ν</th>
<th>Σ_{ij}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure matrix (no electron hopping): EPON 828</td>
<td>3.07 GPa</td>
<td>0.3</td>
<td>(1.11 \times 10^{-9}) S/m if (i = j)</td>
</tr>
<tr>
<td>Isotropic hollow representation of CNT (15,15) armchair</td>
<td>1100 GPa</td>
<td>0.14</td>
<td>(1 \times 10^5) S/m if (i = j)</td>
</tr>
</tbody>
</table>

For the results presented herein, the outer nanotube diameter and thickness were chosen to be 2nm and 0.34nm, respectively, corresponding to CNT (15,15) armchair configuration [72]. The CNT and polymer material models are assumed to be uniform and isotropic in the unstrained state (with no electron hopping) for both the mechanical and electrostatic properties which are provided in Tab. 3.1. In the current study, a 2-scale model will be considered with a homogeneous macroscale nanocomposite subjected to uniform strains with aligned SWCNTs at the nanoscale. The effective properties reported in this study can also be representative of the microscale nanotube bundle response to applied strain if the morphology variation at each scale (macro-micro-nano scale) is addressed.

### 3.2 Electron Hopping/Electrical Tunneling

Several models for CNT/polymer nanocomposites idealize the CNT/polymer matrix as a thin dielectric film separating two conducting surfaces based on a model proposed by Simmons [48]. Physically, there is a potential barrier for the electrons to hop across the polymer layer to another nanotube in its vicinity. Depending on the electronic structure in the vicinity of the electrons, the electrons will be in a certain energy state. As the nanotubes get closer, the electrons in higher energy states start to jump over to the other nanotube under the influence of the electric field. Hence, the thickness of the polymer layer separating two
CNTs plays a key role in determining the probability of electrons hopping, and thus in determining the tunneling (or electron hopping) resistance. If the nanotubes are separated by a distance $d_{CNT-CNT}$, which is greater than the maximum electron hopping range of the electrons associated with the nanotubes ($\delta_{EH_{max}}$), the electrons lose the ability to hop across to the neighboring nanotube. As the separation distance decreases, electrons become capable of jumping across the two nanotubes forming a higher current density path in between the nanotubes. The magnitude of the current density in the intertube region depends on the tunneling resistance and the applied electric field. The key idea is that any driving force that causes the nanotubes to get closer or to move away from each other, e.g. mechanical [32,34,40], electrical [145], magnetic [146] etc., would change the corresponding intertube electron hopping response, thus, changing the macroscale electrical behavior of the nanocomposite.

A linear relationship between the log of tunneling resistance and the thickness of the separating polymer film has been reported in the literature [34] based on Simmons’ model [48]. The relationship is such that as the intertube distance decreases, the current density in the conductive path established between them increases rapidly up to the point of CNT-CNT direct contact. An increase in the intertube distance causes the conductivity of the intertube region to decrease. Using this relation, Li et al. (Fig. 2 in [34]), predicted a linear relation between log of tunneling resistance ($\log[R_{EH}]$) and the thickness of the insulating film ($d_{CNT-CNT}$) with 1.8nm maximum electron hopping range, assuming a constant cross sectional area across which the electron hopping occurs. For the purpose of this study, log of resistivity ($\rho_{EH}$) as a linear function of CNT separation distance (thickness of the insulating medium), i.e. linear $\log[\rho_{EH}]$ vs. $d_{CNT-CNT}$, will be used to find the conductivity across the tunneling region. The conductivity of the intertube region based on the linear $\log[\rho_{EH}] - d_{CNT-CNT}$ curve can be written as

$$\hat{\Sigma}^{(EH)}_{ij}(d_{CNT-CNT}) = \begin{cases} \hat{\Sigma}^{(CNT)}_{ij}(\frac{d_{CNT-CNT}}{\delta_{EH_{max}}}) & d_{CNT-CNT} < \delta_{EH_{max}} \\ \hat{\Sigma}^{(poly)}_{ij}(\frac{d_{CNT-CNT}}{\delta_{EH_{max}}}) & d_{CNT-CNT} \geq \delta_{EH_{max}} \end{cases}$$

where $\Sigma^{(CNT)}_{ij}$ and $\Sigma^{(poly)}_{ij}$ are components of the conductivity tensors for the CNT and pure
polymer (no electron hopping) in its unstrained state, respectively, and () on the subscripts signifies no summation on the index. Fig. 3.2 shows the variation in intertube conductivities with the intertube CNT separation distance \( d^{CNT-CNT} \) when the maximum electron hopping range \( \delta_{max}^{EH} \) is chosen to be 5nm.

![Figure 3.2: Intertube conductivity/resistivity versus CNT separation distance (\( d^{CNT-CNT} \)) curves. [139]](image)

The nanoscale electron hopping effect allows for the electrons to hop from one CNT to another when they are separated by a distance less than the maximum electron hopping range, even in the presence of a dielectric medium in between the CNTs. In some studies [34, 147], the current density between the nanotubes is modeled as an effective intertube resistance, which is approximated by Simmon’s relation [48] as

\[
\hat{R}^{EH} = \frac{\Delta V}{AJ} = \frac{\hbar^2 d}{Ae^2 \sqrt{2m\lambda}} \exp\left( \frac{4\pi d}{\hbar \sqrt{2m\lambda}} \right)
\]  

where \( \Delta V \) is the electrostatic potential difference, \( A \) is the area of cross section with unit normal in the direction of electron hopping, \( J \) is the electrostatic current density between the CNTs, \( \hbar \) is the Plank’s constant, \( d \) is the intertube distance, \( e \) is the quantum of charge, \( m \) is the mass of an electron and \( \lambda \) is the height of the potential barrier for electron hopping. The key parameters that determine the intertube resistance are the intertube distance and the electron hopping barrier potential. A longer intertube distance results in a larger intertube resistance for a given value of electron hopping barrier potential, \( \lambda \). A larger value of the
electron hopping barrier potential results in a smaller maximum electron hopping range \( \delta_{EH}^{max} \), and for a fixed intertube distance results in larger intertube resistance.

In the current work, the position of each of the CNTs in the nanoscale RVEs is tracked at each applied quasi-static strain step. The local conductivity of the polymer matrix in the nanoscale RVEs is modified based on the intertube resistance relation. For a material point \( \hat{x}_i^P \) in the polymer medium, the intertube distance \( d \) is approximated [147] as the sum of the distance to the two nearest CNTs from \( \hat{x}_i^P \). The periodicity of nanoscale microstructure is taken into account by assuming a set of ghost CNTs outside the nanoscale RVE with the same hexagonal arrangement. The electron hopping barrier potential \( \lambda \) depends on the type of CNT and the polymer matrix medium, with values typically between 0.05eV and 2.5eV for Epoxy [12]. Once the electron hopping barrier potential for a given CNT-polymer pair is chosen and the distance \( d \) is determined, the local conductivity of the polymer medium at a material point \( \hat{x}_i^P \) is given by

\[
\hat{\Sigma}_{EH} = \left( \frac{\hat{R}_{EH} A}{d} \right)^{-1} = \left[ \frac{h^2}{e^2 \sqrt{2m\lambda}} \exp \left( \frac{4\pi d}{h} \sqrt{2m\lambda} \right) \right]^{-1}
\]  
(3.4)

where \( \hat{\Sigma}_{EH} \) is the electron hopping augmented local polymer conductivity in the nanoscale RVE. The local conductivity of electron hopping augmented polymer medium evolves with applied strains as the positions of CNTs and the intertube distances change. The evolution of local polymer conductivities with applied strains and the associated changes in local current density pathways lead to an observed effective piezoresistive response in CNT-polymer nanocomposites, as has been observed in other modeling efforts [133,136,139].

### 3.3 Finite Element Modeling, Boundary Conditions and Design of Parametric Study

The mechanical BVP at the nanoscale follows the standard methodology used to solve plane strain mechanical BVPs [148]. The strong form of the governing equation for the nanoscale
electrostatic boundary value problem can be derived using Eqn. 2.42, 2.43 and 2.44 to be

\[ [-\hat{\Sigma}^{(r)}_{ij} \hat{\phi},_j],_i = 0 \]  

(3.5)

where \((r)\) denotes the different electrostatic conductivity tensor corresponding to the SWCNT annulus, matrix or the intertube/electron hopping region. In order to develop the weak form, Eqn. 3.5 is multiplied by a test function \(w\) which is continuous and differentiable in the domain. Applying the finite element approximation with standard linear basis functions \((\psi)\) for triangular elements to represent the test function and the primary variables in terms of nodal variables, the weak form of Eqn. 3.5 is obtained as

\[
\left[ \int_{\hat{\Omega}^E} -\hat{\Sigma}^{(r)}_{ij} \psi_m,i\psi_n,j d\hat{\Omega} \right] \hat{\phi}_n = \int_{\hat{\Gamma}^E} \psi_m \hat{J}_i \hat{n}_i d\hat{\Gamma}
\]

(3.6)

where \(\hat{\Omega}^E\) and \(\hat{\Gamma}^E\) represent the elemental area and boundaries, respectively. In order to implement the electron hopping mechanism in a continuum finite element framework the strains are applied in an incremental fashion through displacement boundary conditions on the nanoscale RVE. The spatial derivatives on the conductivity components have been set to zero in Eqn. 3.6 indicating that the conductivities are piecewise constant over the polymer, CNT and the intertube region for a given strain increment. At every strain increment, the positions of the CNTs within an RVE are tracked and the separation distance between every pair of nanotubes (shortest distance between the outer surfaces of the nanotubes) is evaluated. For an element in the matrix region with the corresponding integration point lying within the region between the nanotubes, the conductivity is modified based on Eqn. 3.2. It is to be noted that if an element were to lie between the intertube region of more than one pair of nanotubes, the conductivity associated with the pair of nanotubes with the minimum separation distance overrides the conductivities which would be assigned based on the other, further separated CNTs.

The approach has been implemented within an in-house finite element code and has been used to study the nanoscale RVEs. These RVEs are subjected to mechanical and electrostatic
boundary conditions with continuity of displacements, tractions, electrostatic potential, electrostatic flux imposed at the SWCNT-matrix interfaces and zero tractions, electrostatic flux conditions are applied at the free SWCNT internal boundaries.

Table 3.2: Mechanical boundary conditions applied on the nanoscale RVE to find effective piezoresistive properties (Ref: Fig. 3.1). [139]

<table>
<thead>
<tr>
<th>Type of Test</th>
<th>Boundary Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane strain tension/</td>
<td></td>
</tr>
<tr>
<td>compression test</td>
<td>Edge AB: ( \dot{u}_2 = 0 )</td>
</tr>
<tr>
<td></td>
<td>Edge BC: ( \dot{t}<em>i = n_j \hat{\sigma}</em>{ij} = 0 )</td>
</tr>
<tr>
<td></td>
<td>Edge CD: ( \dot{u}_2 = \pm \hat{\varepsilon}_0 L )</td>
</tr>
<tr>
<td></td>
<td>Edge DA: ( \dot{t}<em>i = n_j \hat{\sigma}</em>{ij} = 0 )</td>
</tr>
<tr>
<td>Plane strain constrained</td>
<td></td>
</tr>
<tr>
<td>tension/compression test</td>
<td>Edge AB: ( \dot{u}_2 = 0 )</td>
</tr>
<tr>
<td></td>
<td>Edge BC: ( \dot{u}_1 = 0 )</td>
</tr>
<tr>
<td></td>
<td>Edge CD: ( \dot{u}_2 = \pm \hat{\varepsilon}_0 L )</td>
</tr>
<tr>
<td></td>
<td>Edge DA: ( \dot{u}_1 = 0 )</td>
</tr>
<tr>
<td>Plane strain shear test</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Edge AB: ( \dot{u}_1 = 0, \dot{u}_2 = 0 )</td>
</tr>
<tr>
<td></td>
<td>Edge BC: ( \dot{t}<em>i = n_j \hat{\sigma}</em>{ij} = 0 )</td>
</tr>
<tr>
<td></td>
<td>Edge CD: ( \dot{u}_1 = \pm \hat{\varepsilon}_0 L )</td>
</tr>
<tr>
<td></td>
<td>Edge DA: ( \dot{t}<em>i = n_j \hat{\sigma}</em>{ij} = 0 )</td>
</tr>
</tbody>
</table>

The boundary conditions have been chosen to demonstrate the impact of electron hopping on the effective piezoresistive response of the nanocomposite for different cases of uniform loading at the macroscale, which result in displacement and traction boundary conditions for the nanoscale RVE as shown in Table 3.2. The edges AB, BC, CD and DA are indicated in Fig. 3.1, with L and W denoting the length and width of the nanoscale RVE at the corresponding volume fraction. Similarly, the electrostatic boundary conditions have been designed to represent the macroscale uniform electric field required to assess the effective conductivity components for a plane strain transverse RVE, which, when coupled to the applied uniform strain states, will also lead to the determination of the macroscale effective piezoresistive tensor components. Table 3.3 provides the potential and electrostatic flux boundary conditions applied on the nanoscale RVE for cases of electrostatic boundary conditions considered for the current study. For this study, a comparison between unconstrained and constrained uniaxial tension and compression is undertaken to demonstrate tension/compression asymmetry and the influence of different boundary conditions on the piezoresistive response of the nanocomposite. The piezoresistive response under the influence of shear strains is
also considered and contrasted with the uniaxial loading cases. The displacement boundary conditions corresponding to a uniform macroscale strain state used in the current study lead to the exact effective properties for the plane strain tension/compression tests because the bounds of effective property obtained using uniform macroscale strain or uniform macroscale stress fields are coincident for these tests. However, for the in-plane shear test, the bounds are not coincident. For the in-plane shear test, displacement boundary conditions corresponding to uniform macroscale strain, as shown in Table 3.2, leads to the upper bound of effective properties [132].

Table 3.3: Electrostatic boundary conditions applied on the nanoscale RVE to find effective electrostatic properties (Ref: Fig. 3.1). [139]

<table>
<thead>
<tr>
<th>Type of Test</th>
<th>Boundary Conditions</th>
</tr>
</thead>
</table>
| Uniform electric field in the Y direction to obtain $\Sigma_{22}^{\text{Eff}}$ and $\Sigma_{12}^{\text{Eff}}$ | Edge AB: $\Phi = -E_0 L$  
Edge BC: $\hat{n}_i \hat{J}_i = 0$  
Edge CD: $\Phi = E_0 L$  
Edge DA: $\hat{n}_i \hat{J}_i = 0$ |
| Uniform electric field in the X direction to obtain $\Sigma_{11}^{\text{Eff}}$ and $\Sigma_{21}^{\text{Eff}}$ | Edge AB: $\hat{n}_i \hat{J}_i = 0$  
Edge BC: $\Phi = -E_0 W$  
Edge CD: $\hat{n}_i \hat{J}_i = 0$  
Edge DA: $\Phi = E_0 W$ |

The mechanical boundary conditions are applied in an incremental fashion such that the effective electrostatic properties can be calculated at every strain step. However, the potentials applied at the boundaries are kept constant because they act as test electric fields applied on the nanoscale RVE. The change in applied electric field as deformations are applied on the RVE are accounted for by using the current test electric field as the estimate of averaged electric field in the domain. The corresponding conductivity and piezoresistive coefficients are independent of the applied test electric field ($E_0$).

In order to understand the origins of macroscale piezoresistivity in CNT-polymer nanocomposites, it is essential to study the complexities of the electron hopping induced formation/disruption of conductive pathways. The key factors that influence the nanoscale electron hopping and the subsequent evolution of nanoscale electrostatic morphology are
• the initial intertube distance between the nanotubes corresponding to a given nanoscale volume fraction.

• the maximum electron hopping range, which determines the percolation volume fraction and the rate of change in local conductivity due to evolving intertube distances.

• the type of boundary conditions applied to the nanoscale medium which is representative of the local macroscale strain state e.g. uniform macroscale strain state cases leading to plane strain tension/compression or plane strain shear at the nanoscale.

Figure 3.3: Intertube conductivity plots corresponding to linear $\log[\rho^{EH}] - d_{CNT-CNT}^C$ relation (Eqn. 3.2) with the unstrained intertube separation distance marked for the different volume fractions ($V_f$) and maximum electron hopping range ($\delta_{EH}^{max}$). Inset shows the true exponential variation of the intertube conductivity with increasing intertube distance. [139]

In order to observe the effect of each of these factors, the strain induced electron hopping pathways are studied for different volume fractions and varying maximum electron hopping distances. For the nanoscale RVE with regular hexagonal microstructural arrangement, any adjacent pair of nanotubes will have the same intertube distance ($d_{CNT-CNT}$) in the unstrained state. For example, the nanoscale RVEs with CNT volume fractions ($V_f$) of 0.15, 0.25, 0.40 and 0.58 considered herein have corresponding unstrained intertube distances ($d_{CNT-CNT}$) of 3nm, 1.75nm, 1nm and 0.5nm, respectively, such that the nanotubes are
separated by a larger region of polymer matrix for low volume fractions. Based on the maximum electron hopping range \((\delta_{EH}^{max})\), these intertube distances may correspond to percolated or unpercolated nanoscale RVE. In the current work, the percolation threshold is defined as the volume fraction at which the intertube distance becomes equal to the maximum electron hopping range. The percolation volume fractions reported herein correspond to well dispersed uniformly aligned CNTs in polymer matrix or to the bundle effective properties. The experimentally observed percolation volume fractions in the literature can be significantly different because of a departure from uniform alignment and the formation of microscale bundles which may lead to much lower percolation concentrations where the key is microscale dispersion of CNT bundles which is not accounted for in the current description of the RVE. For example, if the maximum electron hopping range is 1.8nm, then the volume fractions of 0.40 and 0.58 will be in a percolated state as the intertube separation distance is less than the maximum electron hopping range, whereas, the volume fractions of 0.15 and 0.25 are in an unpercolated state. Thus, the maximum electron hopping distance determines the percolation volume fraction for the nanoscale RVEs such that an increase in the maximum electron hopping range results in percolation at a lower volume fraction. For example, the transverse percolation volume fraction for \(\delta_{EH}^{max}\) of 1.8nm, 5nm and 10nm for nanotubes arranged in regular hexagonal fashion are 0.25, 0.074, 0.025 respectively. Moreover, the conductivity of the intertube region is directly dependent on the maximum electron hopping range and intertube distance through an exponential relationship as indicated in Eqn. 3.2. A longer maximum electron hopping range results in a smaller exponent such that the relative rate of change in local intertube conductivity is smaller for a given variation in the intertube distance. Fig. 3.3 shows (circled points) the unstrained CNT separation distances corresponding to different volume fractions along the intertube conductivity-separation distance \((\Sigma_{EH} - d_{CNT-CNT})\) curves for maximum electron hopping distances \((\delta_{EH}^{max})\) of 1.8nm, 5nm and 10nm. The effective nanoscale electrostatic and piezoresistive response is observed to be highly influenced by the position of unstrained intertube distance along the \(\Sigma_{EH} - d_{CNT-CNT}\) curves.
3.4 Effect of Different Applied Boundary Conditions on the Effective Piezoresistive Response

3.4.1 Unconstrained Plane Strain Tension/Compression Response

In order to study the effect of uniform macroscale tensile/compressive applied strains, an RVE with a volume fraction of 0.58 is subjected to unconstrained plane strain tension/compression test as described in Table 3.2. The strains are applied in the 2-direction on the nanoscale RVE through incremental displacements of edge CD while edge AB fixed in the 2-direction. The maximum electron hopping range ($\delta_{EH}^{\text{max}}$) is fixed at 5nm such that the nanoscale RVE with unstrained intertube distance of 0.5nm is in the percolated state. It is noted that the current case corresponds to point II in Fig. 3.3. The local nanoscale conductivity contours are shown in Fig. 3.4 for different applied tension/compression states. It is observed that applied tensile strains cause the nanotubes to move further apart from each other in the 2-direction such that the local intertube conductivity is reduced significantly in the intertube regions that connect the vertically adjacent nanotube pairs. As an example, for the CNT pair C1-C2, the intertube distance increases from 0.5nm in the unstrained state to 0.63nm at 5% applied tensile strain as shown in Fig. 3.5a. The increasing intertube distance results in decreasing intertube conductivity between CNTs C1-C2, as shown in Fig. 3.5b, with about 53% drop observed in local intertube conductivity from the unstrained state to 5% applied tensile strain state. The intertube distances and conductivities of other vertically adjacent nanotube pairs like C3-C4, C1-C5 etc. follow the same variation. While the nanotubes get separated in the 2-direction, the nanoscale RVE experiences Poisson’s contraction in the 1-direction bringing the nanotubes closer to each other in the 1-direction such that the intertube distance between the diagonally adjacent CNTs increases at a slower rate. Thus, the conductivity of the diagonal intertube bands decreases at a smaller rate as compared to the vertical intertube bands, as indicated for the diagonal CNT pair C1-C3 in Fig. 3.5b. At 5% applied tensile strain, the local conductivity of the diagonal intertube bands drops by only about 8% as compared to 53% drop in local conductivity of the vertical bands. The relatively higher local conductivity of the diagonal bands overrides the highly reduced
conductivity of vertical intertube bands resulting in small pockets of low conductivity matrix between vertically adjacent nanotubes.

Figure 3.4: Effective conductivity components, $\Sigma_{11}^{Eff}$ and $\Sigma_{22}^{Eff}$, for an RVE with volume fraction of 0.58 with $\delta_{max}^{EH}$ fixed at 5nm (point II in Fig. 3.3) subjected to unconstrained tension/compression test with contour plots of local nanoscale conductivity contours at different strain states. The color bars for the local conductivity contours are modified to be non-linear near the bounds such that the limiting values represent CNT and Polymer conductivity. The contour plots show the deformed configuration with no displacement magnification. [139]

On the other hand, applied compressive strains result in the nanotubes getting closer to each other in the 2-direction while slightly diverging in the 1-direction because of Poisson’s expansion. Thus, while the vertically adjacent nanotube pairs get closer to each other and form high intertube conductivity bands, the diagonally adjacent nanotubes get closer to each other at a much slower rate. As an example, the intertube distance in between the pair C1-C2 is reduced by 0.128nm and thus the C1-C2 intertube conductivity increases by about 116% while the intertube distance between the pair C1-C3 decreases by 0.012nm resulting in only about 7% increase in C1-C3 intertube conductivity. Unlike the applied tension case, the vertical bands of highly increased conductivity override the diagonal band of slightly increased conductivity leading to conductivity contours as shown in Fig. 3.4.

In order to find the effective conductivity components, a test electric field ($E_0$) is applied on the nanoscale RVE in the 1 and 2 direction individually, as described in table 3.3, along
with the incrementally applied strains. The averaged electric field and current density of the nanoscale RVE are then evaluated to find the in-plane effective conductivity components using Eqn. 2.49. The variation in effective conductivity components $\Sigma_{11}^{\text{Eff}}$ and $\Sigma_{22}^{\text{Eff}}$ with applied tensile and compressive strains in the 2-direction (up to 5%) are shown in Fig. 3.4. It is observed that $\Sigma_{22}^{\text{Eff}}$ decreases by about 8% from the unstrained state on application of 5% tensile strains due to the formation of vertical and diagonal bands with lower conductivity. However, for the same state of applied strain on the compressive side, a 67% increase in $\Sigma_{22}^{\text{Eff}}$ is observed. The reason for the change being faster on the compressive side lies in the exponential nature of the $\Sigma^{\text{EH}} - d_{\text{CNT}}$ relation. It can be envisioned that because of the exponential decay of the local intertube conductivity ($\hat{\Sigma}^{\text{EH}}$) with increasing intertube distance, as shown in Fig. 3.3 inset, small disturbance in the intertube distance ($d_{\text{CNT}}$) of the nanotubes on the compressive side (up the curve) will cause a greater change in the local conductivity ($\hat{\Sigma}^{\text{EH}}$) than a small disturbance on the tensile side (down the curve). For example, in the current case with 0.5nm unstrained intertube distance, if the nanotubes get closer by 0.1nm, the intertube conductivity will increase by nearly 90% based on Eqn. 3.2. However, if the nanotubes move further away by 0.1nm, the intertube conductivity decreases by only about 47%. In addition, the vertical bands of highly increased conductivity override the diagonal bands for applied compressive strains. For applied tensile strains, however, the conductivity of the diagonal bands overrides than the conductivity...
of the vertical bands. The asymmetry in variation of local conductivity and the difference in the overriding bands gets reflected for effective conductivity components \( \Sigma_{22}^{\text{Eff}} \) as well, where the rate of change of conductivity on application of compressive strains is higher as compared to applied tensile strains. This asymmetric effect, as will be shown later, gives rise to different effective macroscale gauge factors on application of tensile/compressive strains. The tension-compression asymmetry observed in the current results has been reported from experimental observations in the literature [19], although for tensile-compressive tests performed on randomly oriented CNTs in the polymer medium as opposed to the well dispersed uniformly aligned CNTs considered herein.

In addition to changes in the 2-direction effective conductive properties, the effective conductivity component in the 1-direction \( \Sigma_{11}^{\text{Eff}} \) is observed to follow a different variation from \( \Sigma_{22}^{\text{Eff}} \). In the unstrained state, the CNTs are arranged in a regular hexagonal array in the nanoscale RVE with symmetric electron hopping pathways which results in the effective nanoscale properties to be transversely isotropic i.e. \( \Sigma_{11}^{\text{Eff}} = \Sigma_{22}^{\text{Eff}} \). On application of tensile or compressive strains, while the mechanical properties remain transversely isotropic, the regular hexagonal arrangement of CNTs and corresponding symmetric electron hopping pathways are disturbed causing the effective nanoscale electrostatic properties to lose the transverse isotropy and become electrostatically anisotropic. A larger difference between \( \Sigma_{11}^{\text{Eff}} \) and \( \Sigma_{22}^{\text{Eff}} \) is observed on application of compressive strains, where at 5% applied compressive strain \( \Sigma_{11}^{\text{Eff}} \) is about 12.77% less than \( \Sigma_{22}^{\text{Eff}} \). However, on application of 5% tensile strain, \( \Sigma_{11}^{\text{Eff}} \) is observed to be 1.35% higher than \( \Sigma_{22}^{\text{Eff}} \). Such asymmetric difference in \( \Sigma_{11}^{\text{Eff}} \) and \( \Sigma_{22}^{\text{Eff}} \) is observed because of the difference in the formation electron hopping pathways because of applied strains. On the compressive side, the formation of highly conductive vertical bands augment the current density the 2-direction for the same applied test electric field. While the effective conductivity increases in the 1 direction, indicating increasing current density, the effect is not as strong as the diagonal bands are not as conductive. Thus, it leads to smaller values of \( \Sigma_{11}^{\text{Eff}} \) as compared to \( \Sigma_{22}^{\text{Eff}} \) at the same applied compressive strain state. On application of tensile strains, however, the small pockets of relatively less conductive matrix between vertically adjacent nanotubes lower the current density in the 2-direction. Simultaneously, the overriding conductive bands between diagonally adjacent
nanotubes restricting the drop in the current density in 1-direction resulting in \( \Sigma_{11}^{Eff} \) being slightly higher than \( \Sigma_{22}^{Eff} \).

Finally, \( \Sigma_{12}^{Eff} \) and \( \Sigma_{21}^{Eff} \) are observed to be three to four orders of magnitude smaller than \( \Sigma_{11}^{Eff} \) and \( \Sigma_{22}^{Eff} \) for all cases of tension/compression tests conducted at different \( V_f \) and \( \delta_{max}^{EH} \). Hence, for practical purposes the off diagonal terms will be assumed to be negligible as compared to the on-diagonal terms in the effective conductivity tensor.

3.4.2 Constrained Tension/Compression Response

In order to observe the effect of the different type of boundary conditions on the nanoscale electrostatic and piezoresistive response, constrained plane strain tension/compression tests, as described in Table 3.2, are conducted and compared to the unconstrained tension/compression test. Fig. 3.6a shows the local conductivity contours for the \( \pm 5\% \) strain cases with constrained and unconstrained side edges (BC and DA) and the corresponding variation in effective conductivity (\( \Sigma_{22}^{Eff} \)) with applied strains.

Unlike the unconstrained case, where the nanotubes were allowed to move in the 1-direction because of Poisson’s contraction/expansion, the movement of sides BC and DA are constrained in the 1-direction for constrained plane strain tests. Thus, the intertube distance between the diagonally adjacent nanotubes will be different for the constrained and unconstrained tests at a given applied strain (Fig. 3.6b). As an example, while the intertube distance between CNTs C1 and C3 increased by 0.0137nm for the unconstrained test at 5\% applied tensile strain, it increases by 0.0318nm for the constrained test. In effect, while an 8\% drop in the C1-C3 intertube conductivity was observed for the unconstrained tests, a 17\% drop is observed for the constrained tests at 5\% applied tensile strain as is observed from the local conductivity contours in Fig. 3.6a. Similarly, on application of applied compressive strain, the Poisson’s expansion leading to the 1-direction movement of CNT C3 is restricted. Thus, while the C1-C3 intertube conductivity was observed to increase by about 7\% in the unconstrained test at \(-5\% \) applied strain, it increases by about 20\% for the constrained test. The intertube conductivity of other diagonally adjacent CNT pairs follows the same
Figure 3.6: Comparison of constrained and unconstrained tension/compression cases with volume fraction of 0.58 with $\delta_{EH}^{max}$ fixed at 5nm (point II) a) $\Sigma_{22}^{Eff}$ versus $\varepsilon_{App}^{22}$ with conductivity contours at 5% strain level (legend I: constrained/unconstrained compression; legend II: constrained/unconstrained tension) b) intertube conductivity between CNT pair C1-C2 and C1-C3 for constrained and unconstrained tests c) $\Delta\rho_{22}^{Eff}$ versus $\varepsilon_{App}^{22}$ corresponding to $\Sigma_{22}^{Eff}$ plots in a). [139]
behavior while the vertically adjacent CNTs have nearly the same intertube conductivity variation as for the unconstrained test.

The difference in local intertube conductivities for the constrained and unconstrained tests lead to different effective nanoscale conductivity ($\Sigma_{22}^{Eff}$). For applied constrained tensile strains, a further reduction in the local conductivity of the diagonal bands results in smaller $\Sigma_{22}^{Eff}$. On the other hand, a larger increase in the effective conductivity of the diagonal bands leads to higher $\Sigma_{22}^{Eff}$ for applied compressive strains. However, for applied compressive strains, the higher conductivity of the vertical bands override the diagonal bands of lower conductivity resulting in small vertical line of local conductivity equal to the intertube conductivity of diagonal bands. As these occupy a smaller area in comparison to the case with applied tensile strains, where the diagonal bands override the vertical bands of reduced conductivity, the variation in intertube conductivity of diagonally adjacent CNTs affects the tension side more significantly as compared to the compression side. Hence, at −5% compressive strain, the difference between the constrained and unconstrained cases is only 0.7%, while at 5% applied tensile strain the difference observed is about 8%.

When the effective conductivity response is converted into relative change in resistivity ($\Delta \rho_{22}^{Eff}/\rho_{022}^2$), it is observed that the difference in effective conductivity components for the unconstrained and constrained tests lead to different effective piezoresistive response. Figure 3.6c shows the comparison of relative change in resistivity with applied strains for the unconstrained and constrained tests. As observed for effective conductivity, the difference in $\Delta \rho_{22}^{Eff}/\rho_{022}^2$ is observed to be higher for applied tensile strains (≈100% at +5%) and compared to applied compressive (≈2% at −5%). Thus, the asymmetry observed with respect to the electrostatic response is enhanced when the effective piezoresistive response is considered. It is further noted that, at 5% applied tensile strains, a 20% difference in $\Sigma_{22}^{Eff}$ for the unconstrained and constrained tests caused about a 100% increase in $\Delta \rho_{22}^{Eff}/\rho_{022}^2$ indicating that small variations in effective conductivity because of different types of applied boundary conditions can lead to large variations in the effective piezoresistive response.

The corresponding effective piezoresistive strain tensor coefficient ($\Pi_{22}^{Eff}$) are calculated using the averaged form of the piezoresistive constitutive equation as shown in Eqn. 2.48. The
effective piezoresistive strain coefficient tensor components for the unconstrained plane strain tension/compression tests are calculated using Eqn. 2.51 assuming that for uniform hexagonal microstructure with transversely isotropic properties $\Pi_{11}^{Eff} = \Pi_{22}^{Eff}$ and $\Pi_{12}^{Eff} = \Pi_{21}^{Eff}$. It is further assumed that, for uniform hexagonal arrangement of CNTs, it is possible to identify a similar nanoscale RVE with the longer edge (BC or DA) aligned with the 1-direction such that the same values $\Pi_{ij}^{Eff}$ can be recovered. For exact calculation of $\langle \dot{\varepsilon}_1 \rangle$ from the finite elements, averaged strains need to be extended through hollow CNTs, which is a non-trivial task. For the unconstrained plane strain tests, the $\langle \dot{\varepsilon}_1 \rangle$ can be calculated using $\langle \dot{\varepsilon}_2 \rangle$ recognizing that $\langle \dot{\varepsilon}_1 \rangle = -\nu_{12}^{Eff} \langle \dot{\varepsilon}_2 \rangle$ and $\langle \dot{\varepsilon}_6 \rangle = 0$, where $\nu_{12}^{Eff}$ is found using the Mori-Tanaka method. The two expressions in Eqn. 2.51 can then be simultaneously solved for the effective piezoresistive coefficients. However, for the constrained plane strain test with applied strain in the 2-direction, $\langle \dot{\varepsilon}_1 \rangle = 0$ and $\langle \dot{\varepsilon}_6 \rangle = 0$, and $\Pi_{ij}^{Eff}$ is calculated directly using $\Pi_{22}^{Eff} = \Pi_{11}^{Eff} = \Delta \rho_{ij}^{Eff} / \rho_0 \langle \dot{\varepsilon}_2 \rangle$ and $\Pi_{12}^{Eff} = \Pi_{21}^{Eff} = \Delta \rho_{ij}^{Eff} / \rho_0 \langle \dot{\varepsilon}_2 \rangle$. At 5% applied tensile strain, $\Pi_{22}^{Eff}$ is observed to be 2.52 and 3.83 for the unconstrained and constrained plane strain test, respectively. The negative values of the effective piezoresistive strain tensor coefficients for applied compressive strains signify an increase in effective conductivity while the positive values indicate decreasing effective conductivity. For 5% applied compressive strain, the $\Pi_{22}^{Eff}$ obtained is -10.84 and -8.125 for the unconstrained and constrained plane strain test, respectively. The relative difference in $\Pi_{22}^{Eff}$ is observed to be much smaller for applied compressive strains which can be related to the smaller variation in $\Sigma_{22}^{Eff}$ and $\Delta \rho_{22}^{Eff} / \rho_{22}^{Eff}$ response for compressive strains. The observed difference in $\Pi_{22}^{Eff}$ signifies that the effective piezoresistive strain tensor components are not fixed material properties for CNT polymer nanocomposites, unlike inherently piezoresistive materials, and could be highly dependent on the magnitude of applied strains and the type of boundary conditions.

3.4.3 Shear Response

The piezoresistive response under plane strain simple shear test, as described in Table 3.2, is explored in order to study the evolving conductive network at the nanoscale and to assess the $\Pi_{I6}$ and $\Pi_{6I}$ ($I=1,2,6$) components of the piezoresistive strain tensor coefficients. Fig. 3.7
provides the variation in effective conductivity ($\Sigma^{\text{Eff}}_{22}$) and the relative change in resistivity ($\frac{\Delta\rho^{\text{Eff}}_{22}}{\rho_{22}}$) with applied shear strains for a volume fraction of 0.58 and 5nm maximum electron hopping range (point II). Moreover, the local conductivity contours are presented for positive and negative applied shear strain states. It is observed that the applied shear strains cause the formation of diagonal bands with increased conductivity which dominate the $\Sigma^{\text{Eff}}_{22}$ response such that the effective conductivity increases as a function of applied strains. Evolution of the diagonal bands can be further explained based on the variation of intertube distances between the CNTs which directly affects the local conductivity of the intertube region. Fig. 3.8 shows the varying intertube distance on application of shear strains and the local intertube conductivity for different pairs of nanotubes.

For applied positive shear strains, it is observed that the intertube distance in between CNTs C1 and C3 decreases from 0.5nm in the unstrained state to 0.457nm at 5\% applied shear strain, thus increasing the local conductivity in the C1-C3 intertube region from 4.96E3$S/m$ to 6.41E3$S/m$ i.e. about 30\% increase in local conductivity. The intertube distance between CNTs C1 and C6 follows similarly and a diagonal band of relatively higher conductivity is observed between CNTs C1 and C6 through C3. The intertube distance between CNTs C2 and C7 reduces from 0.5nm to 0.491nm resulting in an increase in the local intertube conductivity from the unstrained state, but the increase is not as high as that for the C1-C3 diagonal. The CNTs C1 and C7, however, diverge as positive shear strains are applied with the intertube distance increasing from 0.5nm to 0.546nm. The increasing C1-C7 intertube distance can be related to formation of a diagonal band of lower conductivity through the C1-C7 diagonal to C4. But, the higher local conductivity along the C3-C6 diagonal overrides the reduced conductivity on the C4-C7 diagonal resulting in small pockets of relatively lower conductivity as seen from the local contours in Fig. 3.7. On application of negative shear strains, the the diagonal intertube bands get flipped such that the C4-C7 diagonal is of higher conductivity while the intertube conductivity of the C3-C6 diagonal is reduced. However, flipping of direction of the increased/reduced conductivity bands does not affect the effective current density on application of test electric fields. Thus, the effective conductivity ($\Sigma^{\text{Eff}}_{22}$) for negative shear follows an increasing behavior similar to the variation because of positive shear with about 8\% increase observed in the effective conductivity at $\pm$5\% applied shear
strain relative to the unstrained state. The formation of diagonal bands of relatively higher conductivity augments the current density in the 1 direction further such that $\Sigma_{11}^{Eff}$ increases by about 10% at $\pm 5\%$ applied shear strain relative to the unstrained state. The difference in the effective conductivity components $\Sigma_{11}^{Eff}$ and $\Sigma_{22}^{Eff}$ for the shear test emphasizes the influence of the type of boundary conditions on the electrostatic symmetry properties of the effective nanocomposite.

Figure 3.7: The $\Sigma_{22}^{Eff}$ and $\Delta\rho_{22}^{Eff}/\rho_{22}^0$ response against applied shear strains for different volume fractions with $\delta_{EH}^{max}$ fixed at 5nm. Conductivity contours ($\hat{\Sigma}_{22}$) are shown corresponding to 0%, $\pm 2\%$, and $\pm 5\%$ applied shear strain states. [139]

The symmetrically increasing $\Sigma_{22}^{Eff}$ results in relative change in resistivity ($\Delta\rho_{22}^{Eff}/\rho_{22}^0$) decreasing symmetrically for positive and negative applied shear strains (Fig. 3.7). It is observed that the effect of applied shear strains on $\Delta\rho_{22}^{Eff}/\rho_{22}^0$ is much smaller in comparison to the tensile/compressive strains, and thus, would lead to smaller effective piezoresistive strain coefficients. The effective piezoresistive strain coefficient tensor components for the unconstrained plane strain shear tests are calculated using Eqn. 2.51 recognizing that for applied shear strains $\langle \hat{\varepsilon}_1 \rangle = 0$ and $\langle \hat{\varepsilon}_2 \rangle = 0$. Then, $\Pi_{16}^{Eff}$ and $\Pi_{26}^{Eff}$ are calculated directly using
Figure 3.8: Variation in (a) intertube distance and (b) intertube conductivity, between individual pairs of nanotubes when an RVE with volume fraction of 0.58 and $\delta_{EH}^{max}$ fixed at 5nm is subjected to the plane strain shear test. [139]

$$\Pi_{16}^{Eff} = \frac{\Delta\rho_{16}^{Eff}}{\rho_0^{16}}$$ and $$\Pi_{26}^{Eff} = \frac{\Delta\rho_{26}^{Eff}}{\rho_0^{26}}.$$ For example, at 5% unconstrained plane strain compression state, $\frac{\Delta\rho_{22}^{Eff}}{\rho_0^{22}}$ was observed to be about -0.4 which was then related to a piezoresistive strain tensor coefficient ($\Pi_{22}^{Eff}$) of -10.84. However, ±5% applied shear strains result in $\frac{\Delta\rho_{22}^{Eff}}{\rho_0^{22}}$ of -0.07 yielding a much smaller piezoresistive strain tensor coefficient ($\Pi_{22}^{Eff}$) of -1.64. The piezoresistive strain coefficient $\Pi_{16}^{Eff}$ is observed to be higher as compared to $\Pi_{26}^{Eff}$ based on the higher increase in effective conductivity in the 1-direction. At ±5%, $\Pi_{16}^{Eff}$ is -1.782 which is 8.65% higher than $\Pi_{26}^{Eff}$, but is still about an order of magnitude smaller than the coefficients observed for plane strain tension/compression tests at the same strain state.

The off-diagonal components effective conductivity components, $\Sigma_{12}^{Eff}$ and $\Sigma_{21}^{Eff}$, are two to three orders of magnitude smaller than the on-diagonal components ($\Sigma_{11}^{Eff}$, $\Sigma_{22}^{Eff}$) and are considered to be negligibly small. Assuming that the off-diagonal conductivity components are zero, the relative change in resistivity component $\frac{\Delta\rho_{12}^{Eff}}{\rho_0^{12}}$, or $\frac{\Delta\rho_{66}^{Eff}}{\rho_0^{6}}$ in Voigt’s notation as in Eqn. 2.51, will be zero. Such observation will restrict the effective piezoresistive strain tensor coefficients $\Pi_{66}^{Eff}$ to be zero indicating that the piezoresistive strain coefficient tensor represented in the Voigt’s notation, $\Pi_{IJ}$ (I,J=1,2,6), is not symmetric.

The results for the plane strain shear test show an asymmetry in effective conductivity and piezoresistive components in the 1 and 2 directions. Moreover, the piezoresistive coefficients are much smaller than those observed earlier in the case of plane strain tension/compression tests, further emphasizing that these coefficients are not fixed material properties and can
be highly dependent on the strain state and type of boundary conditions.

### 3.5 Effect of Maximum Electron Hopping Distance, Nanoscale CNT Volume Fraction on the Effective Piezoresistive Response

#### 3.5.1 Varying Maximum Electron Hopping Range

Figure 3.9: The $\Delta \rho_{22}/\rho_{22}$ response against applied strains in the 2-direction for a volume fraction of 0.58 and varying $\delta_{EH}$. Inset shows the response for smaller compressive strains to be linear. [139]

Recalling from Fig. 3.3 that a longer maximum electron hopping range results in lower percolation volume fractions, it is further noted that the longer $\delta_{EH}$ results in a smaller slope of the $\Sigma^{EH} - d^{CNT-CNT}$ relation based on the exponent in Eqn. 3.2. Thus, for longer $\delta_{EH}$, a fixed increment in CNT separation distance for a given pair of nanotubes will result in a smaller change in local intertube conductivity. For example, in case of 0.58 volume fraction, with the unstrained CNT separation distance of 0.5nm, the local intertube conductivity for a maximum electron hopping range of 1.8nm (point I), 5nm (point II) and 10nm (point III) is about 13 S/m, 4E3 S/m and 2E4 S/m, respectively. If the nanotubes move closer by 0.01nm,
the increase in the intertube conductivity ($\Delta \hat{\Sigma}^{EH}$) for the cases with $\delta^{EH}_{max}$ of 1.8nm, 5nm and 10nm will be 2.60S/m, 267.0 S/m and 654.9S/m. However, when the local conductivity tensors are used to find the local resistivity components, a higher local intertube conductivity leads to a small local intertube resistivity. Then, because the local resistivity for longer $\delta^{EH}_{max}$ is several orders of magnitudes smaller than that for small $\delta^{EH}_{max}$ based on the large difference in unstrained conductivity, the relative change in resistivity ($\frac{\Delta \rho^{EH}_{Eff}}{\rho^{0}_{22}}$) for the smallest $\delta^{EH}_{max}$ is observed to be the highest. As an example, for the cases with $\delta^{EH}_{max}$ of 1.8nm, 5nm and 10nm, the relative change in resistivity is 0.162, 0.062 and 0.031, respectively.

Table 3.4: Effective piezoresistive strain tensor coefficients ($\Pi_{22}^{Eff}$) at different unconstrained uniaxial strain states corresponding to a volume fraction of 0.58 with varying maximum electron hopping range. [139]

<table>
<thead>
<tr>
<th>Applied strain (+tensile,-compressive)</th>
<th>Max. EH range ($\delta^{EH}_{max}$)</th>
<th>1.8nm</th>
<th>5nm</th>
<th>10nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>+5%</td>
<td>11.53</td>
<td>2.52</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>+2%</td>
<td>7.00</td>
<td>2.06</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>-2%</td>
<td>-33.98</td>
<td>-12.21</td>
<td>-4.59</td>
<td></td>
</tr>
<tr>
<td>-5%</td>
<td>-22.93</td>
<td>-10.84</td>
<td>-4.53</td>
<td></td>
</tr>
</tbody>
</table>

The effective piezoresistive response for varying maximum electron hopping range follows from the discussion for the relative change in local resistivity of the intertube region, such that a higher $\delta^{EH}_{max}$ results in smaller magnitudes of $\frac{\Delta \rho^{Eff}_{22}}{\rho^{0}_{22}}$. Fig. 3.9 shows the variation of relative change in effective resistivity ($\frac{\Delta \rho^{Eff}_{22}}{\rho^{0}_{22}}$) with applied unconstrained uniaxial strains for a volume fraction of 0.58 with different $\delta^{EH}_{max}$. Moreover, a nonlinear variation in $\frac{\Delta \rho^{Eff}_{22}}{\rho^{0}_{22}}$ response is observed, especially on the compressive side, indicating that the piezoresistive coefficients will be highly strain dependent. For small strains, however, the variation of $\frac{\Delta \rho^{Eff}_{22}}{\rho^{0}_{22}}$ is observed to be approximately linear. Based on the observed variation in $\frac{\Delta \rho^{Eff}_{22}}{\rho^{0}_{22}}$, it is expected that the piezoresistive strain tensor coefficients will be higher for smaller maximum electron hopping range. For example, at 2% tensile strains the corresponding piezoresistive strain tensor coefficient ($\Pi_{22}^{Eff}$) is observed to be 7.00, 2.06 and 0.65 for the cases with $\delta^{EH}_{max}$ of 1.8nm, 5nm and 10nm, respectively. A comparison of $\Pi_{22}^{Eff}$ for varying maximum electron hopping range at different uniaxial strain states is presented in Table 3.4.
3.5.2 Varying Nanoscale CNT Volume Fraction

The influence of local volume fraction on the piezoresistive response of nanocomposites for a fixed maximum electron hopping range is provided in Fig. 3.10. The results for volume fractions of 0.15, 0.25, 0.4 and 0.58 with $\delta_{max}^{EH}$ fixed at 5nm shown in Fig. 3.10 correspond to points II, V, VIII and XI in Fig. 3.3. For a fixed value of $\delta_{max}^{EH}$, the exponent for intertube conductivity decay (refer Eqn. 3.2 and Fig. 3.3) remains the same and is independent of the nanoscale local volume fractions. However, the rate of change of local intertube conductivity on application of strains is highly dependent on the unstrained intertube distance because of the exponential nature of the $\Sigma^{EH} - d^{CNT-CNT}$ curves. For cases with smaller unstrained intertube distance i.e. for high volume fractions, the rate of change in intertube conductivity with increasing/decreasing intertube is higher. For example, if the maximum electron hopping range is fixed at 5nm, a 0.1nm decrease in the intertube distance will lead to about 3.8E-4S/m, 1.1S/m, 1.5E2S/m and 3.5E3S/m increase in intertube conductivity for 0.15, 0.25, 0.4 and 0.58 volume fractions, respectively. But, if the relative change in intertube resistivities is calculated 0.1nm increase in intertube distances, a constant 47% reduction in $\frac{\Delta\rho^{EH}}{\rho_0^{EH}}$ is observed for all volume fractions. The constant change in local relative intertube resistivity ($\frac{\Delta\rho^{EH}}{\rho_0^{EH}}$) indicates that, unlike the varying $\delta_{max}^{EH}$ cases, the evolving local intertube conductivities do not play a significant role in determining the effective piezoresistive response. However, the region of the nanoscale RVE which is susceptible to conductivity change (i.e. matrix volume fraction) is relatively larger for the cases with lower local CNT volume fractions. For the case with 0.58 volume fraction (Fig. 3.11d), the nanoscale RVE is predominantly occupied by the CNTs which results in a smaller intertube polymer region susceptible to electron hopping induced conductivity change. While 42% of the volume is undergoing change in conductivity for the 0.58 $V_f$ case, slightly under 85% of the volume undergoes conductivity change for the case with 0.15 $V_f$ (Fig. 3.11a). The available volume for electron hopping results in different effective piezoresistive response such that the cases with smaller volume fractions are observed (Fig. 3.10) to have higher $\frac{\Delta\rho^{Eff}}{\rho_0^{22}}$ and thus, will yield higher piezoresistive coefficients. For example, at 2% applied tensile strain, the piezoresistive strain tensor co-efficients ($\Pi^{Eff}_{22}$) are 23.90, 12.18, 6.23 and 2.06 for cases with
volume fractions of 0.15, 0.25, 0.4 and 0.58, respectively. A comparison of the piezoresistive strain coefficient, $\Pi_{22}^{Eff}$, for different volume fractions and applied strain states is presented in Table 3.5.

Figure 3.10: The $\Delta\rho_{22}$ response against applied strains in the 2-direction for different volume fractions (0.58, 0.4, 0.25 and 0.15) with $\delta_{EH}^{max}$ fixed at 5nm. Inset shows the response for small compressive strains to be approximately linear. [139]

Table 3.5: Effective piezoresistive strain tensor coefficients ($\Pi_{22}^{Eff}$) at different uniaxial strain states corresponding to a maximum electron hopping range of 5nm with varying volume fractions. [139]

<table>
<thead>
<tr>
<th>Applied strain (+tensile,-compressive)</th>
<th>Volume fraction ($V_f$)</th>
<th>0.15</th>
<th>0.25</th>
<th>0.4</th>
<th>0.58</th>
</tr>
</thead>
<tbody>
<tr>
<td>+5%</td>
<td></td>
<td>29.83</td>
<td>15.22</td>
<td>7.56</td>
<td>2.52</td>
</tr>
<tr>
<td>+2%</td>
<td></td>
<td>23.89</td>
<td>12.18</td>
<td>6.22</td>
<td>2.06</td>
</tr>
<tr>
<td>-2%</td>
<td></td>
<td>-24.03</td>
<td>-18.70</td>
<td>-16.10</td>
<td>-12.21</td>
</tr>
<tr>
<td>-5%</td>
<td></td>
<td>-19.46</td>
<td>-16.17</td>
<td>-14.15</td>
<td>-10.84</td>
</tr>
</tbody>
</table>

It is further noted that the piezoresistive coefficient $\Pi_{12}^{Eff}$, evaluated by subjecting the nanoscale RVE to applied strains in the 2-direction but investigating for variation in effective conductivity in the 1-direction ($\Sigma_{11}^{Eff}$), follows a similar variation with applied strains as observed for $\Pi_{22}^{Eff}$. However, the magnitude of piezoresistive strain coefficient $\Pi_{12}^{Eff}$ is observed to be smaller than $\Pi_{22}^{Eff}$ indicating that the relative change in resistivity are different.
Table 3.6: Effective piezoresistive strain tensor coefficients ($\Pi_{12}^{\text{Eff}}$) at different uniaxial strain states for varying volume fractions with maximum electron hopping range fixed at 5nm. [139]

<table>
<thead>
<tr>
<th>Applied strain (+tensile,-compressive)</th>
<th>Volume fraction ($V_f$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td>+5%</td>
<td>19.50</td>
</tr>
<tr>
<td>+2%</td>
<td>16.40</td>
</tr>
<tr>
<td>-2%</td>
<td>-17.84</td>
</tr>
<tr>
<td>-5%</td>
<td>-14.89</td>
</tr>
</tbody>
</table>

in 1 and 2 direction. Thus, the overall piezoresistive response of the nanocomposite evolves to an anisotropic response from the transversely isotropic unstrained state. A comparison of the piezoresistive strain coefficient, $\Pi_{12}^{\text{Eff}}$, for different volume fractions and applied strain states is presented in Table 3.6. Further, a larger relative difference in $\Pi_{22}^{\text{Eff}}$ and $\Pi_{12}^{\text{Eff}}$ is observed for smaller volume fractions indicating that the departure from transverse isotropy is more significant for the cases with low volume fractions.

Figure 3.11: The conductivity contours at 5% applied compressive strain and with $\delta_{\text{max}}^{EH}$ fixed at 5nm for varying volume fractions. a) $V_f = 0.15$ a) $V_f = 0.25$ a) $V_f = 0.4$ a) $V_f = 0.58$. It is to be noted that the color bars are different for each of the volume fractions. [139]

In order to study the effect of local nanoscale volume fraction for applied shear strains,
Figure 3.12: The $\frac{\Delta \rho_{22}^{\text{Eff}}}{\rho_0^{22}}$ response against applied shear strains for different volume fractions with $\delta_{\text{max}}^{EH}$ fixed at 5nm (Points II, V, VIII and XI). [139]

plane strain shear tests are performed for varying volume fractions. As observed in uniaxial tension/compression test (Fig. 3.11), the relative volume of the nanoscale RVE susceptible to electron hopping induced conductivity change is larger for smaller volume fractions. However, the higher rate of change in local intertube conductivity for larger volume fractions is observed as a competing mechanism for both uniaxial tension/compression and shear tests. Unlike the case of uniaxial tension/compression, for applied shear strains the interplay of these mechanisms result in higher magnitude of the relative change in resistivity ($\frac{\Delta \rho_{22}}{\rho_0^{22}}$) for higher volume fractions. Thus, the rate of change in local conductivity, based on the unstrained intertube distances, is seen to have a more significant effect on the effective piezoresistive response in case of applied shear strains. A comparison of variation in $\frac{\Delta \rho_{22}}{\rho_0^{22}}$ with applied shear strains is shown in Fig. 3.12 for different volume fractions with the maximum electron hopping range fixed at 5nm. The $\frac{\Delta \rho_{22}}{\rho_0^{22}}$ response is shown only for positive shear strains as the response for negative applied shear strains was observed to be symmetric. The effective piezoresistive strain tensor coefficients follow from the $\frac{\Delta \rho_{22}}{\rho_0^{22}}$ response such that the larger volume fraction has higher effective piezoresistive coefficients. For example, at 2% applied shear strain, the corresponding piezoresistive strain tensor coefficients ($\Pi_{26}^{Eff}$) are -0.851, -1.19, -1.47 and -1.64 for cases with 0.15, 0.25, 0.4 and 0.58 volume fraction, respec-
tively. It is noted further that the piezoresistive coefficients for the shear test are about an order of magnitude smaller than the uniaxial strain tests for all volume fractions and strain states.

### 3.6 Macroscale Effective Gauge Factors

The macroscale effective gauge factors for the nanoscale transverse RVE are generated, as shown in Eqn. 2.64, from the effective resistivity components for varying volume fractions ($V_f$) and maximum electron hopping range ($\delta_{\text{max}}^{EH}$). The effective Poisson’s ratios are found using Mori-Tanaka method [131] with material properties corresponding to the transversely isotropic solid representation of CNTs [135] and isotropic polymer [72]. The effective Poisson’s ratios obtained for the different volume fractions are listed in Table 3.7.

<table>
<thead>
<tr>
<th>Volume Fraction</th>
<th>$\nu_{12}^{\text{eff}}$</th>
<th>$\nu_{23}^{\text{eff}} = \nu_{13}^{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>0.3772</td>
<td>0.2629</td>
</tr>
<tr>
<td>0.25</td>
<td>0.3521</td>
<td>0.2405</td>
</tr>
<tr>
<td>0.40</td>
<td>0.3223</td>
<td>0.2132</td>
</tr>
<tr>
<td>0.58</td>
<td>0.2949</td>
<td>0.1863</td>
</tr>
</tbody>
</table>

The macroscale effective gauge factors for varying $\delta_{\text{max}}^{EH}$ at a volume fraction of 0.58 and for varying volume fractions with $\delta_{\text{max}}^{EH}$ fixed at 5nm are presented in Fig. 3.13a and Fig. 3.13b, respectively. The negative values for the effective gauge factors for applied compressive strains correspond to a decreasing macroscale effective nanocomposite resistance while the positive values of gauge factors signify increasing resistance with applied strain. In the unstrained state, the effective gauge factors cannot be evaluated as the denominator in Eqn. 2.64 tends to zero and the effective gauge factor is unbounded. The variation of macroscale effective gauge factor with applied strain for varying maximum electron hopping range follows from the $\frac{\Delta \rho_{22}}{\rho_{22}^{0}}$ results shown in Fig. 3.9 such that the magnitude of the gauge factors is larger for shorter maximum electron hopping range. The gauge factors for varying volume fractions follow from Fig. 3.10 with the smaller volume fractions resulting in higher
gauge factors. The macroscale effective gauge factors also account for the contribution of macroscale geometrical changes along with the evolving nanoscale conductive/piezoresistive behavior because of electron hopping. The effective macroscale gauge factor for the case without nanoscale electron hopping, i.e. considering only geometric constraints, is also shown Fig. 3.13. The observed effective gauge factor without electron hopping is attributed to the macroscale geometrical changes resulting in effective piezoresistive response i.e. \( \rho_{\text{Eff}}^{22} \left( \varepsilon_0 \right) / \rho_{\text{Eff}}^{22} \left( 0 \right) \) in Eqn. 2.64 is fixed at 1 such that the \( \nu_{ij}^{E_{ij}} \) terms drive the effective gauge factor to a constant value at a given volume fraction e.g. 1.48 for 0.58 \( V_f \). Unlike the geometrical gauge factors, the gauge factors with nanoscale electron hopping are highly dependent on the magnitude of applied strain. Substantial increase in the overall gauge factors is observed relative to the geometrical gauge factors (up to 15 times) when the electron hopping is allowed at the nanoscale indicating that the nanoscale electron hopping plays a significant role in determining the macroscale effective piezoresistive response.

It should be noted that higher macroscale effective gauge factors are observed for cases with smaller unstrained effective conductivity i.e. for shorter maximum electron hopping range and smaller nanoscale local CNT volume fractions. The smaller unstrained effective conductivity is representative of the nanoscale RVE being closer to the percolation threshold. Hence, another interpretation of the results presented in the current study is that higher gauge factors (and piezoresistive strain coefficients) are observed for the cases closer to the electrostatic percolation threshold. This observation relates to the experimental results in the literature [11, 12, 16] which have reported a higher macroscale observed gauge factors closer to percolation based on uniaxial strain tests.

In the current chapter, the effective piezoresistive response is investigated in the transverse direction for well dispersed uniformly aligned CNT-polymer nanocomposites. The results are also representative of idealized microscale CNT bundles with aligned CNTs at high volume fractions. While experimental values have been reported for aligned nanocomposites with microscale bundle formation [20], specific information regarding the microstructural morphology of the microscale bundles is generally not available in the literature. Further, the experimental gauge factors reported are typically for the direction of alignment of CNTs,
Figure 3.13: The effective macroscale gauge factors ($G_{22}^{\text{Eff}}$) versus applied strains for unconstrained tension/compression test a) comparison for $\delta_{EH}^{\text{max}}$ of 1.8nm, 5nm, 10nm at a volume fraction of 0.58 b) comparison for volume fractions of 0.15, 0.25, 0.4, 0.58 with $\delta_{EH}^{\text{max}}$ fixed at 5nm. [139]

which can have significantly different response as compared to the results presented herein for the transverse direction, due to the high aspect ratio of CNTs. The macroscale gauge factors for the transverse direction are not available to the best of the authors' knowledge and thus only behavioral comparison can be made with the experimental observations reported in the literature. However, the important observation here is that the observed gauge factors are of comparable magnitudes to those reported from macroscale experiments (i.e. between 1 and 20 [3, 4, 7, 8, 11–13]) indicating that the current model captures the physics behind the origins of macroscale piezoresistivity in CNT-polymer nanocomposites within a continuum micromechanics framework. The results presented herein indicate that an interplay of local nanoscale CNT volume fractions and maximum electron hopping range could yield macroscale effective gauge factors close to the experimentally observed gauge factors. In addition, the current study strengthens the argument that electron hopping could have the governing influence on the effective piezoresistive response of CNT-polymer nanocomposites.
Chapter 4

Nanocomposite Macroscale Effective Piezoresistive Response Through Analytical Multiscale Modeling

The effective properties obtained in Chapter 3 are representative of nanocomposite effective properties if the entire microstructure was composed of uniformly aligned infinitely long CNTs. However, a typical CNT-Polymer nanocomposite sample processed using nominal dispersion techniques such as shear mixing, sonication, electromanipulation etc., is expected to result in agglomeration of CNTs at the microscale resulting in bundles of CNTs due to inter CNT van der Walls forces. These CNT bundles at the microscale can be randomly oriented or aligned depending on the processing techniques used. The nanoscale effective properties obtained in Chapter 4, then, represent the local microscale bundle properties assuming that the bundles are composed of aligned infinitely long CNTs.

Extending the description of the 2-scale micromechanics based multiscale modeling approach discussed in Chapter 2, a hybrid analytical computational micromechanics model can be setup with 3-scales i.e. the homogeneous nanocomposite medium at the macroscale, randomly oriented or aligned bundles in polymer matrix at the microscale and aligned CNT in polymer matrix at the nanoscale. These three scales have been shown in Fig. 4.1 along with
the key information transferred between the scales for the 3-scale computational micromechanics model. The local strains at the coarser scales are passed down to the finer scales and applied as boundary conditions at the finer scale. The effective properties obtained using energy equivalences at the finer scales are used to update the local properties at the coarser scales. Thus, the three scales get concurrently coupled to each other. However, implementation of the 3-scale concurrent model requires large amounts of data handling and parallelization of architecture for the required computational expense of tracking time history of each subscale RVE over the entire incremental strain path.

For the current work, a hierarchal 3-scale computational micromechanics model is developed coupling the nanoscale and microscale hierarchically and homogenizing the microscale to obtain effective macroscale properties. The nanoscale response is obtained using finite element

Figure 4.1: Macroscale, microscale and nanoscale representative domains and key information transfer between the scales for an idealized 3-scale computational micromechanics model. [139]
based solution over the nanoscale RVE as described in Chapter 4. At the microscale, the nanoscale effective properties are used as local CNT bundle properties. The volume fraction and orientation of microscale CNT bundles in polymer matrix are incorporated by Mori-Tanaka method based analytical homogenization scheme resulting in effective macroscale properties for the CNT-polymer nanocomposites. The results presented in the current work are published in [133] and a similar study is undertaken in [149].

4.1 Microscale RVE with Randomly Oriented Nanotube Bundles

In Chapter 4, the in-plane components of the conductivity tensor for the effective nanoscale were presented using energy equivalence methods. However, the out-of-plane conductivity component in the CNT axial direction is required for a 3D bundle network distribution as is assumed in the current study. The effective conductivity components in the direction of CNT alignment, or normal to the plane of nanoscale RVE, are evaluated using a summation over all electrical material phases accounting for their interactions through the electric field concentration tensor as

$$\hat{\Sigma}^{\text{Eff}} = \hat{\Sigma}^{(m)} + \sum_{K=1}^{R} c_K \left( \hat{\Sigma}_K^{(B)} - \hat{\Sigma}_K^{(m)} \right) \hat{A}_K^{(B)}$$

(4.1)

where $R$ is the total number of discrete electrical phases that arise due to the formation/disruption of electron hopping pathways. The quantities $\hat{\Sigma}_K^{(m)}$ and $\hat{\Sigma}_K^{(B)}$ are the nanoscale matrix conductivity and the conductivity of the Kth electrostatic material phase in the nanoscale RVE, respectively, and the quantities $\hat{A}_K^{(B)}$ denote the Jth orientation electric field concentration tensors. However, under the plane strain assumption for infinitely long CNTs, assuming that the in-plane electron hopping pathways extend in the axial direction through the length of the nanotube bundle, the concentration tensor $\hat{A}_K$ becomes identity and the effective axial conductivity then reduces to the averaged conductivity of the nanoscale RVE. Thus, the axial conductivity component $\Sigma_{33}^{\text{Eff}}$ for the nanoscale RVE is evaluated using
direct volume averaging as shown in Fig. 4.2 for nanoscale CNT volume fraction of 0.58 and a maximum electron hopping range of 5nm.

The key assumption for the microscale RVE is that the nanotube bundles, composed of aligned SWCNTs, are identical, well dispersed and randomly oriented in the polymer matrix and sufficiently long to be regarded as infinitely long in the Mori-Tanaka model. The effective electrical conductivity for the microscale RVE is obtained treating each orientation of a given bundle as a different phase, and averaging over all possible orientations (Fig. 4.3) in a consistent manner such that the orientations of nanotube bundles are accounted for [72, 150–152]. For discrete number of orientations, the effective nanocomposite electrical conductivity can be expressed in terms of summation over all orientations as

\[
\Sigma_{eff} = \Sigma_{(m)} + \sum_{J=1}^{P} c_J \left( \Sigma_{J}^{(B)} - \Sigma_{J}^{(m)} \right) A_J^{(B)}
\]  

(4.2)
where $P$ is the total number of discrete orientations of the nanotube bundle and $c_j^B$ is the volume fraction of nanotube bundles having the $J$th orientation such that

$$\sum_{J=1}^{B} c_j^B = V_f^B$$

(4.3)

where $V_f^B$ is the total microscale bundle volume fraction such that $V_f^B + V_f^m = 1$ in the microscale RVE, where $V_f^m$ is the volume fraction of matrix. The quantities $\bar{\Sigma}_{j}^{(m)}$ and $\bar{\Sigma}_{j}^{(B)}$ are the matrix conductivity and the $J$th orientation nanotube bundle conductivity tensors, respectively, and the quantities $\bar{A}_{j}^{(B)}$ denote the $J$th orientation electric field concentration tensors. The effective microscale electrical conductivity averaging for the $P$ discrete orientations of the microscale bundles can then be found using

$$\bar{\Sigma}_{ij}^{Eff} = \bar{\Sigma}_{ij}^{(m)} + \frac{v_f^B}{4\pi} \sum_{k=1}^{P_1} \sum_{m=1}^{P_2} p^B(\psi_k, \varphi_m) \left( \bar{\Sigma}_{il}^{(B)}(\psi_k, \varphi_m) - \bar{\Sigma}_{il}^{(m)} \right) \bar{A}_{lj}^{B}(\psi_k, \varphi_m) \sin(\varphi_m) \Delta \varphi \Delta \psi$$

(4.4)

where $p^B(\psi_k, \varphi_m)$ is the probability of an orientation at a given set of Euler angles, $\psi_k$ and $\varphi_m$, summed over a discrete number $P_1$ and $P_2$ of respective angles. The components of the electric field concentration tensors, $\bar{A}_{ij}^{B}(\psi_k, \varphi_m)$ can be evaluated using a variety of micromechanics methods. In the present work, they are obtained using the Mori-Tanaka method [131] which is a micromechanics based averaging technique for obtaining concentration tensors that account for interactions among nanotube bundles by modifying the components of the average electric fields in the matrix from their dilute approximation values. The components of the electric field concentration tensors can thus be obtained as

$$\bar{A}_{ij}^{B}(\psi_k, \varphi_m) = \bar{Q}_{im}(\psi_k, \varphi_m) \bar{T}_{mn}^{B} \bar{Q}_{ln}(\psi_k, \varphi_m)$$

$$\left[ (1 - v_f^B)\delta_{jl} + \frac{v_f^B}{4\pi} \sin(\varphi_m) \sum_{r=1}^{P_1} \sum_{s=1}^{P_2} \left( \bar{Q}_{jr}(\psi_r, \varphi_s) \bar{T}_{rs}^{(B)} \bar{Q}_{ls}(\psi_r, \varphi_s) \right) \right]^{-1}$$

(4.5)
where $\delta_{ij}$ is Kroneker delta and $\tilde{T}_{ij}^{(B)}$ is the dilute electric field concentration tensor obtained using the Eshelby’s tensor for infinitely long cylinders, $S_{ml}$, as

$$
\tilde{T}_{mn}^{(B)} = \left[ \delta_{mn} + S_{ml} \left( \tilde{\Sigma}_{lr}^{(m)} \right)^{-1} \left( \tilde{\Sigma}_{rn}^{(B)} - \tilde{\Sigma}_{rn}^{(m)} \right) \right]^{-1}
$$

(4.6)

where $Q_{ij}(\psi_r, \varphi_s)$ are the components of the rotation matrix used to transform the microscale coordinate system with the local nanotube bundle coordinate system. In the current study, the homogeneous macroscale strains applied at the macroscale are assumed to result in uniform homogeneous local strain state at the microscale. Typically, uniform macroscale strain state applied as boundary conditions on the microscale RVE will lead to a non-uniform microscale strain state because of non-uniform microscale microstructure, however, it is assumed that the microscale RVE undergoes a uniform strain state at each of the strain increment. In other words, the applied macroscale strain is considered to be equal to the effective strain in every bundle, which would generally not be true since the matrix and the bundle have different mechanical properties resulting in smaller local strain within the bundles since they are the stiffer phase. If the non-uniform strain state at the microscale is to be accounted for, analytical micromechanics techniques may not suffice for the microscale RVE and a finite element based solution of local microscale strains will be needed which will then be transferred to the nanoscale RVE as displacement boundary conditions. The corresponding local bundle strains are then transformed to the local bundle coordinate system using the rotation matrices which coincides with the coordinate system of the nanoscale RVE. It is further assumed that the microscale nanotube bundles orientation is governed by only the in-plane Euler angle such that the bundles are randomly oriented within the $\tilde{x}_2 - \tilde{x}_3$ plane in the microscale RVE. Thus, the rotation matrix ($Q_{ij}$), the effective bundle conductivity tensor ($\tilde{\Sigma}_{lr}^{(B)}$) and the electric field concentration tensors ($\tilde{A}_{ij}^{(B)}$) retain dependence only on angle $\varphi_i$ while $\psi_i$ is fixed at $\frac{\pi}{2}$. Further, the effective conductivity components for the microscale RVE need to be calculated at each strain increment as the effective nanoscale conductivity used to generate the dilute electric field concentration tensor (Eqn. 4.6) gets modified based on the formation/disruption of electron hopping induced nanoscale conductive pathways. This is achieved by using a heirarchal effective conductivity passing scheme from the nanoscale
to the microscale. For a given state of transformed local strain within a bundle, the strain components which correspond to the transverse in-plane bundle strains are picked from the transformed microscale strain tensor. The effective conductivity components of the nanoscale bundle at that strain are picked by interpolating between the results shown in Fig. 3.4 say if the local bundle volume fraction is chosen to be 0.58. The effective conductivity components are passed hierarchally to the microscale and then used to build the microscale bundle conductivity tensor used in Eqn. 4.4 to evaluate effective microscale properties.

![Averaging procedure for the microscale RVE with different microscale bundle orientations indicating the microscale and local nanotube bundle coordinate systems.](image)

Figure 4.3: Averaging procedure for the microscale RVE with different microscale bundle orientations indicating the microscale and local nanotube bundle coordinate systems. [133]

### 4.2 Macroscale Effective Gauge Factors for Different Dispersion Cases

Two different microscale bundle dispersion cases are studied in the current work. The first case has uniformly dispersed bundles which are randomly oriented in the polymer matrix. The second case had uniformly dispersed bundles which are aligned in the polymer matrix. It is expected that studying these two dispersion cases will lead to some key insights into the microscale microstructure based piezoresistive response of CNT-polymer nanocomposites.
4.2.1 Uniformly Dispersed Randomly Oriented Microscale Bundles with Aligned Nanotubes

The macroscale effective gauge factors, for the case with bundle formation at the microscale, are evaluated using effective resistivity components at the microscale found by averaging over several discrete orientations of microscale bundles. The piezoresistive response of a material point inside the microscale nanotube bundles is similar to that reported for the uniformly aligned nanotubes dispersed in polymer matrix in Chapter 4. For the case with randomly oriented nanotube bundles (Fig. 4.4a), the probability of each orientation, $p^B(\varphi_m)$ in Eqn. 4.4, is fixed at 1 for all discrete orientations of the microscale bundles. On application of uniform strains in the $\tilde{x}_3$ direction at the microscale, it is observed that the effective microscale conductivity components for the $\tilde{x}_2$ and $\tilde{x}_3$ directions follow a different variation with applied strains resulting in a different relative change in resistivity ($\Delta \tilde{\rho}_{ij}^{\text{Eff}} / \tilde{\rho}_{ij}^0$). As an example, for the case with the CNT volume fraction inside the bundles ($V_{CB}^f$) of 0.58 and a maximum electron hopping range ($\delta_{\text{EHmax}}$) of 5nm with the overall nanocomposite volume fraction ($V_f$) fixed at 0.1, $\Delta \tilde{\rho}_{33}^{\text{Eff}} / \tilde{\rho}_{33}^0$ is 2.62E-3 at 5% tension and -2.61E-1 at 5% compressive tension.
strain state. The tension/compression asymmetry observed for the relative change in resistivity follows from the argument that the transverse direction of the nanotube bundles are sensitive to applied strains than the axial direction. For a given microscale nanotube bundle, an applied strain in the local $\hat{x}_3$ direction (Fig. 4.3), which corresponds to the axial direction at the nanoscale, does not cause any change in the nanoscale electron hopping pathways because the transverse strains are fixed at zero and there is no Poisson’s contraction when considering this case. However, a local microscale bundle strain in the $\hat{x}_2$ direction causes the electron hopping pathways to get modified in the nanoscale RVE resulting in changes in conductivities and relative resistivities. It is further observed from Fig. 4.4b that the relative change in resistivity is smaller for the $\hat{x}_2$ direction as compared to the $\hat{x}_3$ direction, i.e. the relative change in resistivity is sensitive to the direction of applied microscale strain. On application of microscale strain in the $\hat{x}_3$ direction, the nanotube bundles oriented along the $\hat{x}_3$ direction do not undergo a change in local bundle conductivity. However, the nanotube bundles oriented along the $\hat{x}_2$ direction, i.e. perpendicular to applied strain, undergo a larger conductivity change in the $\hat{x}_3$ direction (or $\hat{x}_2$ direction in the transverse nanoscale RVE) as compared the axial direction of the bundles. Thus, $\frac{\Delta \rho^E_{33}}{\rho_{33}^0}$ is about 70% higher than $\frac{\Delta \rho^E_{22}}{\rho_{22}^0}$ in magnitude at $\pm 5\%$ applied strain.

\[ \text{Figure 4.5: The effective macroscale gauge factors } (G^E_{33}) \text{ versus applied strains a) comparison for } \delta_{EH} \text{ of 1.8nm, 5nm and 10nm at a volume fraction of 0.58 b) comparison for local CNT volume fraction in microscale bundles of 0.25, 0.4 and 0.58 with } \delta_{EH} \text{ fixed at 5nm. [133] } \]

The effective macroscale gauge factors are obtained based in the variation in effective re-
sistivities at the microscale using Eqn. 2.64. The effective Poisson’s ratios were obtained using the Mori-Tanaka method, however, unlike the case with uniformly dispersed aligned nanotubes, the Poisson’s ratios are calculated by averaging over all possible orientations of the microscale bundles composed of aligned nanotubes. The effective mechanical properties obtained for the uniformly dispersed aligned nanotube case now become local properties of each of the microscale bundles which are averaged through the discrete number of orientations of the microscale bundle accounting for the bundle and nanocomposite CNT volume fraction. For an overall nanocomposite volume fraction of 0.1, the macroscale effective gauge factors are observed to be different for cases with different maximum electron hopping range \(\delta_{EH}^{max}\) and local bundle volume fractions \(V_{f}^{CB}\). The variation in effective macroscale gauge factors for varying \(\delta_{EH}^{max}\) and \(V_{f}^{CB}\) are shown in Fig. 4.5a and Fig. 4.5b, respectively.

It is observed from the results presented in Fig. 4.5, that the macroscale effective gauge factors \(G_{33}\) are about an order of magnitude smaller that the case with uniformly dispersed aligned CNTs. For example, at 5% compressive strain, the macroscale effective gauge factor for the uniformly aligned CNT case was -8.91, however, for the case with randomly oriented microscale bundles the effective gauge factor is only -1.62 for the same 5nm maximum electron hopping range. The reason for low effective gauge factors is that in the case of randomly oriented microscale bundles, electron hopping only takes place inside the bundles resulting in overall macroscale effective gauge factors. There is no electron hopping in between the microscale bundles and given a small bundle volume fraction \(V_{f}^{B}\) the overall effect of electron hopping on the macroscale gauge factors is small resulting in lower gauge factors.

The effective gauge factors, for all cases of local CNT volume fraction in bundles \(V_{f}^{CB}\) and maximum electron hopping range are observed to be smaller on application of tensile strains as compared to compressive strains. For example, at 0.58 \(V_{f}^{CB}\) and 5nm maximum electron hopping range, the effective macroscale gauge factor is 1.20 at 5% applied tensile strain and -1.62 at 5% applied compressive strain. The higher gauge factors for applied compressive strains are consistent with the higher relative change in resistivity for applied compressive strains.

Further, it is observed that unlike the case of uniformly dispersed aligned CNTs, higher CNT
volume fractions in microscale bundles ($V_{CB}^f$) are observed to yield higher macroscale effective gauge factors, which is contrary to the decreasing effective gauge factors for high local volume fractions observed for the uniformly aligned CNTs case. For example, at 0.25, 0.4 and 0.58 local CNT volume fraction in the microscale bundles, the effective macroscale gauge factors are -1.09, -1.17 and -1.62, respectively. For larger $V_{CB}^f$, the effective conductivity for each microscale bundle orientation is governed by the conductivity of the high conductivity nanoscale bundle. Thus, a small change in local bundle conductivity, or effective nanoscale conductivity, will lead to larger change in the microscale effective conductivity for the case with higher $V_{CB}^f$. The same idea can be used to understand the increasing effective gauge factor with increasing maximum electron hopping range at a fixed $V_{CB}^f$ of 0.58 as shown in Fig. 4.5a. At 1.8nm, 5nm and 10nm maximum electron hopping range, the macroscale effective gauge factors are observed to be -1.13, -1.62 and -1.64, respectively. A longer maximum electron hopping range will lead to highly conductive microscale bundles, which will then have the dominant effect on the effective microscale conductivities. The dominance of the nanotube bundle conductivity on the effective microscale conductivity leads to the effective microscale piezoresistive response being more sensitive to the piezoresistive response of the microscale bundles. Hence, higher effective gauge factors are observed for cases with longer maximum electron hopping range. However, while the effective gauge factors for the 5nm maximum electron hopping range is significantly higher (about 30%) than the 1.8nm case, the increase is much smaller as the maximum electron hopping range is changed from 5nm to 10nm (about 1.23%).

4.2.2 Uniformly Dispersed Partially Aligned Microscale Bundles

In addition to randomly oriented microscale bundles, the effective macroscale piezoresistive response for partially aligned microscale bundles (Fig. 4.6a) can be obtained by averaging over discrete number of orientations the microscale bundle by modifying the probability function $p^B(\varphi_m)$ to assign higher weights to a certain orientation during the averaging process. For this study, the probability function was assigned using a normal distribution of probabilities around $\varphi = \frac{\pi}{2}$ i.e. aligning the bundles along the $\tilde{x}_3$ direction. Three different cases
of normal distribution, as shown in Fig. 4.6b, are studied to observe the effect of variation in degree of alignment of microscale bundles. The variation parameter \( \sigma \) governs the width of probability distribution, and thus governs the degree of alignment of microscale bundles such that smaller values of \( \sigma \) yield higher degree of alignment. In contrast, the probability distribution function for the uniformly dispersed, randomly oriented case is a constant line of magnitude 1 representing equal probability of all discrete bundle orientations.

![Figure 4.6: a) Schematic of partially aligned microscale bundles indicating the direction of applied strain b) Different cases of probability distribution of microscale bundle orientations to account for varying degree of alignment.](image)

Fig. 4.7 shows the comparison of macroscale effective gauge factors \( G_{33} \) for the cases with different degree of alignment based on the probability distribution of discrete orientations shown in Fig. 4.6b for the case with \( 0.1V_f \), 5nm maximum electron hopping range and \( 0.58V_f^{CB} \). The macroscale effective gauge factor for the partially aligned microscale bundles are compared to the case with uniformly oriented microscale bundles. It is observed that for lower degree of microscale bundle alignment, the microscale effective gauge factors approach the randomly oriented bundle gauge factors, as was anticipated. The macroscale effective gauge factors are observed to be smaller in magnitude as the degree of alignment of microscale bundles is increased. For example, the macroscale effective gauge factors for variation parameter, \( \sigma \), of 0.1, 0.25, 0.5 and the randomly oriented case are -1.147, -1.185, -1.295 and -1.437, respectively. As the degree of alignment is increased, more microscale bundles
tend to align with the direction of principal strain i.e. $\tilde{x}_3$, resulting in more microscale bundles undergoing local strains in the axial direction. It was assumed in using a 2D transverse nanoscale RVE, owing to the large aspect ratio of CNTs, applied strains in the axial direction of microscale bundles will not cause formation or disruption of nanoscale electron hopping pathways. Thus, as the degree of alignment increases, lesser number of bundles undergo electron hopping induced change in nanoscale effective conductivity, which leads to smaller gauge factors for smaller values of $\sigma$. It is further noted that the effective gauge factors are higher for applied compressive strains as compared to applied tensile strains irrespective of the degree of alignment, as was observed for the randomly oriented microscale bundles.

![Figure 4.7](image.png)

Figure 4.7: The variation in effective macroscale gauge factors ($G_{33}^{Eff}$) with applied tensile compressive strains for different degrees of alignment of microscale bundles compared to the case with randomly oriented microscale bundles. [133]

4.3 Comparison with Experimental Results

It is observed from the results obtained for the uniformly dispersed aligned nanotubes, randomly oriented and partially aligned microscale bundles that the effective piezoresistive response of the CNT-polymer nanocomposite can be significantly different based on the morphology of microstructure at each of the scales. A comparison of the macroscale effective gauge factors obtained from the current study with those available from experimental re-
sults in the literature is shown in Table 4.1. The experimental results provided in Table 4.1 are measured for a 0.75wt% multi walled CNT-polysulfone(PS) films tested in tension with uniform dispersion and electric field induced alignment [20]. In addition, Oliva-Aviles et al. observed an increasing gauge factor as the applied strains were increased up to film fracture, which is consistent with the strain dependent effective macroscale gauge factors obtained in the current study. While the effective gauge factors for the randomly oriented and partially aligned microscale bundle cases are about the same in magnitude, the experimentally observed gauge factors are observed to be slightly higher than those obtained from the current multiscale model. It is to be realized that, for the current study, only one of the mechanisms, i.e. nanoscale electron hopping, is considered in evaluating the macroscale effective gauge factors. Other mechanisms, like inherent CNT piezoresistivity, network piezoresistivity of microscale bundles, plasticity and damage, could affect the macroscale effective gauge factors. The experimental results also indicate towards a higher gauge factor for the aligned nanocomposites. In contrast, the multiscale model in the current study predicts decreasing gauge factors in the alignment direction as the degree of alignment increases. The reason for the difference in observed behavior is attributed to the microstructure morphology obtained in the experimental investigation of the effective gauge factors for aligned CNT-polymer nanocomposites. In the current case, it is assumed that microscale bundles do not interact with each other to form long range bundle filaments or through microscale electron hopping, such that every bundle is isolated in the polymer matrix only interacting through strain or electric field perturbations. In an actual microstructure, such long range filament formation leading to network piezoresistivity and electron hopping pathways in between microscale bundle for high local microscale volume fractions could result in a different effective macroscale gauge factor.

In comparing the effective gauge factors obtained from the current study to those reported in the literature, it should be noted that the relevant information about the microstructure morphology, in terms of thickness and orientation of bundles, is not readily available in the literature. Hence, it is difficult to have a direct comparison of effective gauge factors against those reported in the literature from experimental investigation. However, the magnitudes of the effective gauge factors can be broadly compared to those available from experimental
Table 4.1: Macroscale effective gauge factors ($G^{Eff}$) obtained from the current study for different cases of microstructure morphology compared with those reported in the literature based on 0.75wt% MWCNT-PS nanocomposites tested in tension [20]. [133]

<table>
<thead>
<tr>
<th>Microstructure morphology</th>
<th>Macroscale Effective Gauge factors</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>2% compressive strain</td>
</tr>
<tr>
<td>Current multiscale model</td>
<td>Uniformly aligned CNTs</td>
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<tr>
<td></td>
<td>Randomly dispersed CNT bundles</td>
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<td>Partially aligned CNT bundles</td>
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<tr>
<td>Experimental results [20]</td>
<td>Randomly dispersed CNT bundles</td>
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<tr>
<td></td>
<td>Partially aligned CNT bundles</td>
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results. The effective gauge factors observed in this study are of comparable magnitude to the values reported in the literature (i.e. between 1 and 20 [3, 4, 7, 8, 11–13]). Thus, the results presented herein indicate that an interplay of local nanoscale CNT volume fractions, maximum electron hopping range and microstructure morphology can yield macroscale effective gauge factors close to the experimentally observed gauge factors. In addition, the current study strengthens the argument that electron hopping could have the governing influence on the effective piezoresistive response of CNT-polymer nanocomposites.
Chapter 5

Nanocomposite Piezoresistivity with Interfacial Separation and Damage

The effective macroscale properties of nanocomposites are known to originate from the nanoscale interface characteristics between the individual CNTs and the polymer matrix. For example, the mechanical properties of CNT-polymer nanocomposites are dependent on the functionalization of CNT interface. It is expected that the electrostatic response of nanocomposites will be sensitive to interface characteristics as well. Further, interfacial separation and damage at the nanoscale could lead to additional damage based piezoresistivity in the nanocomposites. In order to study the effect of nanoscale interface separation/damage on the effective electrostatic and piezoresistive response, the nanoscale CNT-polymer interface is modeled through electromechanical cohesive zones in the current work. The results presented in this chapter are published in [136].

5.1 Coupled Electromechanical Cohesive Zones

In addition to mechanical cohesive zones, here we report the development of coupled electrostatic cohesive zones to allow for electron hopping based current density across the separated CNT-polymer interface. A computational continuum micromechanics based method is devel-
oped to study the changing CNT-polymer morphology at the nanoscale along with initiation and evolution of the interfacial separation/damage of the CNT-polymer interface, the subsequent evolution of electron hopping pathways in between nanotubes and their effect on the macroscale piezoresistive response.

5.1.1 Mechanical Cohesive Zones

In order to account for the interfacial damage at the CNT-polymer interface, mechanical cohesive zones (CZ) allowing for interfacial tractions across the separated interface are employed. A bilinear cohesive law is used in the current work to model the CNT-polymer interface behavior based on a molecular dynamics study conducted by Li and Seidel [82] examining the mechanical behavior of a graphene sheet - Polyethylene (PE) interface which relied heavily on the non-bonded (i.e. unfunctionalized) load transfer capabilities. The non-bonded interactions for the graphene-epoxy interface are expected to undergo a similar variation in local interfacial properties. In the study by Li and Seidel, a molecular dynamics based simulation box was set up with an interacting graphene sheet and amorphous PE polymer. The interface traction-separation response was found by fixing the top section of the amorphous PE in space while pulling on the graphene sheet, normal and tangential to the graphene-PE interface, to complete separation. The traction separation curves for purely normal and purely tangential monotonic separation of the CNT-polymer interface are shown in Fig. 5.1a and Fig. 5.1b, respectively. It is observed that the normal traction increases in an apparently linear fashion up to a point of peak traction as the separation distance increases. Thereafter, the normal surface traction decreases to complete separation where it diminishes to zero signifying complete damage of the cohesive zone element. It was indicated in [82] that the observed traction-separation response can be idealized as a bilinear cohesive law with an initial linear region (Region II, Fig. 5.1a) corresponding to the elastic stretching of the polymer ligaments and a subsequent linear region of negative slope (Region III, Fig. 5.1a) signifying a linear decrease in interfacial traction as the cohesive zone progressively gets damaged. The bilinear traction displacement curves used in the current work are quantified by three parameters i.e. peak traction ($t^{max}_n=0.332$GPa), interface separation
at peak traction \( \Delta \tilde{u}_{sw}^{\text{max}} = 0.182 \text{nm} \) and the interface separation at complete separation of the interface \( \Delta \tilde{u}_{\text{max}} = 3.32 \text{nm} \). For the normal traction-separation law, negative values of \( \Delta \tilde{u}_n \) represent non-physical interpenetration of the interface which needs to be discouraged through a larger stiffness for \( \Delta \tilde{u}_n < 0 \). However, in that case the convergence of the solution near the interface may not be easily achieved since stiffness mismatch at the interface in tension and compression are different and leads to local oscillations of the interface. In the current work, the stiffness for \( \Delta \tilde{u}_n < 0 \) is fixed to be the same as the initial linear elastic stiffness of cohesive zones and since this stiffness is large for the specific CNT-polymer interface \[82]\ the interpenetration of the interface is small.

![Figure 5.1](image)

**Figure 5.1:** Cohesive zone (CZ) traction-separation law for CNT-polymer interface undergoing a) purely normal mode of separation b) purely tangential mode of separation as obtained from MD simulations in \[82]\, \[136]\.

The tangential traction-separation law was observed to follow a bilinear behavior as well. Similar to the traction-separation response for purely normal separation, the CZ behavior for purely tangential separation undergoes an initial linear increase in tangential traction as the tangential interface separation increases (Region III, Fig. 5.1b). Thereafter, instead of linearly decreasing after the point of peak traction \( \Delta \tilde{u}_t^{\text{sw}} = 1 \text{nm} \) as was observed for the normal CZ law, the tangential surface traction remains constant at the peak traction \( \tilde{t}_t^{\text{max}} \) of 0.08GPa (Region IV, Fig. 5.1b). The flat plateau region for \( \Delta \tilde{u}_t > \Delta \tilde{u}_t^{\text{sw}} \) corresponds to the amorphous polymer sliding over an infinitely long graphene sheet, as opposed to a
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For the normal mode of separation, if the interface separation becomes less than zero (i.e. inter penetration of surfaces), the stiffness of the cohesive zone is fixed at the initial stiffness of the undamaged cohesive zone in tension (Region I, Fig. 5.1a). However, for tangential separation the traction-separation response is symmetric about the origin i.e. same in either direction of tangential sliding.

Figure 5.2: Cohesive zone (CZ) traction-separation law for CNT-polymer interface with CZ unloading in a) purely normal mode of separation b) purely tangential mode of separation.

[136]

For the case of hexagonally packed CNTs in the nanoscale RVEs, applied boundary conditions on the non-uniform microstructure can lead to complex interface separation response which could lead to localized relaxation of some cohesive zone elements as damage gets initiated in the vicinity. In the case of cyclic loading of the nanoscale RVE, such relaxation of cohesive zones could have an even greater influence on the local and overall response of the nanoscale RVE. Thus, the cohesive zones are allowed to relax (or unload) along the line of constant current stiffness for both normal and tangential separation as is shown in Fig. 5.2a and Fig. 5.2b for purely normal and and purely tangential separation of interface, respectively. For purely normal separation (Fig. 5.2a), the normal traction increases linearly from point A up to point B with the slope of the traction displacement curve ($\tilde{K}_n^{(0)}$) signifying the
initial undamaged linear elastic normal stiffness of the cohesive zone. Thereafter, the normal traction starts to decrease linearly from point B to point C. The current normal stiffness of the cohesive zone at any point after B can be evaluated as the current traction divided by the current separation distance i.e. the slope of the line connecting the current location on the traction-separation curve to the origin. For example, the current stiffness at point C is given by $\tilde{K}_n^{(cur)} = \tilde{t}_C / \Delta \tilde{u}_n^C$. Hence, the current stiffness at any point after the peak traction (point B) will be less than the initial linear elastic stiffness of the cohesive zone ($\tilde{K}_n^{(0)}$) signifying a decreased stiffness as damage gets induced in the cohesive zone. At point C, the direction of applied local displacements on the cohesive zone is reversed and the cohesive zone is allowed to unload along the line connecting point C to the origin i.e. keeping the current stiffness ($\tilde{K}_n^{(cur)}$) constant. If the normal separation distance decreases to the extent that it crosses the origin leading to interpenetration (A-D) the cohesive zone assumes the initial linear elastic stiffness ($\tilde{K}_n^{(0)}$) to restrict non-physical interpenetration of damaged cohesive zones. Some studies have used an exponential stiffness in compression to restrict unrealistic interpenetration for cohesive zone interfaces [78]. If the cohesive zone is loaded again in tension, it follows the initial linear elastic stiffness while it is still interpenetrating (D-A). Thereafter, it follows the damaged current stiffness ($\tilde{K}_n^{(cur)}$) along which it had unloaded and joins the traction-separation curve at point C where it had started the unloading cycle (A-C). Thus, during the unloading/reloading cycle (C-A-D-A-C), no further damage is induced in the cohesive zone. However, if loaded further beyond point C, the cohesive zone follows the line B-C to point E accumulating further damage up to a point where it gets fully damaged (point E) resulting in complete separation of interface with zero normal traction. If the cohesive zone is unloaded from this point the traction across the interface remains zero as long as $\Delta \tilde{u}_n > 0$ and follows the initial compression stiffness if $\Delta \tilde{u}_n < 0$.

A similar loading/unloading behavior of purely tangential cohesive zones is shown in Fig. 5.2b. For purely tangential loading, the cohesive zone undergoes the normal cycle A-B-C. At point C, the loading is reversed and the cohesive zone relaxes along the line of constant current tangential stiffness ($\tilde{K}_t^{(cur)} = \tilde{t}_C / \Delta \tilde{u}_t^C$). However, unlike purely normal cohesive zone separation, if the separation distance becomes negative (i.e. interface sliding in the negative direction), the cohesive zone still follows the current tangential stiffness (A-D). If loaded again, it re-
traces the line of current tangential stiffness (D-A) and rejoins the traction-separation law at point C.

5.1.2 Electrostatic Cohesive Zones

In addition to mechanical cohesive zones, the electrostatic behavior of the CNT-polymer interface is modeled through electrostatic cohesive zones. The response of the electrostatic cohesive zones is coupled with the mechanical cohesive zone such that the local cohesive zone electrostatic properties are dependent on the normal separation of the interface. While the mechanical cohesive zones act effectively as springs connecting the interface between the CNT and polymer allowing for interaction between the CNT and polymer through the surface tractions, the electrostatic cohesive zones are needed for the CNT and polymer to interact electrostatically by allowing a surface normal current density through the separated interface. The electrostatic cohesive zones were used in the current study using a normal current density ($\tilde{J}_n$) - interface normal separation distance ($\Delta\tilde{u}_n$) law. The electron hopping effect can lead to an increased surface normal current density as the electrons hop across the separated interface through the polymer ligaments. In order to account for such effects, a bilinear interfacial resistance ($\tilde{R}$) to normal interface separation is proposed in this study for the case with no electron hopping and extended to nonlinear for interfaces with electron hopping.

For the case where no electron hopping is allowed, the cohesive zone interface is considered to have polymer ligaments connecting the interface resulting in electrostatic current density carrying capacity of the interface. As the interface starts to separate, these ligaments start to stretch elastically for $\Delta\tilde{u}_n < \Delta\tilde{u}_n^{sw}$ such that the cross sectional area of these ligaments varies with interface separation. However, the local resistivity ($\tilde{\rho}$) of the cohesive zone polymer ligament remains constant as no damage is induced for interface separation less than $\Delta\tilde{u}_n^{sw}$. The separation distance at which the onset of damage occurs ($\Delta\tilde{u}_n^{sw}$) is the same for the mechanical and electrostatic cohesive zone interface model, implying that the mechanical damage in filaments connecting the interfaces is accompanied by a changing local electrostatic cohesive zone response. The interfacial resistance for a cohesive zone node pair
for interface separation less than $\Delta \tilde{u}_{n}^{sw}$ is given by

$$\tilde{R}(\Delta \tilde{u}_{n}) = \frac{\tilde{\rho}}{\tilde{A}} \Delta \tilde{u}_{n} \quad \Delta \tilde{u}_{n} \leq \Delta \tilde{u}_{n}^{sw} \quad (5.1)$$

where $\tilde{A}$ is the effective cross sectional area for the cohesive zone node pair. The normal interface separation ($\Delta \tilde{u}_{n}$) acts as the effective length of the polymer ligament connecting the interface. In effect, the interface resistance increases linearly as the interface normal separation increases with a rate given by $\tilde{\rho}/\tilde{A}$. The linear increase in resistance with increasing normal separation distance for undamaged cohesive zone is shown in region II in Fig. 5.3a (between points A and B). It should be noted that the local resistance of the cohesive zone is dependent on the separation distance, thus, every cohesive zone could possibly have a different current resistance for applied displacement boundary conditions on the inhomogeneous nanoscale RVE.

![Figure 5.3](image)

Figure 5.3: a) Variation of cohesive zone interface resistance with increasing normal interface separation for monotonic loading and with cohesive zone relaxation and b) the corresponding cohesive zone normal current density variation with interface separation. [136]

If the normal interface separation becomes larger than $\Delta \tilde{u}_{n}^{sw}$, the cohesive zone starts to get
progressively damaged up to $\Delta \bar{u}_{n}^{\text{max}}$, where it gets completely damaged. The rate of change of resistance with increasing interface separation should be larger than the nominal slope with no interfacial damage ($\zeta$) to account for the damage induced increase in local polymer ligament resistivity. The interfacial separation distance for complete damage ($\Delta \bar{u}_{n}^{\text{max}}$) is the same for both the mechanical and electrostatic cohesive interface laws. For this study, it is assumed that the increase in resistance with cohesive zone damage follows a linear response (region III and IV in Fig. 5.3a) with a higher rate of $\gamma \bar{\rho}/\bar{A}$ where $\gamma \geq 1$. The symbol, $\gamma$, denotes the increase in rate of change of interfacial resistance with interfacial damage, thus, for an undamaged cohesive zone $\gamma = 1$. The interfacial resistance for interface separation larger than $\Delta \bar{u}_{n}^{\text{sw}}$ is given by

$$\tilde{R}(\Delta \bar{u}_{n}) = \tilde{\rho} \Delta \bar{u}_{n}^{\text{sw}} + \frac{\gamma \tilde{\rho}}{\bar{A}} (\Delta \bar{u}_{n} - \Delta \bar{u}_{n}^{\text{sw}}) \quad \Delta \bar{u}_{n} \geq \Delta \bar{u}_{n}^{\text{sw}} \quad (5.2)$$

The local cohesive zone resistivity in region III of Fig. 5.3a is given by the slope of line joining the current position on the interfacial resistance - normal separation curve to the origin, and can be expressed as

$$\tilde{\rho}(\Delta \bar{u}_{n}) = \frac{\Delta \bar{u}_{n}^{\text{sw}}}{\Delta \bar{u}_{n}} + \gamma \tilde{\rho} \left(1 - \frac{\Delta \bar{u}_{n}^{\text{sw}}}{\Delta \bar{u}_{n}}\right) \quad \Delta \bar{u}_{n} \geq \Delta \bar{u}_{n}^{\text{sw}} \quad (5.3)$$

If the cohesive zone starts to unload (or relax) because of localized damage in the inhomogeneous nanoscale microstructure or because of macroscale boundary conditions, it is allowed to unload and reload along the line of constant current resistivity as shown in Fig. 5.3a by the line connecting point C to point A. The point C is where the unloading of the cohesive zone is initiated. The local cohesive zone resistivity is then given by $\tilde{R}_{C}/\bar{A}\Delta \bar{u}_{n}^{C}$ or by Eqn. 5.3 with $\Delta \bar{u}_{n} = \Delta \bar{u}_{n}^{C}$. If the normal interface separation becomes greater than $\Delta \bar{u}_{n}^{\text{max}}$, the polymer ligament connecting the interface is considered to be completely damaged and the interfacial resistance jumps to a very high value approximating infinity, i.e. zero current density across the interface, as shown in region V of Fig. 5.3a. In the case where the cohesive zone interface is interpenetrating (A-D), i.e. $\Delta \bar{u}_{n} < 0$, the interface resistance is fixed at approximately zero, as shown in region I of Fig. 5.3a. It is to be noted that the variation in
surface normal traction shown in Fig. 5.2a and the variation in interfacial resistance shown in Fig. 5.3a, with loading and unloading of the cohesive zone, correspond to the same time variation of applied displacement boundary condition. Fig. 5.2a and Fig. 5.3a represent the coupled electromechanical response of the cohesive zone, i.e. they begin to damage and are fully damaged at the same relative normal displacement values ($\Delta \tilde{u}^{\text{sw}}_n$ and $\Delta \tilde{u}^{\text{max}}_n$).

The current density across a separating CNT-polymer interface is dependent on the variation of interface resistance with increasing interface normal separation. Fig. 5.3b shows the surface normal current density for a zoomed interface separating CNT-polymer phases with a CNT block interacting with a polymer polymer block through the interface. A test electric field is applied across the CNT-polymer interface as shown in the local potential contour in Fig. 5.3b. In the unstrained state, the CNT being highly conductive retains the potential applied at the bottom edge and the potential drop happens across the polymer medium uniformly. There is negligible potential drop at the interface in the unstrained state because the cohesive zone resistance is nearly zero. As the interface separation increases, the resistance of the interface increases such that a larger potential drop happens in the cohesive zone. The surface normal current density decreases from the unstrained state from point A-B, after which the rate of decreasing surface normal current density is larger which in accordance with a steeper increase in the interfacial resistance. At complete separation, as the interfacial resistance goes to infinity, the surface normal current density drops to zero and remains at zero for any change in interface separation. Once completely damaged, the electromechanical cohesive zone loses its capability to carry any tractions or current density, even in the case of unloading of the cohesive zones. However, if on unloading, the interface interpenetrates ($\Delta \tilde{u}_n < 0$) the resistivity goes to zero as would be anticipated.

In order to allow for electron hopping across the separated interface, the local resistivity ($\tilde{\rho}$) of the cohesive zone in Eqn. 5.1,5.2 and 5.3 is modified to the electron hopping based local resistivity of the polymer medium ($\tilde{\rho}^{\text{EH}}$). If the polymer node of the cohesive zone node pair lies in an element which is within the intertube region i.e. has electron hopping based augmented conductivity, the cohesive zone material inherits the same conductivity/resistivity. Thus, the bilinear law for resistance with increasing interface separation becomes a non-
linear function of interface separation as the interfacial resistivity ($\tilde{\rho}$) changes along with the normal interface separation ($\Delta\tilde{u}_n$), resulting in faster rate of increase of local cohesive zone resistivity.

The variation of interfacial resistance with increasing normal interface separation is shown in Fig. 5.4a for different maximum electron hopping ranges ($\delta_{EH}^{max}$). The initial intertube distance between the CNT pair is taken to be 1nm such that the intertube separation distance at a certain interface separation ($\Delta\tilde{u}_n$) becomes 1nm+$\Delta\tilde{u}_n$. The local resistivity of the cohesive zone is then evaluated based on the electron hopping relation shown in Eqn. 3.2. The 1nm $\delta_{EH}^{max}$ case is observed to follow the same variation of interfacial resistance as the case with no electron hopping (No EH) because the electron hopping range is less than the intertube distance for all values of interface separation. Similarly, the 2nm and 3.5nm $\delta_{EH}^{max}$ cases are observed to converge to the case with no electron hopping as they move out of the electron hopping range at 1nm and 2.5nm, respectively. From Eqn. 3.2, it is observed that for a fixed intertube distance ($d^{CNT-CNT}$), given that the polymer conductivity is several orders of magnitude smaller than the CNT conductivity, a larger $\delta_{EH}^{max}$ will result in larger
conductivity (or smaller resistivity). Thus, at any given interface separation in Fig. 5.4a, the larger electron hopping range has smaller interfacial resistance because of smaller electron hopping resistivity. At the point of complete separation of the interface (i.e. $\Delta \tilde{u}_n = \Delta \tilde{u}^{max}_n$), the interfacial resistivity jumps to a large value approximating infinity for all electron hopping ranges. In other words, the electrostatic cohesive zones are still active and represent infinite resistance even when the mechanical cohesive zone gets completely damaged. The normal interface current density is evaluated by applying a test electric field across the interface as depicted in Fig. 5.3b. The interfacial current density follows from the interfacial resistance such that for a fixed interface separation a larger electron hopping range (or smaller local cohesive zone local resistivity) leads to a larger interface normal current density, as shown in Fig. 5.4b.

5.2 Nanocomposite Piezoresistivity with Interfacial Separation Under Monotonic Loading

The finite element based micromechanics model described for the electron hopping framework with electromechanical cohesive zones at the CNT-polymer interface is used to identify the key factors behind the strain and interface separation/damage based macroscale piezoresistivity in response to applied macroscale strains. This is achieved by performing tests on the nanoscale RVE, varying key modeling parameters e.g. applied boundary conditions, maximum electron hopping ranges and electromechanical cohesive zone parameters, to assess the effect of each of these parameters on the effective nanocomposite piezoresistive response.

5.2.1 Unconstrained Plane Strain Tension/Compression Test

In order to study the effect of interface separation on the effective electrostatic properties of the CNT-polymer nanocomposite for applied uniform macroscale tension/compression, the nanoscale RVE with a volume fraction of 0.4 is subjected to unconstrained plane strain tension/compression tests. A detailed description of the applied boundary conditions for the
unconstrained plane strain tension/compression test is provided in [139]. The key idea is that the sides BC and AD are free to move in the $\hat{x}_1$ direction while displacement boundary conditions, representative of macroscale uniform strain state, are applied in edges AB and CD of the nanoscale RVE (Fig. 3.1) in the $\hat{x}_2$ direction. The maximum electron hopping range ($\delta_{EH}^{max}$) is fixed at 5nm for the current test. The nanoscale RVE with a volume fraction of 0.4 is composed of hexagonally packed CNTs with an unstrained intertube distance of 1.01nm between every adjacent pair of nanotubes. The intertube distances in the unstrained state, and for the applied ±5% uniaxial strain, are observed to be within the maximum electron hopping range i.e. the nanoscale RVE is above the percolation threshold for the current plane strain tension/compression test with local intertube polymer and cohesive zone conductivities dependent on the electron hopping conductivity as shown in Eqn. 3.2. In some of our earlier work [133,139], it was shown that the uniform local macroscale strains applied to the nanoscale RVE as displacement boundary conditions lead to a change in the nanoscale intertube distances for the nanoscale RVE with perfectly bonded interface, resulting in an increased effective conductivity when subjected to compressive strains and a reduced effective conductivity for applied tensile strains. It was further observed that the change in effective conductivity was closely related to the formation of vertical and diagonal bands of increases/reduced conductivity in the polymer medium representative of electron hopping across the nanotubes.

For the current work with interface separation, two primary factors govern the effective electrostatic properties 1) electron hopping based local intertube conductivity 2) local interfacial resistance after interface separation. Both of these factors determine the local current density pathways in the nanoscale RVE when subjected to a test electric field to find the effective electrostatic properties. Fig. 5.5a shows a comparison of intertube distances for perfectly bonded interface and with interface separation between a pair of vertically and diagonally adjacent nanotubes. The variation of electron hopping based local intertube conductivities corresponding to the intertube distances are shown in Fig. 5.5b. For applied compressive strains, a vertical band of increased conductivity forms between the vertically adjacent nanotubes (C1-C2,C3-C4 etc.) resulting in an increase in the effective conductivity components. For applied tensile strain, the intertube distances between the vertically and
Figure 5.5: a) Variation of intertube distances for CNT pairs C1-C2 and C1-C3 with applied strain for the perfectly bonded interface and with interface separation and b) local conductivity of the corresponding electron hopping pathways. [136]

Diagonally adjacent nanotubes increase, but the change in the intertube distance between the diagonally adjacent nanotubes (C1-C3,C1-C7 etc.) is smaller. Thus, the local electron hopping conductivity of the diagonal band overrides the reduced conductivity in the vertical bands resulting in small pockets of highly reduced conductivity in between the vertically adjacent nanotubes. The intertube distances for the vertically adjacent C1-C2 pair with interface separation is observed to be very close to those observed for the C1-C2 pair with perfectly bonded interface. This indicates that the electron hopping based vertical bands have the same local conductivity for either case. However, the intertube distance between diagonally adjacent CNTs (like C1-C3) is observed to follow a slightly different variation for the case with interface separation and with perfectly bonded interface. At 5% applied tension, the intertube distance between C1-C3 pair increases by 0.37% for the perfectly bonded interface case resulting in 2.23% increase in the local intertube conductivity as compared to the unstrained state. However, for the case with interface separation, the C1-C3 intertube distance increases by 2.09% resulting in 11.9% increase in the local intertube conductivity. Thus, it is expected that the effective conductivity components will undergo a larger change
from the unstrained state for the case with interface separation. It is to be noted that for the ±5% applied strain applied to the nanoscale RVEs, the normal and tangential interface separation of all cohesive zone elements is less than $\Delta u_n^{sw}$ and $\Delta u_t^{sw}$, respectively, indicating that cohesive zones do not get damaged for the ±5% applied strain states.

Although the interface cohesive elements do not get damaged for the strains applied, i.e. they retain the same resistivity as the electron hopping augmented polymer in the vicinity, they introduce a third phase in the nanoscale RVE. After interface separation, the nanoscale RVE is composed of the CNTs, electron hopping augmented polymer and the interface cohesive zone elements. The interfacial resistance at the separated CNT-polymer interface effects the local current density (Fig. 5.6) resulting in electrostatic properties different from the perfectly bonded interface case. On application of tensile strains, the interface separation of cohesive zone element CZ2 (Fig. 5.5 inset) increases resulting in higher interfacial resistance as discussed in Sec. 5.1.2. On application of compressive strains, the cohesive zone CZ2 remains in compression (slight interpenetration) with nearly zero interfacial resistance, but the cohesive zone CZ1 undergoes interface separation resulting in higher interfacial resistance. Thus, the current density pathways in the $\hat{x}_1$ direction get inhibited faster than those in the $\hat{x}_2$ direction. In addition, the intertube distance for the diagonally adjacent pair is observed to be smaller for the separated interface (Fig. 5.5), resulting in higher local intertube conductivity in the polymer medium between diagonally adjacent nanotube pairs. The local current density contours are presented in Fig. 5.6a,b at different strain states for the perfectly bonded interface in comparison to cases with interface separation. Fig. 5.6a shows the local current density contour for the component $\hat{J}_1$ when a test electric field is applied in the $\hat{x}_1$ direction. The current density contours show the same overall behavior, but with slight differences in the local current density components for the perfectly bonded and separated interface cases. It is to be noted that the averaged current density from contours shown in Fig. 5.6a is used in Eqn. 2.49 to find the $\Sigma_{11}^{Eff}$ component of effective conductivity. Similarly, Fig. 5.6b shows the local current density contours for component $\hat{J}_2$ when the test electric field is applied in the $\hat{x}_2$ direction. The averaged current density from Fig. 5.6b is used to evaluate the $\Sigma_{22}^{Eff}$ component of effective conductivity. Based on the difference in the local current density in the nanoscale RVE, it is expected that the effective conductivity
components for the perfectly bonded and with interface separation will be different.

![Figure 5.6: Local current density contours for the nanoscale RVE with and without interface separation at different applied strain states.](image)

(a) local current density in the $\hat{x}_1$ direction with applied test electric field in the $\hat{x}_1$ direction and (b) local current density in the $\hat{x}_2$ direction with applied test electric field in the $\hat{x}_2$ direction. [136]

Fig. 5.7 presents a comparison of the effective conductivity components for nanoscale RVE with perfectly bonded and with interface separation for up to 5% applied tensile/compressive strain. In addition, the local conductivity contours are presented at different tensile and compressive strain states in order to correlate the effective conductivity to the electron hopping based evolving local conductivities. A correspondence between the evolving local nanoscale electrostatic properties with the effective conductivity components was established for a nanoscale RVE with perfectly bonded interface in [139]. In comparison to the perfectly bonded case, the effective conductivity components follow a different variation when subjected to plane strain tension compression tests allowing for interface separation. It is observed that the $\Sigma_{11}^{Eff}$ and $\Sigma_{22}^{Eff}$ components have the same initial values for the unstrained state because of uniform hexagonal arrangement of CNTs and symmetric electron hopping pathways in the nanoscale RVE resulting in transversely isotropic in-plane effective properties. On application of tensile/compressive strains the nanoscale RVE deviates from the transversely isotropic behavior as the nanoscale microstructure evolves such that $\Sigma_{11}^{Eff}$ and $\Sigma_{22}^{Eff}$ components follow a different variation with applied strain.
Figure 5.7: Effective conductivity components for the nanoscale RVE subjected to unconstrained plane strain tension/compression tests with perfectly bonded interface in comparison to the tests allowing for interface separation. Local conductivity contours showing the electron hopping induces formation/disruption of conductive pathways for different applied strain states. A zoomed view of local interfacial separation around CNT C1 at 5% applied tension. [136]
When the local cohesive zone interfaces are in contact they are expected to have zero resistance or infinite conductivity based on the discussion in Sec. 5.1.2. For the current work, the infinite conductivity of the interface at zero separation is approximated by using a value five orders of magnitude larger than local CNT conductivity. However, despite this assumption, the interface has a small finite resistance even when it is not separated (in contact or interpenetrating). Thus, in the unstrained state, $\Sigma_{11}^{Eff}$ and $\Sigma_{22}^{Eff}$ are observed to be 15.34% smaller for the case with interface separation as compared to that observed with perfectly bonded interface. On application of 5% tensile strain, $\Sigma_{11}^{Eff}$ reduces by about 17% from the unstrained state for the case with interface separation, whereas for perfectly bonded interface $\Sigma_{11}^{Eff}$ reduces by only about 5%. Similarly, the $\Sigma_{22}^{Eff}$ component decreases by about 25% with the separated interfaces and only about 17% for the perfectly bonded case, compared to the respective unstrained state effective conductivities. In compression, the $\Sigma_{22}^{Eff}$ component of applied conductivity increases by 117% for perfectly bonded interface and 133% for the case with interface separation. The difference in the variation of effective conductivity components in compression is partly due to the difference in the C1-C3 intertube distance, since the C1-C2 interface separation is essentially the same, and partly due to the interpenetration observed at the CNT-polymer interface. The results indicate that the interface separation leads to a higher deviation from the unstrained state transversely isotropic behavior in both tension and compression. In addition, the relative change in effective conductivity components from the unstrained state governs the macroscale piezoresistive response indicating that the perfectly bonded and separated interfaces cases will lead to different macroscale effective gauge factors, and therefore an ability to distinguish between deformation and interface separation.

### 5.2.2 Constrained Plane Strain Tension/Compression Test

The nanoscale RVE is subjected to constrained plane strain tension/compression tests in order to understand the difference in evolving interface separation, electron hopping pathways and their impact on the effective piezoresistive response of CNT-polymer nanocomposites when subjected to different applied boundary conditions. The key difference in boundary
conditions from the unconstrained tests (presented in section 5.2.1) is that the sides BC and AD are constrained not to move in the \( \hat{x}_1 \) direction while displacement boundary conditions, representative of macroscale uniform strain state, are applied in edges AB and CD of the nanoscale RVE (Fig. 3.1). With perfectly bonded interface \([139]\), the effective electrostatic and piezoresistive response for the constrained and unconstrained tension/compression was observed to be different because of the difference in evolution of intertube distances for the two cases. The difference in evolving intertube distances led to the formation of electron hopping pathways with different local conductivities, which were then reflected in the effective electrostatic response. For the current work allowing interface separation, in addition to the difference in evolving intertube distances, the difference in evolution of interfacial separation at the CNT-polymer interfaces for the two cases leads to the difference in effective electrostatic and piezoresistive response of the nanoscale RVE.

Allowing interface separation, the variation of intertube distances with applied constrained/unconstrained plane strain test cases is shown in Fig. 5.8a. It is observed that the intertube distance C1-C2 follows the same variation for both constrained and unconstrained tension/compression tests. However, the intertube distance, C1-C3 is observed to increase at a faster rate for applied constrained tension as compared to the unconstrained tension. A faster increase in the intertube distance results in a faster reduction in local electrical conductivity of the bands between diagonally adjacent nanotubes for the constrained test. For applied compressive strain, the C1-C3 intertube distance decreases faster from the unstrained state for the constrained test resulting in larger local conductivity in the diagonal electron hopping bands at any compressive strain state as compared to the unconstrained tests. In addition to the intertube distances, the interface separation at the CNT-polymer interface is observed to be different for the constrained/unconstrained plane strain tension/compression tests. As an example, the interface normal separation \( (\Delta \tilde{u}_n) \) is presented in Fig. 5.8b for two sets of cohesive zone node pairs, CZ1 and CZ2, as indicated in Fig. 5.8c. It is observed that the cohesive zone normal separation for both CZ1 and CZ2 and the other cohesive zone node pairs are much smaller than the interface separation needed to initiate damage in the cohesive zone \( (\Delta \tilde{u}_{n}^{sw} = 0.182\text{nm}) \). Thus, the cohesive zones are operating in their undamaged linear part of the cohesive zone law for the applied ±5% applied strains for con-
Figure 5.8: a) Comparison of intertube distances, C1-C2 and C1-C3, for the constrained and unconstrained cases, b) comparison of interface normal separation of the local cohesive zone CZ1 and CZ2 for applied constrained/unconstrained strains and c) state of local interface separation around CNT C1 for ±5% applied constrained/unconstrained strain. [136]

strained/unconstrained tests. Fig. 5.8c shows the interface separation at ±5% strain state around CNT C1 for the unconstrained and constrained plane strain tests. The interface normal separation for cohesive zone CZ2 is observed to follow a similar variation for both constrained and unconstrained test. However, for the CZ1 cohesive zone, a significant difference is observed in the normal interface separation. On application of tensile strain, CZ1 is observed to undergo interpenetration with -0.023nm interface separation at 5% applied strain for the unconstrained test. However, the constraints on edges BC and DA restrict Poisson’s contraction of the nanoscale RVE resulting in the transverse direction experiencing tensile strains leading to interfacial separation at the CZ1 interface. For the constrained test, the CZ1 cohesive zone is observed to undergo tension (separation) with 5.76E-4nm
interface separation at 5% applied constrained tension. Similarly, in compression, the CZ1 cohesive zone was observed to undergo interface separation with 0.023 nm separation at 5% unconstrained compressive strain. However, for the constrained compression test, the CZ1 cohesive zone undergoes interpenetration with -5.76E-4 nm interface separation.

Figure 5.9: Comparison of effective conductivity components for the nanoscale RVE with and without interface separation subjected to constrained/unconstrained tension/compression tests. a) $\Sigma_{11}^{\text{Eff}}$ and b) $\Sigma_{22}^{\text{Eff}}$. [136]

Fig. 5.9 shows the effective conductivity components for the constrained and unconstrained plane strain tension/compression tests with interface separation in comparison to the perfectly bonded interface cases. The electrostatic properties are observed to evolve from the same nominal conductivity in the unstrained state to different effective conductivities for the constrained/unconstrained plane strain tension/compression tests. With interface separation, it is observed that the effective conductivity components reduce faster from the unstrained state conductivity for the case with applied strains for the constrained tension test. For example, at 5% applied tension, $\Sigma_{11}^{\text{Eff}}$ and $\Sigma_{22}^{\text{Eff}}$ components of effective conductivity are observed to be smaller than the unconstrained tension case by 10.52% and 9.39%, respectively. Similarly, in compression, $\Sigma_{11}^{\text{Eff}}$ and $\Sigma_{22}^{\text{Eff}}$ components of effective conductivity are observed to be larger than the unconstrained tension case by 10.03% and 1.82%, respectively. The observed difference indicates that the nanoscale RVE deviates from the electrostatically transversely isotropic material symmetry faster when subjected to constrained plane strain.
tension/compression. Thus, the effective electrostatic properties for the nanocomposite are observed to be boundary condition dependent. However, the difference between the effective conductivity components is observed to be smaller for the nanoscale RVE with interface separation as compared to the perfectly bonded interface. For example, at 5% applied tensile strain, the difference in $\Sigma_{11}^{Eff}$ component between the constrained and unconstrained tests for perfectly bonded interface is about 19% as compared to about 10% difference for with interface separation. Similarly, the difference in $\Sigma_{22}^{Eff}$ component at 5% applied tensile strain is about 16% with perfectly bonded interface as compared to about 10% with interface separation. These observations indicate that the boundary condition dependent evolving interface separation can significantly affect the material symmetry properties in addition to the strain dependent electron hopping mechanism.

![Figure 5.10: Comparison of relative change in resistivity components for the nanoscale RVE with and without interface separation subjected to constrained/unconstrained tension/compression tests. a) $\Delta \rho_{11}^{Eff} / \rho_{0}^{Eff}$ and b) $\Delta \rho_{22}^{Eff} / \rho_{0}^{Eff}$. [136]](image)

The electrostatic conductivity components are used to evaluate the relative change in resistivity to relate the variation in conductivity components to the effective piezoresistive response of CNT-polymer nanocomposites. Fig. 5.10a,b show the relative change in resistivity for the effective resistivity components in the $\hat{x}_1$ and $\hat{x}_2$ direction, respectively, for constrained/unconstrained tests with perfectly bonded interfaces and with interface separation. A positive magnitude of the relative change in resistivity signifies that the effective nanocomposite is less conductive from its unstrained state while a negative magnitude repre-
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tsents an increase from unstrained conductivity. The variation of relative change in resistivity with applied strain represents the piezoresistive response of the nanocomposite through to the piezoresistive strain tensor coefficients \( \Pi_{ij}^{\text{eff}} \) as shown in Eqn. 2.51. From Fig. 5.10a,b, it is observed that the relative change in resistivity is higher with interface separation as compared to the corresponding perfectly bonded interface cases. As an example, for 5% applied tension, \( \Delta \rho_{11}^{\text{eff}} / \rho_0^{\text{eff}} \) is higher for the unconstrained tension test with interface separation by about 280% as compared to the perfectly bonded case. Similarly, for 5% applied tension, a 148% increase in the magnitude of \( \Delta \rho_{22}^{\text{eff}} / \rho_0^{\text{eff}} \) is observed with interface separation as compared to the perfectly bonded interface. The difference between relative change in resistivity in the \( \hat{x}_2 \) direction (\( \Delta \rho_{22}^{\text{eff}} / \rho_0^{\text{eff}} \)) for the damaged and undamaged interface cases is observed to be smaller on application of compressive strains, especially for the unconstrained tests. As an example, for the unconstrained test, at 5% compression the difference in \( \Delta \rho_{22}^{\text{eff}} / \rho_0^{\text{eff}} \) is observed to be about 6% as compared to 148% increase at 5% tension. In contrast, the \( \Delta \rho_{11}^{\text{eff}} / \rho_0^{\text{eff}} \) component undergoes a much larger 39% increase as compared to the perfectly bonded case at 5% compression. Such observations indicate that a small difference in the effective electrostatic properties can yield a large change in the effective piezoresistive properties for CNT-polymer nanocomposites. In addition, the sensitivity of the properties to evolving nanoscale interface separation can be related to higher piezoresistive response with weak interfaces/interfacial damage in CNT-polymer nanocomposites.

It is further observed that the piezoresistive response for the constrained tests is larger than that obtained from the unconstrained tests indicating that the type of boundary condition applied can significantly alter the effective piezoresistive response observed at the macroscale. For example, at 5% applied tensile strain, \( \Delta \rho_{11}^{\text{eff}} / \rho_0^{\text{eff}} \) for the unconstrained test with interface separation is observed to be 0.21 while for the constrained test it is 0.34, i.e. about 69% higher. Similarly, \( \Delta \rho_{22}^{\text{eff}} / \rho_0^{\text{eff}} \) for the constrained test at 5% applied tensile strain is observed to be about 40% higher than that observed for the unconstrained tension test. For applied compressive strains, a similar behavior is observed with the larger piezoresistive response for the constrained tests as compared to the unconstrained tests. The difference in the piezoresistive response of the nanocomposite for constrained and unconstrained tests arises from the difference in the variation of effective conductivity components with applied
strain. The observed difference in piezoresistive properties indicates that the piezoresistive strain coefficients \( \Pi_{ij}^{ff} \) are not material properties as they are dependent on the type of applied macroscale boundary conditions.

### 5.2.3 Effect of Maximum Electron Hopping Range on the Effective Piezoresistive Response and Macroscale Effective Gauge Factors

In addition to the type of boundary conditions, the maximum electron hopping range was observed to have a significant effect on the effective piezoresistive response of CNT-polymer nanocomposites with perfectly bonded interface [139]. The effective piezoresistive response with perfectly bonded interfaces was observed to be dependent on several factors such as the exponential nature \( \Sigma^{EH} - d^{CNT-CNT} \) relation, the unstrained effective conductivities and the slope of the \( \Sigma^{EH} - d^{CNT-CNT} \) curve at a given unstrained intertube distance corresponding to the chosen volume fraction. In addition to these, the piezoresistive response for the nanoscale RVE depends on the local cohesive zone properties for the separated interface when subjected to applied strains. For the current work, three different maximum electron hopping ranges \( \delta_{\text{max}}^{EH} \) of 1.8nm, 5nm, 10nm are chosen based on the reported values in the literature [25,33–35,38]. Fig. 3.3 shows the variation local intertube conductivity associated with electron hopping as a function of the intertube distance. It is to be noted that Fig. 3.3 has a logarithmic axis for \( \Sigma^{EH} \) and that the true nature of the \( \Sigma^{EH} - d^{CNT-CNT} \) is highly exponential, such that the slope of \( \Sigma^{EH} - d^{CNT-CNT} \) curves shown in Fig. 3.3 represent the exponent for the decaying intertube conductivity with intertube distance. The intertube distance for an RVE with a volume fraction of 0.4 in the unstrained state is 1.01nm which corresponds to the points I,II,III marked in Fig. 3.3 for 1.8nm, 5nm and 10nm maximum electron hopping range, respectively. It is observed that the intertube conductivities in the unstrained state differ by several orders of magnitude such that a longer electron hopping range has a larger unstrained intertube conductivity. A larger unstrained conductivity leads to higher effective conductivities in the unstrained state for cases with longer maximum...
electron hopping range. The piezoresistive response, however, is dependent on the change in the electrostatic conductivity from the unstrained state. Thus, one of the governing factors is the slope of the $\sum^{EH} - d^{CNT-CNT}$ at the given unstrained intertube distance and maximum electron hopping range. The slope (or exponent) is observed to be higher for smaller maximum electron hopping range, and thus, a larger piezoresistive response is observed for smaller $\delta^{EH \text{max}}$ cases.

![Figure 5.11](image)

Figure 5.11: Comparison of relative change in resistivity components for the nanoscale RVE with and without interface separation subjected to unconstrained tension/compression tests with maximum electron hopping ranges ($\delta^{EH \text{max}}$) of 1.8nm, 5nm and 10nm. a) $\Delta \rho^{eff}_{11}/\rho^{eff}_{0}$ and b) $\Delta \rho^{eff}_{22}/\rho^{eff}_{0}$. [136]

The relative change in resistivity for the components in $\hat{x}_1$ and $\hat{x}_2$ directions is shown in Fig. 5.11a and b, respectively, for unconstrained plane strain tension/compression test with and without interface separation. $\Delta \rho^{eff}_{11}/\rho^{eff}_{0}$ and $\Delta \rho^{eff}_{22}/\rho^{eff}_{0}$ are observed to have higher magnitudes for the cases with interface separation as compared to perfectly bonded cases for all electron hopping ranges. For example, $\Delta \rho^{eff}_{11}/\rho^{eff}_{0}$ for the RVE with interface separation is observed to be 390%, 277% and 224% higher than the perfectly bonded interface cases for maximum electron hopping ranges of 1.8nm, 5nm and 10nm, respectively, at 5% applied tension. While $\Delta \rho^{eff}_{22}/\rho^{eff}_{0}$ increases by 41%, 39% and 48% at 5% applied compression relative to the unstrained state, $\Delta \rho^{eff}_{22}/\rho^{eff}_{0}$ increases by only 1%, 5% and 18% for maximum electron hopping ranges of 1.8nm, 5nm and 10nm respectively. The results observed in Fig. 5.11
indicate that the difference in the effective piezoresistive response of the nanocomposite to applied strain and interface separation is highly sensitive to the maximum electron hopping range for the specific CNT-polymer material system.

Figure 5.12: Comparison of macroscale effective gauge factors for the nanoscale RVE with and without interface separation subjected to unconstrained tension/compression tests with maximum electron hopping ranges ($\delta_{\text{max}}^{EH}$) of 1.8nm, 5nm and 10nm. a) $G_{12}^{Eff}$ and b) $G_{22}^{Eff}$. [136]

The piezoresistive response observed through the relative change in resistivity components for the different maximum electron hopping ranges is converted to macroscale effective gauge factors in order to compare to gauge factors obtained from macroscale experiments from uniform tension/compression tests. Fig. 5.12 shows the macroscale effective gauge factors, $G_{12}^{Eff}$ and $G_{22}^{Eff}$, when the nanoscale RVE is subjected to unconstrained plane strain tension/compression tests with different maximum electron hopping ranges with and without interface separation. Following from the relative change in resistivity variation with applied strain (Fig. 5.11), the macroscale effective gauge factors for the nanoscale RVE with interface separation are observed to have larger magnitudes than the perfectly bonded interface cases. The variation of macroscale effective gauge factor with applied strains is observed to be highly nonlinear and dependent on applied strain. In compression, the effective gauge factors $G_{12}^{Eff}$ are observed to be significantly larger for the case with interface separation from
the corresponding perfectly bonded case as compared to $G_{22}^{Eff}$ because of the local interface separation around the CNT-polymer interface. A shorter electron hopping range is observed to undergo a larger increase in the effective gauge factor components as compared to longer electron hopping ranges, even though the local interface separation evolves identically in the cases with different maximum electron hopping ranges. For example, for 1.8nm, 5nm and 10nm maximum electron hopping ranges, the increase in $G_{22}^{Eff}$ from the undamaged case is observed to be 8.95, 2.76 and 1.64, respectively, at 5% applied tension. Thus, the change in effective gauge factor is observed to be dependent on the maximum electron hopping range which relates to the electron hopping based variation in interfacial resistance of the local cohesive zones. In addition, the effective gauge factors for the different maximum electron hopping ranges are observed to be sensitive to the state of interfacial separation. For example, the difference in $G_{22}^{Eff}$ between the damage and undamaged cases is observed to be about 39%, 41% and 46% at 1%, 2% and 5% applied tensile strain i.e. larger percent change with increasing interfacial separation.

5.2.4 Accelerated Damage Test Cases

The plane strain tension/compression tests, presented so far, have been restricted to a maximum strain of ±5%. A maximum applied strain of ±5% is chosen because the linear constitutive relationship used for the polymer is applicable within that range. However, for applied ±5% strain the local cohesive zones are observed to be operating in the linear elastic region of the traction displacement law, i.e. the interface separation distance for the cohesive zones is less than the separation distance for initiation of damage in the cohesive zones ($\Delta \tilde{u}_n \leq \Delta \tilde{u}_{sw}$) as is observed from Fig. 5.8b. Thus, the MD based cohesive zones [82] are active in the initial linear elastic (A-B in Fig. 5.1a) or the undamaged region of the traction-separation response. In order to demonstrate the full capability of the proposed modeling framework presented herein, up to ±20% strains are applied so that the interface separation gets larger than $\Delta \tilde{u}_{sw}$ leading to initiation and accumulation of damage in the cohesive zones. It is expected that much of the applied strain would be absorbed in the CNT-polymer interface separation, and thus would result in smaller strain state in the polymer region of
the nanoscale RVE.

In addition to applying larger magnitudes of strain, a set of damage test cases with a parametric set of cohesive zone parameters are developed with faster damage initiation to explore the full capability of the modeling framework presented herein. For the CNT-polymer interface discussed herein, the parameters are obtained from MD based tests of the interface at 100K. At a higher temperature, say 300K, the cohesive zone parameters are expected to be different leading to faster damage initiation [85]. The MD based study by Li and Seidel [82] does not account for damage of MD bonds, but relies on disentanglement of polymer chains at the interface. If a damage model were to be incorporated in such a study, it is expected that critical parameters governing cohesive zone damage (e.g. \( \Delta u_n^{sw} \)) will be different, leading to faster damage initiation. In addition, the parameters for the electromechanical cohesive zones which govern the effective electrostatic properties can be different depending on the specific CNT-polymer material system, CNT functionalization, degree of crosslinking in the polymer and the nanocomposite processing conditions. In the current work, test cases have been designed to illustrate the impact of electromechanical cohesive zone parameters in the effective electrostatic and piezoresistive response of CNT-polymer nanocomposites. The volume fraction for the nanoscale RVEs is fixed at 0.4 and the maximum electron hopping range is chosen to be 5nm for the accelerated damage tests similar to the discussion in the previous sections.

The local cohesive zone parameters used for the different test cases are presented in Table 5.1 with different mechanical and/or electrostatic rates of cohesive zone damage. The constrained/unconstrained plane strain tension/compression test discussed so far correspond to the Test Case I shown in Table 5.1. The electrostatic damage parameter \( \gamma \), as discussed in Sec. 5.1.2, defines the rate of increase of interface resistance as the local cohesive zone gets damaged and can be considered separately from mechanical damage rate of the cohesive zone. The difference would arise because the nanoscale electron hopping could result in damage of electrostatic cohesive zone to proceed at a different rate than the mechanical cohesive zone i.e. \( \gamma \) becomes an unknown parameter at the nanoscale electrostatic interface. Test Case II undergoes the same mechanical cohesive zone traction-separation law, but the electrostatic
damage parameter $\gamma$ is increased 10 times from 5 to 50 such that the the local interfacial resistance of the cohesive zones after damage initiation (i.e. $\Delta \tilde{u}_n > \Delta \tilde{u}_n^{sw}$) increases 10 times faster in comparison to the results discussed so far. For Test Case III, the parameter $\gamma$ is fixed at 5, however, $\Delta \tilde{u}_n^{sw}, \Delta \tilde{u}_t^{sw}$ and $\Delta \tilde{u}_n^{max}$ are reduced 10 times from 0.182nm, 1nm, 3.32nm to 0.0182nm, 0.1nm and 0.332nm, respectively, reflective of the cohesive zone response at elevated temperatures. Thus, while the electrostatic resistance increases at the same rate as the results in the earlier sections, the damage initiation for the electromechanical cohesive zones is 10 times faster. Finally, for Test Case IV the damage initiates 10 times faster and the electrostatic cohesive zone resistance increases 10 times faster after local cohesive zone damage initiation. Fig. 5.13 shows the evolution of interface separation in the cohesive zones for Case I and the evolution of local current density component ($\hat{J}_2$) in response to applied strain in the $\hat{x}_2$ direction for different strain states.

Table 5.1: Electromechanical cohesive zone parameters for the different test cases designed to study the key features of interfacial separation, damage initiation, evolution and the resulting effective piezoresistive response. [136]

<table>
<thead>
<tr>
<th>Test Case</th>
<th>$\Delta \tilde{u}_n^{sw}$ (nm)</th>
<th>$\Delta \tilde{u}_t^{sw}$ (nm)</th>
<th>$\Delta \tilde{u}_n^{max}$ (nm)</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.182</td>
<td>1.00</td>
<td>3.32</td>
<td>5</td>
</tr>
<tr>
<td>II</td>
<td>0.182</td>
<td>1.00</td>
<td>3.32</td>
<td>50</td>
</tr>
<tr>
<td>III</td>
<td>0.0182</td>
<td>0.10</td>
<td>0.332</td>
<td>5</td>
</tr>
<tr>
<td>IV</td>
<td>0.0182</td>
<td>0.10</td>
<td>0.332</td>
<td>50</td>
</tr>
</tbody>
</table>

Figure 5.13: Local state of interface separation in the nanoscale RVE for different applied strain states with the same electromechanical cohesive zone interface parameters (Test Case I in Tab. 5.1). The contours show the local current density in the $\hat{x}_2$ direction. [136]

The variation of effective conductivity components with applied strain for the different test cases are shown in Fig. 5.14 in comparison to the effective conductivity components with per-
fectly bonded CNT-polymer interface. It is observed that for applied compressive strains, the electrostatic properties follow the same variation for the effective conductivity components, $\Sigma^{\text{Eff}}_{11}$ and $\Sigma^{\text{Eff}}_{22}$, because the interface separation/interpenetration at the CNT-polymer interface is identical and all the test cases have the same electromechanical cohesive zone law in compression, as was discussed in Sec. 5.1.2. In tension, however, the variation in effective conductivity components deviates after a specific applied tensile strain. For example, the effective conductivity components $\Sigma^{\text{Eff}}_{11}$ and $\Sigma^{\text{Eff}}_{22}$ follow identical variation for Test Cases I and II up to about 14% applied tensile strain. After that, some of the local cohesive zones start to undergo damage initiation such that Test Case II, with higher rate of increasing interface resistance, undergoes a larger decrease in the effective conductivity components. At 20% applied tensile strain, $\Sigma^{\text{Eff}}_{11}$ for Test Case II is observed to be about 6% smaller than Test Case I while $\Sigma^{\text{Eff}}_{22}$ for Test Case II is observed to be about 11% smaller. For Test Case III, the damage initiates much earlier at about 2.5% applied tensile strain state such that the effective conductivity components deviate from Test Case I owing to the higher rate of interfacial resistance increase after damage. It is observed that Test Case III undergoes a larger change in effective conductivity components as compared to Test Case II. The $\Sigma^{\text{Eff}}_{11}$ component for Test Case III is observed to be 21% smaller than Test case I and $\Sigma^{\text{Eff}}_{22}$ is observed to be 23% smaller at 20% applied tensile strain. The effective conductivity components for Test Case IV, with accelerated damage initiation and interfacial resistance increase, deviates from the other test cases at about 2.5% applied tensile strain state as was observed for Case III. However, the rate of decrease of effective conductivity components for Test Case IV after that is much larger due to faster increase in interfacial resistance with $\gamma=50$. At 20% strain state, both $\Sigma^{\text{Eff}}_{11}$ and $\Sigma^{\text{Eff}}_{22}$ are observed to be about 50% smaller than the effective conductivity at the same strain state for Test Case I.

The difference in electrostatic behavior is further reflected in the effective piezoresistive response of nanoscale RVE. Fig. 5.15 shows the relative change in resistivity in the $\hat{x}_1$ and $\hat{x}_2$ directions for the different test cases in comparison to the undamaged case. As compared to the undamaged nanoscale RVE, the effective piezoresistive response for the four test cases with interfacial damage are observed to be higher. For example, at 20% applied tensile strain, the relative change in resistivity component in the $\hat{x}_1$ direction, $\Delta \rho^{\text{Eff}}_{11} / \rho^{\text{Eff}}_{11}$, is observed to be
Figure 5.14: Comparison of effective conductivity components with perfectly bonded inter-
face and for different test cases with interfacial separation and damage as shown in Tab. 5.1.
a) $\Sigma_{11}^{Eff}$ and b) $\Sigma_{22}^{Eff}$. [136]

Figure 5.15: Comparison of relative change in resistivity components with perfectly bonded
interface and for different test cases with interfacial separation and damage as shown in
Tab. 5.1. a) $\Delta \rho_{11}^{Eff}/\rho_{0}^{Eff}$ and b) $\Delta \rho_{22}^{Eff}/\rho_{0}^{Eff}$. [136]
34%, 45%, 83% and 216% for Test Case I, II, III and IV, respectively. It is further observed that the piezoresistive response is larger in the $\hat{x}_2$ direction, i.e. the direction of applied strain, based on the larger variation observed in $\Sigma_{22}^{\text{Eff}}$ component with applied strains. At 20% applied tensile strain in the $\hat{x}_2$ direction, $\Delta \rho_{22}^{\text{Eff}} / \rho_0^{\text{Eff}}$, is observed to be 4.79, 5.54, 6.53 and 10.66 as compared to $\Delta \rho_{11}^{\text{Eff}} / \rho_0^{\text{Eff}}$ which is 2.65, 2.88, 3.63 and 6.25 for Test Case I, II, III and IV, respectively. A larger change in the $\hat{x}_2$ components of effective conductivity is observed because the interface separation around nanotubes is higher for cohesive zones primarily oriented in the $\hat{x}_2$ direction, resulting in larger interface resistance for conductive paths oriented in the $\hat{x}_2$ direction, especially after interfacial damage initiates.

![Figure 5.16: Comparison of macroscale effective gauge factors with perfectly bonded interface and for different test cases with interfacial separation and damage as shown in Tab. 5.1. a) $G_{12}^{\text{Eff}}$ and b) $G_{22}^{\text{Eff}}$. [136]](image)

The variation of macroscale effective gauge factors, $G_{12}^{\text{Eff}}$ and $G_{22}^{\text{Eff}}$, for the four test cases are shown in Fig. 5.16 in comparison to the the case with perfectly bonded interface. The expressions macroscale effective gauge factors for the constrained plane strain tension/compression test are different from Eqn. 2.64 and 2.65. For constrained plane strain tension/compression test, the effective gauge factors are obtained using Eqn. 2.52, however, unlike the unconstrained tests $< \dot{\varepsilon}_{11} > = 0$ because the sides are constrained. Thus, the expression for effective gauge factors used for the results in Fig. 5.16 are
\[
\begin{align*}
G_{12}^{\text{Eff}} &= \frac{1}{\varepsilon_0} \left[ \frac{\rho_{22}^{\text{Eff}}(\varepsilon_0)}{\rho_{22}^{\text{Eff}}(0)} (1 + \varepsilon_0) - 1 \right] \\
G_{22}^{\text{Eff}} &= \frac{1}{\varepsilon_0} \left[ \frac{\rho_{22}^{\text{Eff}}(\varepsilon_0)}{\rho_{22}^{\text{Eff}}(0)} \frac{1}{1 + \varepsilon_0} - 1 \right]
\end{align*}
\]

(5.4)

It should be noted that \(G_{12}^{\text{Eff}}\) and \(G_{22}^{\text{Eff}}\) for constrained plane strain tension/compression test are not dependent on the effective Poisson’s ratio components. It is observed that for all of the cases including the undamaged case, the gauge factors are highly nonlinear, applied strain dependent and much larger than the nominal geometric gauge factor of about 1.5. The nominal geometric gauge factors are obtained by fixing \(\frac{\rho_{22}^{\text{Eff}}(\varepsilon_0)}{\rho_{22}^{\text{Eff}}(0)} = 1\) in Eqn. 2.64, 2.65, for non inherently piezoresistive materials. In the current work, the intertube electron hopping and interfacial separation/damage leads to \(\frac{\rho_{22}^{\text{Eff}}(\varepsilon_0)}{\rho_{22}^{\text{Eff}}(0)}\) being higher than 1 resulting in higher gauge factors. As the applied tensile strain on the nanoscale RVE is incrementally increased, the macroscale effective gauge factors are observed to increase because of the formation/disruption of conductive pathways at the nanoscale. In addition, for the different test cases with interfacial damage, damage initiation and evolution significantly affects the macroscale effective gauge factors. Higher effective gauge factors are observed in the direction of applied strain i.e. the \(\hat{x}_2\) direction compared to the transverse direction based on the higher relative change in resistivity in the \(\hat{x}_2\) direction. The electrostatic and piezoresistive response is observed to be asymmetric in the direction of applied strains (\(\hat{x}_2\)) and in the transverse direction based on the local evolution of cohesive zone damage. The different test cases indicate that local electromechanical cohesive zone parameters for the specific nanocomposite material system governing cohesive zone damage initiation, damage evolution and the local cohesive zone properties (e.g. rate of mechanical and electrostatic damage) for a given state of interface separation/damage state can significantly vary the effective nanocomposite piezoresistive response.

In conclusion, the effective piezoresistive response and the effect of interfacial damage accumulation is significantly dependent on the nanoscale local microstructure. A larger volume
fraction results in larger differences in the loading/unloading curves because of interfacial damage accumulation. The effective piezoresistive response and effect of interfacial damage accumulation is significantly dependent on the electron hopping barrier potential such that a smaller barrier potential (or longer maximum electron hopping range) results in larger differences in the loading/unloading curves. The rate of electrostatic damage at the nanoscale CNT-polymer interface affects the difference in loading/unloading response such that a faster electrostatic damage leads to larger damage accumulation effect. Over multiple loading cycles, if the amplitude of maximum applied strains is constant, then effective properties cycle along the unloading path of the first cycle. Over multiple loading cycles, if the maximum amplitude of applies strains increases every cycle, the effective response is closely governed by the amount of interfacial damage accumulated in every subsequent cycle.
Chapter 6

Nanocomposite Piezoresistivity Under Cyclic Loading

Several experimental studies have attempted to characterize the piezoresistive response of CNT-polymer nanocomposites [11,12,19,24–28] and CNT doped fiber reinforced composite laminates [9,29] under cyclic loading conditions. Ku-Herrera and Aviles [19] applied small number of quasi-static cyclic tensile loading tests within small deformation range on multi-walled CNT (MWCNT)-vinyl ester nanocomposite samples and observed close correlation between the applied strains and change in macroscale resistance. It was further observed that there is insignificant lag or hysteresis in the piezoresistive response for the small applied tensile strains. Nofar et al. [24] applied a larger number of strain cycles on MWCNT-Epoxy nanocomposites and observed that the residual change in nanocomposite resistance in the undeformed state increases with the number of strain cycles, indicating that the nanocomposite damage can be correlated to the change in macroscale resistance for CNT-polymer nanocomposites. In both of these studies, the maximum strain amplitude was constant. Vega et al. [27] applied cyclic strains on single-walled CNT(SWCNT)-epoxy nanocomposites with incrementally increasing maximum strain amplitude. They observed that the relative change in resistance increases with increasing strain amplitude in addition to hysteresis effect i.e. the difference in loading/unloading paths. The authors attributed the observed response to interfacial separation phenomenon at the CNT-polymer interface.
In the current work, the focus is on studying the effect of cyclic loading conditions and exploring the role of interfacial damage initiation, evolution and accumulation in the macroscale effective piezoresistive response for the nanocomposites within the computational micromechanics framework. The nanoscale CNT-polymer interface is modeled using electromechanical cohesive zones to allow for surface tractions and current density across the separated interface. It is expected that loading and unloading paths of the cohesive zones at the interface within the non-homogeneous microstructure when subjected to cyclic loading will lead to complex interactions at the nanoscale CNT-polymer interface. The current work aims to capture these complex interactions and the subsequent evolution of the effective piezoresistive response. Some of the results presented in this chapter are published in [153] and others are a part of a manuscript under review for publication [154].

6.1 Cyclic Loading of Electromechanical Cohesive Zones

In order to introduce the mechanics of imperfect CNT-polymer interface at the nanoscale, the interface is modeled using electromechanical cohesive zones [136]. The mechanical response of the interface is prescribed in terms of normal/tangential traction-separation laws at the interface obtained from MD based study conducted by Li and Seidel [82]. The electrostatic side of the coupled electromechanical cohesive zones is obtained using arguments based on the deformation and subsequent damage based resistance of polymer ligaments connecting across the interface. A detailed description of transitioning from MD results to interface traction-separation laws and development of the coupled electrostatic counterpart is presented in Chapter 5. However, some of the key features of the coupled electromechanical cohesive zones will be discussed here for completeness.

Fig. 6.1 demonstrates the cohesive zone laws governing the mechanical interface response of the CNT-polymer interface. Fig. 6.1a shows the normal mode (or Mode I) traction-separation response for the CNT-polymer interface obtained from the MD results and idealized into a bilinear form [136]. The normal traction increases from point A to point B i.e. for normal interface separation ($\Delta u_n$) less than 0.182nm (point B). At point B, which is also denoted
by $\Delta \tilde{u}_{sn}^w$, the normal traction reaches its peak value of 0.332GPa [82]. As long as the normal interface separation is less than $\Delta \tilde{u}_{sn}^w$, the cohesive zone undergoes a linear elastic response with the an undamaged stiffness $\tilde{K}_n^{(0)}$. The region A-B denotes the range of elastic stretching of the entangled polymer chains when subjected to forces separating graphene and polymer normal to the interface. After point B, the normal traction of the cohesive zone starts to reduce as the cohesive zone begins to get damaged which in the MD model is representative of disentanglement of amorphous polymer chains. This phenomenon is accompanied by decreasing traction, which for the purpose of the current study is idealized as linear reduction (B to F) keeping the normal mode separation energy (area under the normal traction - normal separation curve) consistent with the MD simulations. From point B to point F of the traction separation response, the cohesive zone gets progressively damaged such that the current normal stiffness of the interface ($\tilde{K}_n^{(cur)}$) is given by the line connecting the current point on line BE to the origin. As an example, at point C in the normal traction - separation response shown in Fig. 6.1a, the current normal interface stiffness is given by
the slope of line CA ($\tilde{K}_n^{(1)}$). Now, if the cohesive zone was to unload from point C, because of local rearrangement of forces or because of cyclic loading conditions, it will unload along the line CA. When reloaded, it reloads along AC and then follows the progression from C to E. It is evident that in the process of unloading and reloading, no additional damage is induced in the cohesive zone and the interface stiffness remains constant at the $\tilde{K}_n^{(1)}$, i.e. the stiffness of the cohesive interface at the point it started to unload (point C in Fig. 6.1a). If the cohesive zone unloads again from point E, it unloads along the line EA with the current stiffness, $\tilde{K}_n^{(2)}$, back to point A and reloads along line AE. The stiffness of the cohesive zone in the second unloading cycle is less than that in the first unloading cycle ($\tilde{K}_n^{(1)} > \tilde{K}_n^{(2)}$) because of added interfacial damage in going from C to E. If the interface normal separation continues to increase after point E, the normal traction follows its progression to point F. At point F, all of the polymer chains get disentangled such that there is no interaction between the graphene and the polymer medium. Thus, at this point the interface is completely damaged and does not support any normal traction. Even if the cohesive zone unloads from this point, it will not support normal traction. If the cohesive zone undergoes interpenetration, i.e. $\Delta \tilde{u}_n < 0$, then the stiffness of the cohesive zone is fixed to be equal to the initial undamaged stiffness, $\tilde{K}_n^{(0)}$, to avoid non-physical interpenetration of the cohesive interface.

The traction-separation response for tangential interface separation (Mode II) is shown in Fig. 6.1b. The tangential traction increases linearly from point A to point B ($\Delta \tilde{u}_t^{sw}=1\text{nm}$) up to a peak traction of 0.08GPa [82]. It is to be noted that the peak traction for the tangential mode of separation is much smaller than the peak traction for the normal mode of separation. Once the cohesive zone reaches peak traction due to elastic deformation of the polymer chains, it starts to slide on the graphene sheet resulting in a constant tangential traction for any subsequent increase in tangential separation as shown in Fig. 6.1b between points B and G. At any tangential separation, the current stiffness of the tangential cohesive zone element is given by the line connecting the current point on the cohesive zone law to the origin, as indicated for point C and point E. If the cohesive zone was to unload, it will follow this path of constant stiffness without accumulating any further damage during the unloading and reloading cycle, as was the case with normal mode of separation. During the first unloading/reloading cycle (CA) the local cohesive zone stiffness is found as the slope of
the line connecting CA i.e. $\tilde{K}_t^{(1)}$. Similarly, for the second loading/unloading cycle the local stiffness is given by $\tilde{K}_t^{(2)}$, such that the local stiffness decreases from the initial tangential stiffness as the interface gets damaged i.e. $\tilde{K}_t^{(0)} < \tilde{K}_t^{(1)} < \tilde{K}_t^{(2)}$. During the unloading cycles, if the cohesive zone slides tangentially into the other direction i.e. $\Delta \tilde{u}_t < 0$, then the current slope of the unloading path is retained. As an example, after unloading from C to A if the cohesive zone slides into the other direction the current stiffness is maintained and the tangential traction follows the line AD with local stiffness of $\tilde{K}_t^{(1)}$. The restoring tangential tractions, however, are negative based in the chosen coordinate system because of the reversal in direction of interface separation.

Figure 6.2: (a) Interfacial resistance variation with normal interface separation with no electron hopping [136] (d) Interfacial resistance variation with normal interface separation with electron hopping for different electron hopping barrier potential ($\lambda=0.05\text{eV},0.5\text{eV}$) assuming that the averaged intertube distance is 1nm in the undeformed state [136]. The maximum electron hopping range ($\delta_{EH}^{max}$) with $\lambda$ of 0.5eV and 0.05eV is 4.54nm and 13.87nm, respectively. Figures (a),(b) also show the unloading path on load reversal for cyclic loading cases or local cohesive zone relaxation. [154]

While the mechanical cohesive zones support normal and tangential traction over the sep-
arated interface, the coupled electrostatic cohesive zones allow for surface normal current density across the interface. In general, before the interface gets completely damaged leading to complete separation between the CNT and the polymer medium, it should allow for current density across the separated interface. In addition, electron hopping across the separated interface would augment the interface normal current density similar to the electron hopping based augmentation of the intertube polymer medium discussed in Chapter 4. In order to allow for surface normal current density, electrostatic cohesive zones are incorporated at the CNT-polymer interface. The electrostatic response of the interface is coupled with the mechanical response of the interface such that interface normal current density is dependent on the normal interface separation ($\Delta \tilde{u}_n$). Additionally, the onset of interfacial damage of the mechanical normal mode cohesive zones ($\Delta \tilde{u}_n^{sw}$) coincides with the onset of damage of the electrostatic cohesive zones. Analogous to the form chosen for the mechanical traction-separation laws, a bilinear model for cohesive zone normal resistance is used for the electrostatic counterpart in the absence of electron hopping, as shown in Fig. 6.2a. The initial linear region (A-B) of the electrostatic cohesive zone interface is considered to have resistivity equal to the polymer resistivity ($\tilde{\rho}^P$) such that the local interface resistance is given by

$$\tilde{R}(\Delta \tilde{u}_n) = \frac{\tilde{\rho}^P}{A} \Delta \tilde{u}_n \quad \Delta \tilde{u}_n \leq \Delta \tilde{u}_n^{sw}$$  \quad (6.1)$$

where $A$ is the effective cross sectional area for the cohesive zone. The normal interface separation ($\Delta \tilde{u}_n$) acts as the effective length of the polymer ligament connecting the interface. Unlike the bilinear traction-separation law where the normal traction decreases after the peak traction is reached (at point B, $\Delta \tilde{u}_n = \Delta \tilde{u}_n^{sw}$), the interfacial resistance keeps increasing but at a faster rate than the initial linear elastic separation region. The faster rate of increase of interfacial resistance after the onset of damage is a reflection of diminishing current density across the interface with increasing damage in the polymer ligaments connecting the interface. The interfacial resistance for $\Delta \tilde{u}_n > \Delta \tilde{u}_n^{sw}$ is expressed as
\[ \tilde{R}(\Delta \tilde{u}_n) = \frac{\tilde{\rho}^P}{A} \Delta \tilde{u}^w_n + \gamma \frac{\tilde{\rho}^P}{A} (\Delta \tilde{u}_n - \Delta \tilde{u}^w_n) \quad \Delta \tilde{u}_n \geq \Delta \tilde{u}^w_n \]  

(6.2)

The symbol, \( \gamma \), denotes the amplification factor in rate of change of interfacial resistance after the onset of interfacial damage, i.e. for an undamaged cohesive zone \( \gamma = 1 \). On complete mechanical separation (point E in Fig. 6.2a), there is no further current density across the interface reflected in the sudden jump in the interfacial resistance to infinity. Infinite resistance is approximated by a numerically very high number for interfacial resistivity, several orders of magnitude higher than the electron hopping augmented local polymer resistivity. Similar to the mechanical interface model, if the cohesive zones unload, the cohesive zone resistance follows the line connecting the current point on the surface normal resistance-separation curve to the origin (along CA). Finally, electron hopping is allowed across the cohesive zones by using the electron hopping augmented local polymer resistivity (\( \tilde{\rho}^{EH} \) instead of \( \tilde{\rho}^P \)) to evaluate the interfacial resistance in Eqn. 5.1, 5.2. This results in an exponential variation in the normal interfacial resistance with increasing normal interface separation following from the exponential nature of electron hopping based conductivity/resistivity-intertube distance relation. Fig. 6.2b shows the variation of interfacial resistance for different values of electron hopping barrier potential, \( \lambda \), where the average intertube distance in the undeformed state is 1nm. With increasing interface normal separation, the intertube distance increases resulting in an exponentially increasing local polymer resistivity which, in conjunction with the undamaged/damaged state of the cohesive zone, leads to several orders of magnitude change in the interfacial resistance before full separation.

In order to quantify interfacial damage in the nanoscale RVE, an averaged damage parameter \( (D_{avg}) \) is defined by averaging the local damage in each of the cohesive zone finite element node pairs which constitute the nanoscale interface. The averaged damage parameter is mathematically expressed as

\[ D_{avg} = \frac{1}{\tilde{A}^I} \int_{\tilde{A}^I} D(\tilde{x})d\tilde{A}^I \]  

(6.3)

where \( \tilde{x} \) is any point lying at the CNT-polymer interface, \( \tilde{A}^I \) is the total cohesive zone in-
terface area perpendicular to the direction of normal interface separation, i.e. cohesive zone differential width multiplied by the plane strain thickness, and $D(\tilde{x})$ is the local damage parameter defined at interface location $\tilde{x}$. Integrating the damage state across the entire CNT-polymer interface allows for representation of each cohesive zone in the averaged damage parameter, where every cohesive zone may possibly have a different state of damage depending on the local interface separation. $D(\tilde{x})$ is defined based on the bilinear mechanical cohesive zone law used in the current study as

$$D(\tilde{x}) = \begin{cases} 1 & \Delta \tilde{u}_n(\tilde{x}) \leq \Delta \tilde{u}_{sw}^n \\ 1 - \frac{\Delta \tilde{u}_n(\tilde{x}) - \Delta \tilde{u}_{sw}^n}{\Delta \tilde{u}_{sw}^n - \Delta \tilde{u}_{sw}^n} & \Delta \tilde{u}_{sw}^n \leq \Delta \tilde{u}_n(\tilde{x}) \leq \Delta \tilde{u}_{sw}^n \\ 0 & \Delta \tilde{u}_{sw}^n \leq \Delta \tilde{u}_n(\tilde{x}) \end{cases}$$

(6.4)

The micromechanics based finite element framework is used to find the effective electrostatic and piezoresistive response for the nanoscale CNT-polymer RVEs discussed in Chapter 4. In addition to the different nanoscale local microstructure, the effect of different interfacial mechanical cohesive zone laws, electron hopping barrier potential ($\lambda$), cohesive zone electrostatic damage parameter ($\gamma$) and application of multiple loading cycles is studied to explore the key features of the complex nanoscale interactions resulting in the effective piezoresistive response.

### 6.2 Preliminary Discussion of CNT-Polymer Nanocomposite Cyclic Piezoresistivity

The nanoscale representative volume element, as shown in Fig. 3.1, is subjected to constrained plane strain tension compression tests [139] in order to study the evolution of electrostatic properties with applied uniform macroscale strains. A set of tests have been designed for the nanoscale RVE in order to bring out the key features of the modeling framework and the evolution/accumulation of interfacial damage. In the previous implementation of the model for monotonic loading, it was noted that the MD based traction-separation
response evaluated by Li and Seidel [82] leads to the onset of interfacial damage only at very high strain states. However, while the MD model accounts for separation at the interface, the MD bonds themselves do not have a damage model, and thus can stretch indefinitely. In a more realistic case, the MD bonds would start to break even before the polymer chains start to get disentangled resulting in faster interfacial damage. Also, for a different set of CNT-polymer interface, damage may initiate much faster based on the local atomistic morphology of the interface materials. Thus, accelerated mechanical damage models were used and compared with the original interfacial description by Li and Seidel [82] based on these arguments and for demonstration of key features of the modeling framework. In the current work, the accelerated mechanical damage models will be studied in addition to that by Li and Seidel [82] and the perfectly bonded interface cases.

![Figure 6.3](image.png)

Figure 6.3: a) Local conductivity ($\Sigma$) contours and b) the local current density ($\hat{J}_2$) contours for a nanoscale RVE with accelerated damage with volume fraction 0.4, $\gamma$=5 and 1 cycle of applied strain with 5% maximum tensile strain (Test Case III in Tab. 6.2). [153]

Tab. 6.2 outlines the set of test cases used for the current work. Case I in Tab. 6.2 uses the cohesive zone parameters obtained from Li and Seidel [82]. For applied 5% tensile strain in the current study, the cohesive zone does not start damaging, but it does introduce a third electrostatic interface material phase defined by the interfacial resistance-separation curves resulting in differences in effective properties from the perfectly bonded interface cases. It is to be recalled that $\gamma$ defines the rate of damage of the coupled electrostatic cohesive zones,
such that a larger value of $\gamma$ results in faster electrical damage leading to faster reduction in current density across the interface. Thus, for test case I, any value of $\gamma$ does not change the effective response because $\Delta \tilde{u}_n < \Delta \tilde{u}^{sw}_n$ for 5% maximum tensile strain. However, the accelerated damage cases (II,III,IV) undergo interfacial damage initiation and evolution for applied 5% maximum tensile strain, and thus, would result in a different effective response for different value of $\gamma$.

Table 6.1: Electromechanical cohesive zone parameters for the different test cases designed to study the key features of interfacial separation, damage initiation, evolution and the resulting effective piezoresistive response. [153]

<table>
<thead>
<tr>
<th>Test Case</th>
<th>$\Delta \tilde{u}^{sw}_n$ (nm)</th>
<th>$\Delta \tilde{u}^{sw}_t$ (nm)</th>
<th>$\Delta \tilde{u}^{max}_n$ (nm)</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.182</td>
<td>1.00</td>
<td>3.32</td>
<td>1,5,10</td>
</tr>
<tr>
<td>II</td>
<td>0.0182</td>
<td>0.10</td>
<td>0.332</td>
<td>1</td>
</tr>
<tr>
<td>III</td>
<td>0.0182</td>
<td>0.10</td>
<td>0.332</td>
<td>5</td>
</tr>
<tr>
<td>IV</td>
<td>0.0182</td>
<td>0.10</td>
<td>0.332</td>
<td>10</td>
</tr>
</tbody>
</table>

Fig. 6.3a shows the local conductivity contours for the nanoscale RVE where the local inter-tube conductivity between the CNTs is modified based on electron hopping relation resulting in non-homogeneous evolving matrix local conductivity. The evolution of local conductivity can be observed from Fig. 6.3a such that at larger applied tensile strains, the local conductivity is smaller. The evolution of local conductivity components leads to evolution of local current density within the nanoscale RVE as shown in Fig. 6.3b in the direction of applied strain ($\hat{x}_2$) for different applied strain states. The local current density is observed to get smaller as the magnitude of tensile strain is increased similar the local electron hopping based conductivity. After load reversal, the local current density starts to increase as the intertube distances between the CNTs get smaller resulting in higher local conductivity. The key observation from the local current density contours is that at 2% applied strain while loading, the current carrying pathways between the vertically adjacent nanotubes are locally more conductive than at 2% strain in the unloading cycle. This is because of interfacial damage which develops at the CNT-polymer interface leading to increased interfacial resistance and smaller current density in vertical pathways. The averaged current density and the applied electric field at each strain increment is used to calculate the effective conductivity components for the nanoscale RVE. Such observation about changes in local conductivity
Figure 6.4: Effective conductivity component ($\Sigma_{22}^{\text{Eff}}$) for a nanoscale RVE with volume fraction of 0.4 subjected to one loading/unloading cycle with 5% maximum applied strain with non-accelerated and accelerated damage cases shown in Tab. 6.2 (a) for $\delta_{\text{EH}}^{\text{max}} = 1.8\text{nm}$ as a function of solution time (b) for $\delta_{\text{EH}}^{\text{max}} = 1.8\text{nm}$ as a function of applied strain (c) for $\delta_{\text{EH}}^{\text{max}} = 5\text{nm}$ as a function of solution time (d) for $\delta_{\text{EH}}^{\text{max}} = 5\text{nm}$ as a function of applied strain. [153]

and current density contours will eventually lead to differences in the effective conductivity components during loading and unloading cycle.

The effective conductivity component in the direction of applied strain ($\Sigma_{22}^{\text{Eff}}$) is shown in Fig. 6.4 over one cycle of applied strain with 5% maximum applied strain for a maximum electron hopping range of 1.8nm and 5nm. The variation in $\Sigma_{22}^{\text{Eff}}$ is shown as a function of solution time where the applied tensile strain increases (loading) linearly from unstrained state to 5% at solution time equals to 50. After solution time of 50, the applied strain decreases linearly from 5% to the unstrained state (unloading) at solution time equals 100. Fig. 6.4a,c show the variation of $\Sigma_{22}^{\text{Eff}}$ with solution time and Fig. 6.4b,d present the same variation as a function of applied strain for maximum electron hopping ranges of 1.8nm and
Figure 6.5: Relative change in resistivity \( \frac{\Delta \rho_{\text{Eff}}^{\text{f}}}{\rho_0^{\text{f}}} \) for a nanoscale RVE with volume fraction of 0.4 subjected to one loading/unloading cycle with 5\% maximum applied strain with non-accelerated and accelerated damage cases shown in Tab. 6.2 (a) for \( \delta_{\text{EH}}^{\max} = 1.8\text{nm} \) as a function of solution time (b) for \( \delta_{\text{EH}}^{\max} = 1.8\text{nm} \) as a function of applied strain (c) for \( \delta_{\text{EH}}^{\max} = 5\text{nm} \) as a function of solution time (d) for \( \delta_{\text{EH}}^{\max} = 5\text{nm} \) as a function of applied strain. \[153\]

5\text{nm}, respectively. The first key observation is that the conductivity component is four orders of magnitudes higher for 5\text{nm} maximum electron hopping range as compared to 1.8\text{nm}. The difference arises because of the several orders of magnitude difference in the local intertube conductivity with higher maximum electron hopping range \[139\]. During the loading cycle, the intertube distances between CNT pairs increase resulting in increasingly smaller electron hopping based local conductivity. On unloading, the local conductivity increases because of decreasing intertube distances. The evolution of local conductivity gets reflected in the effective conductivity components such that the effective conductivity of the nanoscale RVE decreases during loading cycle and increases during the unloading cycle.
It is further observed that the effective conductivity variation for the non-accelerated case and for the accelerated damage case with $\gamma=1$ is the same for all strain states. For the non accelerated damage case, the interface does not get separated enough to get damaged and operates in the initial linear elastic region of the traction-separation response. For the accelerated damage case with $\gamma=1$, even though the cohesive zone gets damaged, the rate of change in resistance is the same as that for the undamaged case i.e. the bilinear interfacial resistance-separation is linear for $\gamma=1$ following the initial slope (refer Fig. 6.1c). Thus, the effective conductivity components are the same at each strain state for the two cases. For the accelerated damage cases, as $\gamma$ increases, the effective conductivity component undergoes a larger variation from the unstrained state because of faster increase in the interfacial resistance for higher $\gamma$. At 5% applied tension for 1.8nm maximum electron hopping range, $\Sigma_{22}^{Eff}$ is observed to be 61.2%, 65.3% and 69.2% smaller than the unstrained effective conductivity for $\gamma$ of 1, 5 and 10, respectively. With 5nm maximum electron hopping range, while higher $\gamma$ yields larger change in the effective conductivity from the unstrained state as well, the magnitude of change is observed to be smaller. At 5% applied tension for 1.8nm maximum electron hopping range, $\Sigma_{22}^{Eff}$ is observed to be 32.2%, 41.5% and 49.3% smaller than the unstrained effective conductivity for $\gamma$ of 1, 5 and 10, respectively.

The variation in $\Sigma_{22}^{Eff}$, when plotted against the applied strain state, is observed to follow different path during unloading for $\gamma$ of 5 and 10. For $\gamma=1$, the unloading path in Fig. 6.1c is the same as the loading path, thus the cohesive zones locally relax along the same path which gets reflected in the effective conductivity components. For $\gamma$ of 5 and 10, the unloading path is different from the loading path such that the local cohesive zone resistance is higher during unloading at the same interface separation. This results in a smaller effective conductivity component when unloading is observed at the same strain state. For a larger value of $\gamma$, the unloading path would lead to larger value of resistance at the same interface separation, thus resulting in larger difference in effective conductivity components for the loading/unloading curves. Fig. 6.4b,d show that the effect of interfacial damage accumulation on the effective conductivity components is larger for higher value of $\gamma$ (i.e. faster cohesive zone electrostatic damage) and is larger for longer maximum electron hopping range.
Figure 6.6: Macroscale effective gauge factors ($G_{22}^{\text{eff}}$) for a nanoscale RVE with volume fraction of 0.4 subjected to one loading/unloading cycle with 5% maximum applied strain with non-accelerated and accelerated damage cases shown in Tab. 6.2 (a) for $\delta_{\text{EH max}}^{\text{EH}}=1.8\text{nm}$ as a function of solution time (b) for $\delta_{\text{EH max}}^{\text{EH}}=1.8\text{nm}$ as a function of applied strain (c) for $\delta_{\text{EH max}}^{\text{EH}}=5\text{nm}$ as a function of solution time (d) for $\delta_{\text{EH max}}^{\text{EH}}=5\text{nm}$ as a function of applied strain. [153]
The effective conductivity component \( \Sigma_{22}^{Eff} \) in the direction of applied strain is further converted to the relative change in resistivity with respect to the unstrained state \( \frac{\Delta \rho_{22}^{Eff}}{\rho_0} \) in the direction of applied strain to examine the piezoresistive behavior for the different cases. Fig. 6.5 shows the response for the relative change in resistivity as a function of solution time and applied strain. The results are presented for the cases listed in Tab. 6.2 along with the perfectly bonded interface case. All of the damage cases, non-accelerated and accelerated, are observed to undergo a larger piezoresistive response than the case with perfectly bonded interface as was shown in the authors’ earlier work [136]. For the cyclic loading cases, the perfectly bonded interface case and the non-accelerated damage case do not undergo any interfacial damage (even if there is interfacial separation for non-accelerated damage case) and do not show any damage accumulation effect in the relative change in resistivity curves. The accelerated damage case with \( \gamma = 1 \) does not show any damage accumulation effect and is coincident with the non-accelerated damage case because of reasons discussed earlier in the discussion for the effective conductivity component. However, following from the effective conductivity variation the accelerated damage cases with \( \gamma = 5, 10 \) do show damage accumulation effect such that the relative change in resistivity in the loading cycle is smaller than that in the unloading cycle resulting in different loading/unloading paths. Shorter maximum electron hopping range is observed to undergo larger change in resistivity relative to the unstrained state. However, the effect of interfacial damage is better captured for the longer electron hopping range case because of a larger difference in the loading/unloading pathways.

The experimental results presented in the literature generally present macroscale gauge factors instead of the relative change in resistivity response. In order to allow for comparisons with results in the literature, the relative change in resistivity is further converted to the effective gauge factors using the relation presented in Eqn. 2.64. The corresponding results are presented in Fig. 6.6 and follow much of the same features which were discussed for the effective conductivity and the relative change in resistivity. Larger gauge factors are observed for shorter maximum electron hopping range and damage accumulation effect is observed for the accelerated damage cases such that the loading/unloading paths are different. The key idea here is that the interfacial damage at the nanoscale results in a different
piezoresistive response at the macroscale and on unloading and reloading the path would be different. Thus, interfacial damage accumulated over a number of cycles could be assessed at the macroscale by analyzing the macroscale effective gauge factors and can be differentiated from the strain-based piezoresistive response.

While it is observed that the interfacial damage evolution and accumulation leads to quantifiable difference in the macroscale effective properties, the amount of interfacial damage induced because of applied strains needs to be quantified. In order to quantify interfacial damage in the nanoscale RVE, an averaged damage parameter \( D_{\text{avg}} \) is defined by averaging the local damage in each of the cohesive zone finite element node pairs which constitute the nanoscale interface. The averaged damage parameter is mathematically expressed as

\[
D_{\text{avg}} = \int_{\Gamma^I} D(\tilde{x})d\Gamma^I
\]

where \( \tilde{x} \) is any point lying at the CNT-polymer interface \( (\Gamma^I) \) and \( D(\tilde{x}) \) is the local damage parameter defined at interface location \( \tilde{x} \). \( D(\tilde{x}) \) is defined based on the bilinear mechanical cohesive zone law used in the current study as

\[
D(\tilde{x}) = \begin{cases} 
1 & \Delta \tilde{u}_n(\tilde{x}) \leq \Delta \tilde{u}_{n}\text{sw} \\
\left[\frac{\Delta \tilde{u}_n(\tilde{x}) - \Delta \tilde{u}_{n}\text{sw}}{\Delta \tilde{u}_{n}\max - \Delta \tilde{u}_{n}\text{sw}}\right] & \Delta \tilde{u}_{n}\text{sw} \leq \Delta \tilde{u}_n(\tilde{x}) \leq \Delta \tilde{u}_{n}\max \\
0 & \Delta \tilde{u}_{n}\max \leq \Delta \tilde{u}_n(\tilde{x})
\end{cases}
\]

The averaged damage parameter for the cases discussed in Tab. 6.2 have been shown in Fig. 6.7 as a function of solution time when subjected to cyclic loading with 5% maximum applied strain. For the non-accelerated damage case, it was discussed earlier that the interface does not undergo any damage but it does separate within the initial linear elastic region of the bilinear cohesive law. This is also observed from the averaged damage parameter in Fig. 6.7 where \( D_{\text{avg}} \) remains at 1 for the non-accelerated damage case for the entire applied strain cycle. On the other hand, for the accelerated damage cases the value of the averaged damage parameter reduces from 1 to about 0.92 i.e. the CNT-polymer interface in the nanoscale RVE undergoes about 8% damage. Furthermore, it is observed that all of
the interfacial damage is accumulated during the loading cycle i.e. before solution time of 50. In the unloading cycle, no further damage is accumulated which is consistent with the damage description within the cohesive zones. The key idea is to show that small interfacial damage amounts can result in large differences in the effective gauge factors. Thus, \( D_{avg} \) provides a quantifiable correlation of the interfacial damage with the observed changes in the macroscale gauge factors.

![Averaged interfacial damage parameter for the nanoscale RVE when subjected to one cycle of applied tensile strain with a maximum strain of 5%.](153)

**Figure 6.7:** Averaged interfacial damage parameter for the nanoscale RVE when subjected to one cycle of applied tensile strain with a maximum strain of 5%. [153]

In the discussion so far, the nanoscale RVE has been subjected to a maximum tensile strain of 5%. For under 5% applied strains, the non-accelerated cohesive zone model obtained using the MD results by Li and Seidel [82] undergoes linear elastic interfacial separation but does not undergo interfacial damage. Hence, the accelerated damage models were incorporated at the nanoscale interface to subject the nanoscale interface to faster damage initiation within 5% applied tensile strain. Another way to induce interfacial damage at the nanoscale interface is to use the original non-accelerated bilinear cohesive zone law i.e. test case I in Tab. 6.2, and subject the nanoscale RVE to larger applied strains. It was shown in our earlier work [136] that at least about 15% strain needs to be applied to the nanoscale RVE to initiate interfacial damage using the non-accelerated cohesive law. Furthermore, in the results presented so far, the nanoscale RVE has been subjected to only one cycle of applied strains. In order to study the effect interfacial damage for multiple cycles of applied strains using the non-accelerated MD based cohesive zone law, the nanoscale RVE is subjected to 4 cycles of tensile strain test with increasing strain from 20% in the first cycle to 50% in
the last, with an electron hopping range of 5nm. The variation of applied strain with the solution time is presented in Fig. 6.8a.

The maximum applied strain is increased in every subsequent cycle to induce further damage at the interface. If the applied strain is kept constant in each cycle, the effective properties cycle along the unloading path after the first cycle because no further damage is induced at the CNT-polymer interface during unloading and reloading after the first loading cycle. Fig. 6.8b shows the variation in effective conductivity component ($\Sigma_{22}^{Eff}$) with applied strain as a function of solution time. It is observed that $\Sigma_{22}^{Eff}$ decreases from the unstrained state during each loading cycle and increases back to the unstrained state conductivity during
the unloading cycle at the end of which the interface comes into contact. Furthermore, the effective conductivity is observed to progressively decrease at the highest strain states as the applied strain states in the cycles increase. For example, at the peak strain states of 20%, 30%, 40% and 50% applied strain cycles, the effective conductivity is observed to be 77.7%, 88.9%, 94.5% and 97% smaller than the unstrained state conductivity. The decreasing conductivity value at the peak strains is because in every subsequent cycle further interfacial damage is induced at the nanoscale CNT-polymer interface with the nanoscale RVE.

The relative change in resistivity shown in Fig. 6.8c is observed to be higher in every subsequent loading cycle as more damage gets induced at the interface. For example, at the peak strain states of 20%, 30%, 40% and 50% applied strain cycles, the relative change in resistivity is observed to be 3.5, 8.0, 17.0 and 33.0, respectively. Effective gauge factors follow a similar variation to the relative change in resistivity as shown in Fig. 6.8d, with higher gauge factors in every subsequent cycle. Fig. 6.9 shows the effective gauge factors plotted as a function of applied strain instead of the solution time to observe the effect of interfacial damage accumulation through the difference in loading/unloading cycles. The inset shows a zoomed version of the response for smaller strains (under 20% applied strain). It is observed
that in every subsequent unloading and reloading cycles the effective gauge factor follows a different loading/unloading path. The effective macroscale gauge factors are observed to be increasingly higher in every subsequent cycle because of damage accumulation at the nanoscale interface. For example, at 10% applied tensile strain, the effective gauge factor is observed to be 13.57, 14.94, 17.28 and 18.78 for cycles 1, 2, 3 and 4, respectively. The key idea is that at large applied strains even the interface with non-accelerated damage undergoes interfacial damage accumulation and shows much of the same effect on the effective gauge factors as was observed for the accelerated damage cases.

6.3 Exploration of Different Factors Influencing Cyclic Piezoresistivity

6.3.1 Effect of Nanoscale Local Microstructure

The local nanoscale CNT microstructure has a significant influence on the effective electrostatic and piezoresistive piezoresistive response of the nanocomposites [139, 147]. For the current work, the nanoscale local volume fraction and the regular/random distribution of aligned nanotubes are explored as nanoscale microstructure metrics. Differences in nanoscale local volume fractions have been shown [139] to result in a different effective electrostatic and piezoresistive response for CNT-polymer nanocomposites. As an example, a nanoscale volume fraction of 0.15 has been observed to result in more than one order of magnitude larger piezoresistive response as compared to 0.58 volume fraction [139]. In addition, the distribution of CNTs at the nanoscale, i.e. regular hexagonal array and random dispersion, have been shown [147] to result in significant differences in the macroscale effective properties for CNT-polymer nanocomposites. In order to study the effect of the nanoscale local microstructure, nanoscale hexagonal plane strain RVEs are constructed at two different local volume fractions of 0.4 and 0.1. At 0.1 volume fraction, two different RVEs with randomly distributed CNTs [147] are generated in addition to the hexagonal RVEs. Fig. 6.10 shows the four nanoscale RVEs, drawn to scale, which are studied in the current work. The nanoscale
CNT-polymer interface is allowed to separate and subsequently damage when strains are applied on the nanoscale RVE in the form of displacement boundary conditions due to the presence of electromechanical cohesive zones [136] at the interface. With damage restricted to the CNT-polymer interface, cyclic tensile strains are applied in order to understand the correlation between interfacial separation/damage accumulation and evolution of the effective electrostatic and piezoresistive response.

It has been shown [136] that the nanoscale CNT-polymer interface separation leads to several times higher effective piezoresistive response and macroscale gauge factors as compared to perfectly bonded nanoscale interface. For the MD based nanoscale interface traction-separation law, it was observed that for applied 5% tensile strain while the interface undergoes separation, it does not get damaged i.e. $\Delta \tilde{u}_n \leq \Delta \tilde{u}^\text{sw}_n$ such that the nanoscale interfaces are in the initial linear elastic region of the traction separation curves shown in Fig. 6.1a.

In order to explore the effect of interfacial damage on the effective piezoresistive, accelerated damage models were incorporated at the CNT-polymer interface. In the current work, both the non-accelerated MD based models and accelerated damage models are studied to evaluate the key differences in the effective piezoresistive response of the nanocomposites when subjected to cyclic loading conditions, in particular the effect of interfacial damage accumulation. The mechanical cohesive zone parameters for the accelerated damage case are chosen such that the interfacial damage initiates much faster and the nanoscale RVE undergoes interfacial damage even for 5% applied tensile strain. Tab. 6.2 shows the mechanical
cohesive zone parameters for the non-accelerated and accelerated damage cases used in the current study.

Table 6.2: Mechanical cohesive zone parameters for the different test cases designed to study the key features of interfacial separation, damage initiation, evolution and the resulting effective piezoresistive response. [154]

<table>
<thead>
<tr>
<th>Test Case</th>
<th>$\Delta u_{sw}^n$ (nm)</th>
<th>$\Delta u_{sw}^t$ (nm)</th>
<th>$\Delta u_{max}^n$ (nm)</th>
<th>$t_{\max}^n$ (GPa)</th>
<th>$t_{\max}^t$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non Acc. Damage</td>
<td>0.182</td>
<td>1.00</td>
<td>3.32</td>
<td>0.332</td>
<td>0.08</td>
</tr>
<tr>
<td>Acc. Damage</td>
<td>0.0182</td>
<td>0.10</td>
<td>0.332</td>
<td>0.0332</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Each of the nanoscale RVEs is subjected to one cycle of constrained plane strain tension with linearly increasing tensile strain up to a maximum of 5% and linearly decreasing strain to the unstrained state. The quasi static strains are applied on the nanoscale RVEs incrementally using displacement boundary conditions [139] such that the effective electrostatic properties can be investigated at each strain step using test electric fields applied in form of electrostatic boundary conditions [139] in the $\hat{x}_1$ and $\hat{x}_2$ direction. The averaged current density in each direction ($\hat{x}_1, \hat{x}_2$) is found from the finite element solution of the coupled electromechanical problem and is used to find the effective conductivity components for the nanoscale RVEs [139]. Fig. 6.11 shows the local current density contours for the four nanoscale RVEs on application of the test electric fields when the nanoscale RVEs are subjected to 5% tensile strain. The electron hopping barrier potential for the tests is fixed at 0.5eV and the accelerated damage model which is implemented at the interface along with the electrostatic damage parameter, $\gamma$, which is fixed at 5. Fig. 6.11a shows the local contours of current density component in the $\hat{x}_1$ direction ($\hat{J}_1$) when the test electric field is applied in the $\hat{x}_1$ direction. Similarly, Fig. 6.11b shows the local contours of current density component in the $\hat{x}_2$ direction ($\hat{J}_2$) when the test electric field is applied in the $\hat{x}_2$ direction. It is to be noted that the local current density in the matrix medium is highly dependent on the electron hopping augmented local polymer conductivity [139,147]. It is observed that the RVEs with regular hexagonal packing have symmetric local current density contours because of symmetry in microstructure which in turn leads to symmetrical electron hopping pathways. For the nanoscale RVEs with random CNT distribution, the intertube electron hopping pathways lead to different local conductivities based on the intertube distances. It is further observed
Figure 6.11: (a) Local contours of current density component, $\hat{J}_1$, when the test electric field is applied in the $\hat{x}_1$ direction for the nanoscale RVEs and (b) local contours of current density component, $\hat{J}_2$, when the test electric field is applied in the $\hat{x}_2$ direction for the nanoscale RVEs. The local current density contours presented here are for nanoscale RVEs undergoing interface separation with the accelerated damage model shown in Tab. 6.2 with interfacial electrostatic damage parameter, $\gamma$, of 5. An electron hopping barrier potential of 0.5eV is used for this test and the nanoscale RVE is subjected to 5% applied tensile strain. [154]
that the local current density in the RVE with 0.4 CNT volume fraction is larger because of smaller intertube distances and larger local conductivity of the electron hopping augmented current density pathways as compared to the hexagonal and randomly distributed 0.1 volume fraction RVEs. Thus, the local CNT-polymer microstructure highly influences the current density pathways across the nanoscale RVEs. While the current density pathways in random RVE 1 are more distributed, random RVE 2 has one primary current density pathway in both the \( \hat{x}_1 \) and \( \hat{x}_1 \) direction. Such variation in the local current density contours results in different effective electrostatic properties for the nanoscale RVEs. The effective conductivity components, \( \Sigma_{11}^{\text{Eff}} \) and \( \Sigma_{22}^{\text{Eff}} \), for the nanoscale RVE in the unstrained state and at 5% applied strain are presented in Tab. 6.3 for the accelerated and non-accelerated interfacial damage cases. It is observed that the hexagonal nanoscale RVEs at 0.4 and 0.1 volume fraction are approximately transversely isotropic in the unstrained state, i.e. \( \Sigma_{11}^{\text{Eff}} = \Sigma_{22}^{\text{Eff}} \), because of the uniform hexagonal arrangement of nanotubes. However, the random RVEs at 0.1 volume fraction are anisotropic even in the unstrained state because of the random CNT distribution. On application of tensile strains, however, even the hexagonal RVEs lose their transversely isotropic symmetry and evolve into an orthotropic material medium.

Table 6.3: Comparison of effective conductivity components for the nanoscale RVE in the unstrained state and at 5% applied tensile strain for each of the nanoscale microstructure cases with non-accelerated and accelerated interfacial damage. The variation of effective conductivity components with applied strains is presented in Fig. 6.14,6.15. [154]

<table>
<thead>
<tr>
<th>Applied strain</th>
<th>( \Sigma_{11}^{\text{Eff}} ) (S/m)</th>
<th>( \Sigma_{22}^{\text{Eff}} ) (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-Acc./Acc.</td>
<td>Acc. ( \gamma = 5 )</td>
</tr>
<tr>
<td>0.4 ( V_f ) hex</td>
<td>19.50</td>
<td>13.12</td>
</tr>
<tr>
<td>0.1 ( V_f ) hex</td>
<td>2.03E-7</td>
<td>1.13E-7</td>
</tr>
<tr>
<td>0.1 ( V_f ) rand1</td>
<td>4.13E-6</td>
<td>1.04E-6</td>
</tr>
<tr>
<td>0.1 ( V_f ) rand2</td>
<td>1.44E-6</td>
<td>6.02E-7</td>
</tr>
</tbody>
</table>

A zoomed in picture of the local interface separation around the CNTs is shown in Fig. 6.12 for the 0.1 volume fraction hexagonal RVE, random RVEs 1 and 2, 5% applied tensile strain. It is observed that the interface separation is different at different CNT-polymer interface spatial location. Thus, the local damage at the CNT-polymer interface is quantified by averaging the local cohesive zone damage at the entire nanoscale CNT-polymer interface.
using Eqn. 6.3.6.4. A $D_{avg}$ of 1 signifies that the nanoscale interface has not undergone any damage. Even though there may be interfacial separation at the nanoscale CNT-polymer interface, but it is possible that the interface separation at every point on the nanoscale interface is less than $\Delta \tilde{u}_{sw}$ such that all cohesive zones are operating within the initial linear elastic region of the normal traction-separation response such that $D_{avg}$ remains at 1. If damage initiates at any point of the nanoscale interface, the averaged damage index starts to reduce from the nominal value of 1. If $D_{avg} < 1$, the averaged damage accumulated at the nanoscale interface is given by $1 - D_{avg}$. The evolution of the of the averaged damage index in the nanoscale RVEs with applied strain is shown in Fig. 6.13. It is observed that for the MD based non-accelerated damage cases, $D_{avg}$ remains at 1 through the entire strain cycle for a maximum applied tensile strain of 5% for each of the nanoscale RVEs. As was indicated earlier, with the MD based non-accelerated damage model the nanoscale interface was observed to separate but it would operate within the initial linear elastic region for a maximum applied tensile strain of 5%, leading to an average damage index of 1 in the entire cycle. For the accelerated damage cases, $D_{avg}$ remains at 1 for some initial period of the strain cycle until approximately 1.5% tensile strain is applied on the nanoscale RVEs, but then it starts to reduce from the nominal value of 1 as the nanoscale interface starts to...
undergo damage. The averaged damage index monotonically decreases up to the maximum applied strain state, after which it remains constant during the unloading cycle because no further damage is induced in the cohesive zones during unloading. The amount of damage accumulated in the nanoscale RVEs with different local microstructure is observed to different because of the differences in local volume fractions and the distribution of CNTs. For the hexagonal RVEs with a volume fraction of 0.4 and 0.1 at 5% applied tensile strain, $D_{\text{avg}}$ was observed to be 0.92 and 0.89, respectively. Thus, the nanoscale interface in the hexagonal RVE at 0.4 volume fraction undergoes about 8% damage accumulation while the 0.1 volume fraction RVE undergoes around 12% interfacial damage accumulation. The random RVEs at 0.1 volume fraction were observed to undergo about 9% interfacial damage accumulation with $D_{\text{avg}}$ of about 0.91 at 5% applied tensile strain and during the unloading cycle.

![Graph showing the evolution of averaged damage parameter](image)

**Figure 6.13:** Evolution of averaged damage parameter for the accelerated and non-accelerated interfacial damage cases (Tab. 6.2) for the different nanoscale RVEs when subjected to one cycle of applied tensile strain with maximum 5% applied strain. [154]

The interfacial damage accumulation at the nanoscale interface leads to evolution of interfacial resistance though the electrostatic cohesive law along with the evolution of local electron hopping pathways. Evolution of interfacial resistance because of damage accumulation with applied strains gets reflected in the effective electrostatic properties of the nanoscale RVEs such that the effective properties follow a different variation during loading and unloading for the accelerated damage cases. Fig. 6.14 shows the evolution of effective conductivity component in the direction of applied strain, $\Sigma_{22}^{\text{Eff}}$, when quasi static strain cycle with a
maximum amplitude of 5% strain is applied on the nanoscale RVEs for both non-accelerated and accelerated damage model. It is observed that the effective conductivity component, $\Sigma_{22}^{Eff}$, reduces from the unstrained state effective conductivity for both accelerated and non-accelerated damage cases and for all nanoscale RVEs. The reduction in effective conductivity is due to strain induced increase in intertube distances leading to smaller local conductivity in the electron hopping augmented intertube pathways [139]. In addition to the electron hopping pathways, the local interfacial separation and damage leads to increased interfacial resistance at the nanoscale interfaces such that the effective conductivity component becomes progressively smaller during the loading cycle. During the unloading cycle, the intertube distances start to decrease resulting in increased electron hopping based local conductivity such that $\Sigma_{22}^{Eff}$ increases during the unloading cycle.

The nanoscale local interfacial damage leads to the difference in response for the non-accelerated and accelerated damage cases such that the effective conductivity for the accelerated damage cases is smaller than those for non-accelerated damage cases. As an example, $\Sigma_{22}^{Eff}$ for the 0.4 volume fraction hexagonal nanoscale is observed to be 9.05 S/m for the non-accelerated damage case as compared to 7.91 S/m for the accelerated damage case at 5% applied strain state i.e. 12.13% smaller. Thus, about 8% interfacial damage accumulation in nanoscale RVE as shown in Fig. 6.13 leads to about 12% reduction in the effective conductivity component. Similar observation can be made for the 0.1 volume fraction RVEs, however, for these RVEs the difference between the accelerated and non-accelerated damage case is observed to be much smaller. For the 0.1 volume fraction hexagonal RVE, random RVE 1 and random RVE 2, $\Sigma_{22}^{Eff}$ with accelerated damage is observed to be about 3%, 2% and 6%, respectively. The difference in the conductivity component at 5% applied strain for the non-accelerated and accelerated cases indicated that interfacial damage at the nanoscale leads to differences in evolution of electrostatic properties. Furthermore, for the accelerated damage cases, the loading and unloading paths are observed to be different because of non-reversible interfacial damage accumulation. As an example, for the 0.4 volume fraction hexagonal RVE, at 2.5% applies strain $\Sigma_{22}^{Eff}$ is observed to be 13.01 S/m during while loading and 12.37 S/m while unloading, i.e. about 5% smaller. Thus, even at the same applied strain state, the irreversible damage accumulation at the nanoscale interface leads to
Figure 6.14: Evolution of effective conductivity component, $\Sigma_{22}^{Eff}$, with applied strain cycle in the $\hat{x}_2$ direction for the non-accelerated and accelerated damage cases (Tab. 6.2) with $\lambda=0.5eV$ and $\gamma=5$ for (a) 0.4 $V_f$ hexagonal RVE (b) 0.1 $V_f$ hexagonal RVE (c) 0.1 $V_f$ random RVE 1 and (c) 0.1 $V_f$ random RVE 2. Electron hopping augmented local conductivity contours are presented for each nanoscale microstructure case at 5% applied tensile strain state. It is to be noted that the local conductivity contours for both the non-accelerated and accelerated interfacial damage cases are exactly the same. [154]
a reduced value of effective conductivity component. If the nanoscale RVE is loaded again it follows the curve along which it had unloaded in the previous cycle representative of interfacial damage accumulation. Similar to the 0.4 volume fraction RVE, $\Sigma_{22}^{Eff}$ at 2.5% applied strain during unloading is observed to be about 1.5%, 1% and 2.5% smaller as compared to the loading cycle for 0.1 hexagonal RVE, random RVE 1 and random RVE 2, respectively. The difference in the loading and unloading pathways indicates that the interfacial damage accumulation at the nanoscale leads to irreversible changes in the effective properties of the nanocomposite.

Figure 6.15: Evolution of effective conductivity components, $\Sigma_{11}^{Eff}$ and $\Sigma_{22}^{Eff}$, with applied strain cycle in the $\hat{x}_2$ direction for the accelerated damage cases (Tab. 6.2) with $\lambda=0.5eV$ and $\gamma=5$ for (a) 0.4 $V_f$ hexagonal RVE (b) 0.1 $V_f$ hexagonal RVE (c) 0.1 $V_f$ random RVE 1 and (c) 0.1 $V_f$ random RVE 2. Electron hopping augmented local conductivity contours are presented for each nanoscale microstructure case at 5% applied tensile strain state. It is to be noted that the local conductivity contours for test electric fields in $\hat{x}_1$ and $\hat{x}_2$ are exactly the same. [154]
The nanoscale local electron hopping effect and interfacial damage also affects the symmetry properties of the nanoscale RVE such that both $\Sigma_{11}^{\text{Eff}}$ and $\Sigma_{22}^{\text{Eff}}$ components of the nanoscale RVE evolve from their unstrained state values. While the effective conductivity components presented in Tab. 6.3 show that the effective conductivity components evolve from the unstrained state to 5% applied strain, Fig. 6.15 shows the evolution of $\Sigma_{11}^{\text{Eff}}$ alongside $\Sigma_{22}^{\text{Eff}}$ for comparison of evolution of microstructure symmetry properties with applied strain. Much like the $\Sigma_{22}^{\text{Eff}}$ component, $\Sigma_{11}^{\text{Eff}}$ shows the effect of interfacial damage initiation, evolution and accumulation for all of the nanoscale RVEs. The hexagonal RVEs at 0.4 and 0.1 volume fraction (Fig. 6.15a,b) were transversely isotropic in-plane ($\hat{x}_1 - \hat{x}_2$ plane) such that $\Sigma_{11}^{\text{Eff}}$ and $\Sigma_{22}^{\text{Eff}}$ were the same in the unstrained state. On application of tensile strains, both of the conductivity components evolve due to changes in electron hopping pathways and interfacial separation/damage leading to anisotropic material symmetry. The random RVEs (Fig. 6.15c,d) at 0.1 volume fraction are orthotropic even in the unstrained state such that $\Sigma_{11}^{\text{Eff}}$ and $\Sigma_{22}^{\text{Eff}}$ are different because of the non-symmetric electron hopping pathways. On application of strains, each of the conductivity components evolve such that the difference in $\Sigma_{11}^{\text{Eff}}$ and $\Sigma_{22}^{\text{Eff}}$ becomes smaller for these specific random nanoscale RVEs unlike the hexagonal RVEs. In addition to the evolution of microstructure symmetry, $\Sigma_{11}^{\text{Eff}}$ is also observed to undergo different loading and unloading cycles because of irreversible interfacial damage accumulation. However, much like $\Sigma_{22}^{\text{Eff}}$, the difference between the loading and unloading pathways differs for the different RVEs.

The observations made for the effective conductivity components further get reflected in the variation of relative change in resistivity components ($\Delta \rho_{11}^{\text{Eff}}/\rho_0^{\text{Eff}}, \Delta \rho_{22}^{\text{Eff}}/\rho_0^{\text{Eff}}$). The evolution of the relative change in resistivity components can be used to evaluate the effective piezoresistive strain tensor components using the averaged form of the piezoresistivity equation [139]. For a non piezoresistive effective material, the relative change in resistivity is zero at all strain states. However, for CNT polymer nanocomposites at the nanoscale, the electron hopping effect and the interfacial damage lead to non zero relative change in resistivity with applied strain, and hence, non zero piezoresistive strain tensor coefficients.

Fig. 6.16a and b show the evolution of relative change in resistivity components $\Delta \rho_{11}^{\text{Eff}}/\rho_0^{\text{Eff}}$ and $\Delta \rho_{22}^{\text{Eff}}/\rho_0^{\text{Eff}}$, respectively, through the applied strain cycle. It is observed that the 0.4
volume fraction hexagonal RVE leads to smaller piezoresistive response in both the $\hat{x}_1$ and $\hat{x}_2$ direction as was observed in some earlier studies [139]. However, the effect of interfacial damage accumulation is observed (Fig. 6.16b) to be larger in the 0.4 volume fraction case in the direction of applied strain ($\hat{x}_2$) following from the observed variation in the effective conductivity components. For example, at 2.5% applied tensile strain, $\Delta \rho_{22}^{Eff}/\rho_0^{Eff}$ is observed to be approximately 15%, 3%, 2% and 5% larger than the loading cycle for the 0.4 volume fraction hexagonal RVE, 0.1 volume fraction hexagonal RVE, random RVE 1 and random RVE 2, respectively. Similarly, the $\Delta \rho_{11}^{Eff}/\rho_0^{Eff}$ component at 2.5% applied tensile strain is observed to be less than 1% larger during the unloading cycle for the 0.1 and 0.4 volume fraction hexagonal RVEs. For random RVE 1 and 2 at 0.1 volume fraction the difference is approximately 12% and 2% respectively. Several factors govern the observed higher sensitivity to interfacial damage accumulation at larger volume fraction including differences in the local electron hopping augmented conductivities and evolving interfacial damage. However, the key reason for the larger difference in loading/unloading paths for higher volume fraction is that the area fraction of the cohesive interface is significantly greater for higher local volume fraction, such that the interface has a larger effect on the volume averaged current density components used to determine the effective properties.
Finally, the effective piezoresistive response of the nanocomposite RVEs presented in Fig. 6.16 is expressed in terms of macroscale effective gauge factors using Eqn 2.64, 2.65 to provide a more widely reported unit for observed effective piezoresistivity in the literature. Similar to the relative change in resistivity components, the effective gauge factors are observed to exhibit a difference in the loading and unloading cycles indicating the effect of irreversible interfacial damage accumulation on the effective piezoresistive response. For example, the gauge factor, $G_{22}^{Eff}$ for the 0.4 volume fraction hexagonal RVE is observed to be 20.8 and 24.0 during the loading and unloading cycle, respectively, at 2.5% applied strain state i.e. about 15% larger. Similarly, at 2.5% applied strain $G_{22}^{Eff}$ is observed to be approximately 3%, 1% and 5% larger during the unloading cycle for 0.1 volume fraction hexagonal RVE, random RVE 1 and random RVE 2, respectively. $G_{12}^{Eff}$ on the other hand is observed to be insignificantly larger at 2.5% applied tensile strain during unloading except for 0.1 volume fraction random RVE 1 for which it is observed to be approximately 14% larger. The hysteresis-like response observed in the effective piezoresistive response over one cycle of applied strain has also been reported in the literature [27] based on experimental observations. Such observations indicate that the irreversible interfacial damage accumulation at the nanoscale interface gets captured in the effective piezoresistive response for CNT-polymer nanocomposites. Furthermore, the degree of sensitivity of the effective properties on the
interfacial damage accumulation during cyclic loading is highly dependent on the nanoscale local volume fraction and microstructure distribution.

### 6.3.2 Effect of Electron Hopping Barrier Potential

In addition to the nanoscale local microstructure, the electron hopping barrier potential ($\lambda$) has been observed to have a significant influence on the effective electrostatic and piezoresistive response of CNT-polymer nanocomposites for both perfectly bonded and imperfect interfaces [136,139]. The electron hopping barrier potential determines the maximum range of electron hopping and the local conductivity of electron hopping augmented conductive pathways. In addition, the interfacial resistance for the separated nanoscale CNT-polymer interface is modeled using the bilinear interfacial resistance-normal separation response highly dependent on the local electron hopping augmented conductivity. In order to study the effect of the electron hopping barrier potential on the damage accumulation when the nanocomposite is subjected to cyclic loading conditions, plane strain constrained tension tests are performed on the 0.1 volume fraction nanoscale RVEs with $\lambda=0.05$eV for comparison with the results presented in Sec. 6.3.1 for which $\lambda=0.5$eV was used. The maximum electron hopping range with $\lambda=0.5$eV and $\lambda=0.05$eV is 4.54nm and 13.87nm respectively. Thus, the electron hopping augmented local conductivity is higher for the nanoscale RVE with $\lambda=0.05$eV. As an example, for the 0.1 volume fraction hexagonal RVE, the intertube distance between the adjacent CNTs in the unstrained state is 3.41nm. The local conductivity of the electron hopping pathways is observed to be $4.16 \times 10^{-7}$ S/m and 2.85 S/m with $\lambda=0.5$eV and $\lambda=0.05$eV, respectively. The several orders of magnitude difference in the local conductivity leads to changes in effective electrostatic properties of the nanoscale RVE. Similarly, the evolving intertube distances on application of strain lead to differences in the effective piezoresistive response. A 1% increase in the intertube distance leads to 19.49% and 6.42% change in the local intertube conductivity for a $\lambda=0.5$eV and $\lambda=0.05$eV, respectively. Thus, a larger value of $\lambda$ or shorter electron hopping range leads to larger relative change in local conductivities resulting in a larger piezoresistive response. Fig. 6.18a shows the variation of relative change in resistivity when the 0.1 volume fraction nanoscale RVEs are subjected to cyclic tensile...
strain with a maximum 5% applied strain. The cohesive zones undergo accelerated damage with the electrostatic damage parameter, $\gamma$, fixed at 5. Following from the smaller relative change local conductivity at larger $\lambda$, $\frac{\Delta \rho_{22}^{Eff}/\rho_0^{Eff}}{\rho_0^{Eff}}$ is observed to be smaller at 5% applied strain for $\lambda=0.05$eV as compared to the case with $\lambda=0.5$eV presented in Fig. 6.16b. At 5% applied strain, the magnitude of $\frac{\Delta \rho_{22}^{Eff}/\rho_0^{Eff}}{\rho_0^{Eff}}$ for $\lambda=0.05$eV is observed to be 0.506 while for $\lambda=0.5$eV it is observed to be 2.02 for the 0.1 volume fraction hexagonal nanoscale. Such observation in the relative change in resistivity lead to larger gauge factors with larger $\lambda$ or smaller electron hopping range as observed from Fig. 6.18b where the effective gauge factors are observed to be much smaller than those presented in Fig. 6.17b. At 5% applied strain, the effective gauge factors are observed to be 11.63 and 42.63 with a $\lambda$ of 0.05eV and 0.5eV, respectively.

![Figure 6.18: Evolution of (a) relative change in resistivity component, $\Delta \rho_{22}^{Eff}/\rho_0^{Eff}$, and (b) effective gauge factor, $G_{22}^{Eff}$, with applied strain cycle in the $\hat{x}_2$ direction for the accelerated damage cases (Tab. 6.2) with $\lambda=0.05$eV, $\gamma=5$ for 0.1 $V_f$ hexagonal RVE, random RVE 1 and random RVE 2. [154]](image)

While the effective piezoresistive response is observed to be larger with larger value of $\lambda$, the effect of interfacial damage accumulation at the nanoscale interface is observed to have a more significant effect on the effective response for smaller $\lambda$, or longer maximum electron hopping range. For $\lambda=0.5$eV, at 2.5% applied strain $G_{22}^{Eff}$ was observed to be about 3%, 1% and 5% larger during the unloading cycle for 0.1 volume fraction hexagonal RVE, random RVE 1 and random RVE 2, respectively. In comparison, at 2.5% applied strain $G_{22}^{Eff}$ is observed to be
approximately 8.5%, 5% and 10% larger during the unloading cycle indicating that interfacial damage accumulation leads to a larger difference in the loading and unloading paths for a smaller value of $\lambda$. While several factors influence the effective piezoresistive response of the nanoscale RVE during loading and unloading, the electron hopping barrier potential effects the local intertube conductivity and subsequent interfacial resistance of the nanoscale CNT-polymer interface undergoing separation and damage. It was indicated that the local interface resistance of the nanoscale RVE is a function of the interface normal separation, the local intertube electron hopping conductivity/resistivity and the electrostatic interfacial damage parameter, $\gamma$. The evolution of normal interface separation for the two cases with a $\lambda$ of 0.5eV and 0.05eV remains the same because the mechanical cohesive zone traction-separation laws are the same for both of the cases. However, the local intertube resistivity and its evolution with applied strain for the two different values of $\lambda$ are significantly different, which leads to a larger damage accumulation effect on the effective properties for smaller values of $\lambda$. Such observations indicate that different polymer medium in the nanocomposite with different electron hopping barrier potential can lead to varying degree of sensitivity in effective response of the nanocomposite on the interfacial damage accumulation. The key observation here is that while a larger value of $\lambda$ (or shorter maximum electron hopping range) results in a larger piezoresistive response on application of strain, it leads to smaller difference in the loading/unloading paths for cyclic loading in the presence of nanoscale interfacial damage.

### 6.3.3 Effect of Interfacial Electrostatic Damage Parameter

In addition to the local nanoscale microstructure and the electron hopping barrier potential, the electrostatic damage parameter, $\gamma$, is observed to have a significant influence on the effective piezoresistive response of CNT-polymer nanocomposites [136]. When subjected to cyclic loading, the nanoscale interface follows the bilinear interfacial resistance-normal separation response shown in Fig. 6.1c where the slopes of the bilinear curve are dependent on the current local electron hopping augmented resistivity of the cohesive zones. When subjected to cyclic loading, the cohesive zone unloads along the line of constant resistiv-
ity. Fig. 6.19 shows a comparison of interfacial resistance as a function of normal interface separation undergoing the loading and unloading cycles for the cohesive zones for the non-accelerated damage case and the accelerated damage cases with $\gamma=5,10,20$. It is observed that the MD based non accelerated damage case does not change in slope as interfacial damage does not initiate for small interface separations. However, the accelerated damage cases follow the bilinear response indicating that the interfacial cohesive zones get damaged after $\Delta \tilde{u}_{sw}=0.0182\text{nm}$ as indicated in Tab. 6.2. The rate of increasing interfacial resistance after damage initiates in the cohesive zones depends on the electrostatic damage parameter, $\gamma$, such that a higher value of $\gamma$ leads to a larger increase in the interfacial resistance. Following from the higher resistance, the cohesive zone with larger $\gamma$ undergoes the largest damage accumulation because of a larger difference in the loading and unloading pathways for the accelerated damage cases as seen from Fig. 6.19. As an example, at 0.015nm normal interface separation, the interfacial resistance is observed during the unloading cycle is observed to be 112%, 252% and 532% higher during the unloading cycle as compared to the loading cycle for accelerated damage cases with a $\gamma$ of 5,10 and 20, respectively.

![Figure 6.19: Comparison of interfacial resistance as a function of normal interface separation undergoing the loading and unloading cycles (similar to Fig. 6.2a) for the cohesive zones for the non-accelerated damage case and the accelerated damage cases with $\gamma=5,10,20$.
](image)

The relative difference in the interfacial resistance for loading and unloading cycles for dif-
different values of $\gamma$ leads to differences in electrostatic and piezoresistive response. Fig. 6.20a shows the variation of relative change in resistivity with applied strains with different values of $\gamma$ for the nanoscale hexagonal RVE with 0.1 volume fraction. It is observed that $\frac{\Delta \rho_{22}^{\text{Eff}}}{\rho_0^{\text{Eff}}}$ is higher in magnitude for the accelerated damage cases as compared to the non-accelerated damage cases because the nanoscale interface undergoes damage, i.e. $\Delta \tilde{u}_n > \Delta \tilde{u}_{sn}$, for the accelerated damage cases leading to higher interfacial resistance. In addition, the difference between the loading and unloading curves is observed to be larger with higher values of $\gamma$ following from the larger relative difference in the interfacial resistance of individual cohesive zones for loading/unloading cycles shown in Fig. 6.19. For example at 2.5% applied tensile strain, $\frac{\Delta \rho_{22}^{\text{Eff}}}{\rho_0^{\text{Eff}}}$ is observed to be about 3%, 6% and 8.5% larger during the unloading cycle for accelerated damage cases with a $\gamma$ of 5, 10 and 20, respectively. The observed results indicate that a larger value of $\gamma$ leads to a larger change in the piezoresistive response because of interfacial damage accumulation.

![Figure 6.20](image.png)

Figure 6.20: Evolution of (a) relative change in resistivity component, $\frac{\Delta \rho_{22}^{\text{Eff}}}{\rho_0^{\text{Eff}}}$, and (b) effective gauge factor, $G_{22}^{\text{Eff}}$, with applied strain cycle in the $\hat{x}_2$ direction for the accelerated damage cases (Tab. 6.2) with $\lambda=0.5$eV, for the 0.1 volume fraction hexagonal nanoscale RVE with non-accelerated damage case and accelerated damage case with $\gamma=5,10,20$. Inset in Fig. 6.20a shows a zoomed version of $\frac{\Delta \rho_{22}^{\text{Eff}}}{\rho_0^{\text{Eff}}}$ between 1.5% and 2.5% applied tensile strain. [154]

The variation of the effective gauge factors with applied strains for the non-accelerated damage case and accelerated damage cases with a $\gamma$ of 5, 10 and 20 are shown in Fig. 6.20b.
Following from the strain dependent variation of relative change in resistivity, $G_{22}^{Eff}$ is observed to show a higher damage accumulation effect in the loading/unloading cycles for larger values of $\gamma$. For example, at 2.5% applied tensile strain $G_{22}^{Eff}$ is observed to be 3%, 6% and 8% larger during the unloading cycle as compared to the loading cycle for the accelerated damage cases with $\gamma$ of 5, 10 and 20, respectively. The results indicate that the electrostatic damage of cohesive zones and the subsequent change in interfacial resistance leads to a significant effect on the electrostatic and piezoresistive response of CNT-polymer nanocomposites.

6.3.4 Effect of Multicyclic Loading Conditions

In the discussion so far, the evolution of electrostatic and piezoresistive response of CNT-polymer nanocomposites has been studied for one cycle of applied strains with a maximum tensile strain amplitude of 5%. The effect of interfacial damage accumulation over 1 cycle of applied strains has been observed to be highly dependent on the nanoscale local volume fraction, nanoscale CNT distribution, the electromechanical response of nanoscale interface to separation/damage and the electron hopping barrier potential. In order to study the effect of multiple cycles of applied strains, the nanoscale hexagonal RVE at a volume fraction of 0.1 is subjected to multiple cycles of quasi-static applied tensile strains. For multiple cycles of applied strains, if the maximum amplitude of applied tensile strains in the cycles is fixed, then interfacial damage at the nanoscale CNT-polymer interface is accumulated only in the first cycle of applied strains for the accelerated damage cases because the local cohesive zones load and unload along the same path i.e. CA in Fig. 6.1a. Thus, the effective properties of the nanoscale RVEs follow the same evolution as the unloading cycle of the first cycle of applied strain for all subsequent cycles in which no additional damage accumulation occurs. However, if the magnitude of maximum applied tensile strains is increased in every subsequent cycle [27], then additional damage gets accumulated at the nanoscale interface resulting in a different loading/unloading response for every applied strain cycle e.g. the local cohesive zone unloads/reloads along path CA in the first cycle and along EA in the next (Fig. 6.1a). In order to observe the evolution of applied multicyclic strains with increasing maximum
strain amplitude, six cycles of quasi-static tensile strains are applied on the nanoscale RVE with the maximum amplitude increasing from 5% to 10% incrementing at 1% in every cycle.

Figure 6.21: Evolution of averaged damage parameter for the accelerated interfacial damage case for the 0.1 volume fraction hexagonal nanoscale RVEs when subjected to six cycles of applied tensile strain with maximum applied strain increasing by 1% incrementally from 5% to 10%. [154]

The evolution of interfacial separation around a CNT in the 0.1 volume fraction hexagonal nanoscale RVE is presented in Fig. 6.22 in the unstrained state and at the maximum amplitude of each applied strain cycle i.e. 5% to 10% in increments of 1%. It is observed that the interfacial separation around the CNT increases progressively in every cycle, and thus, additional interfacial damage gets accumulated in every subsequent cycle. Fig. 6.21 shows the evolution of averaged interfacial damage index ($D_{avg}$) over the six cycles of applies tensile strains. It is observed that about 10% interfacial damage is accumulated in the nanoscale CNT-polymer interface during the first loading-unloading cycle with a maximum strain amplitude of 5%. In the subsequent cycles, the amount of interfacial damage accumulation is smaller because the nanoscale interface reloads along the line of constant resistivity until it gets back to the point where unloading started on the previous cycle before accumulating further damage on the current cycle. For the subsequent cycles, i.e. cycle 2 to cycle 6, about 3.5% additional interfacial damage is accumulated in every cycle with 1% increment in the maximum applied strains. The amount of additional interfacial damage accumulated in ev-
Figure 6.22: Zoomed picture showing the evolution of local interface separation around a CNT in the 0.1 volume fraction hexagonal nanoscale RVE in the unstrained state and at the maximum strain amplitude of the six cycles of applied tensile strain with maximum applied strain increasing by 1% incrementally from 5% to 10%. The electron hopping barrier potential used for the current test is 0.5eV and the interface is modeled using the accelerated interfacial damage model presented in Tab. 6.2 with $\gamma=5$. Local current density component, $J_2$, is presented here for comparison over several cycles of applied strain with interfacial damage accumulation in each cycle. [154]
ery cycle directly correlates the difference in effective properties for the loading/unloading parts of applied strains.

The evolution of relative change in resistivity and effective gauge factors with applied strains is presented in Fig. 6.23a for the nanoscale hexagonal RVE at 0.1 volume fraction with the electron hopping barrier potential of 0.5 eV and 0.05 eV, as a function of quasi-static solution times. It is observed that the magnitude of relative change in resistivity at the peak value of applied strains increases in every cycle. As an example, for $\lambda = 0.5\text{eV}$, $\Delta \rho_{22}^{Eff}/\rho_{0}^{Eff}$ is observed to be 2.03, 2.58, 3.15, 3.79, 4.41 and 4.87 at the peak strains i.e. 5% to 10% incrementing at 1% in every cycle. The observed increase in $\Delta \rho_{22}^{Eff}/\rho_{0}^{Eff}$ with increasing strain amplitudes in every cycle is due to the larger intertube distances at higher applied strains affecting the local conductivity of electron hopping pathways and additional damage accumulation at the nanoscale interfaces as shown in Fig. 6.21. The local current density in and around a CNT in the nanoscale hexagonal RVE decreases at the maximum strain amplitude of each cycle as shown in Fig. 6.22, and thus leads to larger change in effective conductivity/resistivity as compared to the unstrained state. Similar to the relative change in resistivity, larger effective gauge factors are observed at the peak strains. For example, at the peak strains, $G_{22}^{Eff}$ is observed to be 42.2, 45.3, 48.0, 51.0, 53.4 and 54.57 for $\lambda = 0.5\text{eV}$. The increase in effective gauge factors with increasing strain amplitude can be qualitatively correlated to the increasing relative change in resistance with the number of applied load cycles in [27]. For $\lambda = 0.05\text{eV}$, the evolution of effective properties is observed to follow a similar variation, however, the magnitude of relative change in resistivity and effective gauge factors is smaller as discussed in Sec 6.3.2.

In order to observe the effect of damage accumulation over multiple cycles of applied strains with increasing amplitudes, the effective gauge factors are presented as a function of applies strains in Fig. 6.23b, for an electron hopping barrier potential of 0.5 eV and 0.05 eV. It is observed that the effective gauge factors for the nanoscale RVE increase over every cycle of applied strains as additional damage is induced in the nanoscale CNT-polymer interfaces. For example, at 2.5% applied strain for $\lambda = 0.05\text{eV}$, the effective gauge factor ($G_{22}^{Eff}$) is observed to be 9.25, 10.07, 10.22, 10.37, 10.53 and 10.68 in the loading cycles for cycle 1 to
Figure 6.23: (a) Evolution of relative change in resistivity ($\Delta \rho_{22}^{\text{Eff}} / \rho_0^{\text{Eff}}$) and effective gauge factors ($G_{22}^{\text{Eff}}$) for the accelerated interfacial damage case for the 0.1 volume fraction hexagonal nanoscale RVEs when subjected to six cycles of applied tensile strain with maximum applied strain increasing by 1% incrementally from 5% to 10% as a function of quasi-static solution times for $\lambda = 0.5\text{eV}, 0.05\text{eV}$. (b) Evolution of effective gauge factors ($G_{22}^{\text{Eff}}$) for the accelerated interfacial damage case for the 0.1 volume fraction hexagonal nanoscale RVEs when subjected to six cycles of applied tensile strain with maximum applied strain increasing by 1% incrementally from 5% to 10% as a function of applied strains for $\lambda = 0.5\text{eV}, 0.05\text{eV}$. (c) Inset I from Fig. 6.23b showing zoomed picture of increasing gauge factors in every cycle for $\lambda = 0.5\text{eV}$ and (d) Inset II from Fig. 6.23b showing zoomed picture of increasing gauge factors in every cycle for $\lambda = 0.05\text{eV}$. [154]
The increasing effective gauge factors indicate that the additional damage induced at the nanoscale interfaces over several cycles affects the effective piezoresistive response of the nanoscale RVE. It is further observed that the damage accumulation effect, in terms of difference in the loading/unloading pathways, is more significant in the first cycle of applied strains for either of electron hopping barrier potentials. From Fig. 6.21, it was observed that the amount of damage accumulation in the first cycle was much larger (10%) as compared to the subsequent cycles of applies strains (3.5%). The amount of additional damage accumulated over each cycle of applied strains correlates to the relative increase in effective gauge factors during the loading/unloading cycle for each cycle of applied strain. Following from additional damage accumulation, at 2.5% applied strain for $\lambda=0.05\text{eV}$, the difference between the effective gauge factors in the loading and unloading cycles is observed to be about 9% in the first cycle of applied strains and about 1.5% in every subsequent cycle of applied strain.

Such observations indicate that damage accumulation at the nanoscale interface over several cycles of applied strain could substantially affect the effective piezoresistive response of the nanocomposite and is closely related to amount of interfacial damage accumulated over each cycle. Thus, under dynamic loading conditions, the effective piezoresistivity of the CNT-polymer nanocomposites may evolve over several cycles depending on the amount of interfacial damage accumulated in the previous cycles resulting in a hysteresis-like behavior as was observed in [27]. It is anticipated that quantification of such hysteresis-like behavior could lead to development of nanocomposite sensors and sensing system with better interpretation of the observed behavior of remaining structural life under cyclic loading conditions.
Chapter 7

Multiscale Modeling of Nanocomposite Bonded Energetic Materials

In the current work, the electro-mechanical characterization of surrogate hybrid sugar-MWNT-epoxy composites is conducted in order to provide proof of concept for in-situ strain and damage sensing in nanocomposite bonded explosives. In addition, effective piezoresistive response of NCBX materials is studied computationally using a micromechanics based hierarchical multiscale framework where the nanocomposite binder is modeled through electromechanical cohesive zones representative of effective CNT-polymer piezoresistive response. It is expected that the results presented in the current work will provide basis to explore optimum NCBX microstructure for in-situ detection of strain and damage state. The results presented in this chapter are published in [155].
7.1 Model Description

7.1.1 Modeling Assumptions and RVEs

A modeling idealization of separation of scales in NCBX nanocomposites goes through an effective homogeneous macroscale medium transitioning through the explosive crystal grain structure at the microscale [95] to the nanocomposite binding medium which has microstructural features (CNTs and CNT bundles/agglomerates) at the nanoscale [139]. At the microscale explosive grains are bound together with polymer nanocomposite with large grain volume fractions. Thus, the polymer nanocomposite binder medium can effectively be thought of as a thin interface connecting the explosive crystals. The effective electromechanical response of the binding interface should then represent the effective electromechanical response of the CNT-polymer nanocomposite.

Figure 7.1: a) Identification of grains from SEM photographs of neat-72 vol.% sugar-epoxy fracture surface, b) a 31-grain RVE inspired from the SEM microstructure morphology image in (a) and c) an idealized 10-grain RVE generated using Voronoi Tesselation. [155]

In the current work, the effective properties of CNT bundles [71,135,136,139] will be used in a micromechanics based homogenization framework to allow for random/aligned orientations of these bundles within the polymer matrix. The effective electromechanical properties of randomly oriented/aligned CNT-polymer nanocomposites obtained are then used to appropriately model the interfacial nanocomposite binder response. For the computational
modeling of the explosive grain structure at the microscale, representative volume elements (RVEs) are constructed based on a) idealized Voronoi Tessellation and b) based on the SEM micrograph obtained in the current work. Fig. 7.1a shows an idealized 10-grain RVE generated using Voronoi Tessellation. Fig. 7.1b shows the SEM micrograph overlaid with the identified crystal/grain structure used in building a 31-grain microscale RVE shown in Fig. 7.1c. It is to be noted that the idealized 10-grain RVE is constructed at a much smaller scale (∼10µm) as compared to the 31-grain RVE for demonstration with true micron sized grains which are typical to some explosive materials [92–94]. The microscale RVEs shown in Fig. 7.1a,c are meshed using 3-noded linear triangular finite elements where each grain edge is resolved using 10 coincident node pair across the interface. The constitutive response of these initially coincident node pairs is governed by CNT-polymer nanocomposite governed electromechanical cohesive laws which are dependent on the nanocomposite binder electromechanical properties and estimates of initiation and evolution of damage at the microscale.

7.1.2 Imperfect Interface Modeling Through Cohesive Zones

The nanocomposite binder medium between the explosive grains is modeled using electromechanical cohesive laws representing the electromechanical response of CNT-polymer nanocomposites through normal and tangential traction-separation laws combined with a normal interfacial resistance-interfacial separation law. These laws are constructed using micromechanics based homogenization techniques to evaluate the initial electromechanical properties of the CNT-polymer nanocomposites in addition to material properties such as experimentally observed fracture toughness.

The cohesive interface response for the mechanical boundary value problem (BVP) is described in terms of bilinear normal and tangential traction-separation response as shown in Fig. 7.2. The normal traction-separation response, shown in Fig. 7.2a, features an initial region of linearly increasing normal traction as the interface separation increases (A-B). This region represents the part of the interface response where the effective nanocomposite acts like a linear-elastic material for small magnitude of strains with no damage based reduction
in the nanocomposite effective stiffness. The local cohesive zone stiffness in the undamaged initial linear elastic region is constant ($\tilde{K}_0^n$). Normal traction increases until it reaches the point of peak traction ($\tilde{t}_{n}^{\text{max}}$ at B with interface separation, $\Delta \tilde{u}_{n}^{\text{sw}}$) where local cohesive zone damage starts to initiate in the form of a linear reduction in normal interfacial traction from the point of peak traction. The local cohesive zone stiffness at any general point, C, on the traction separation curve is then given by ($\tilde{K}_n^C = \tilde{t}_n^C / \Delta \tilde{u}_n^C$), such that $\tilde{K}_n^C \leq \tilde{K}_0^n$. The decreasing stiffness of the cohesive interface following the path B-C-D is representative of damaging nanocomposite binder medium where local damage results in reduced interface stiffness. The linear reduction in interfacial normal tractions with increasing interface separation continues until the normal interface separation becomes zero at D, at a normal interface separation of $\Delta \tilde{u}_{n}^{\text{max}}$, i.e. complete failure of the cohesive zones.

The tangential traction-separation law, shown in Fig. 7.2b, features a similar bilinear behavior with an initial linear increase in tangential traction with increasing tangential interfacial separation in either direction (A-B). The local tangential stiffness of the cohesive zone in this region is constant and is given by $\tilde{K}_0^t$. However, once the tangential traction reaches the maximum value of $\tilde{t}_{t}^{\text{max}}$ at B, with an interface separation of $\Delta \tilde{u}_{t}^{\text{sw}}$, the tangential traction undergoes a flat plateau region with constant tangential traction (BC) representing tangential sliding of the interface under frictional contact. The tangential stiffness at any general
point is given by \( \tilde{K}_C^t = \tilde{t}_C^t / \Delta \tilde{u}_C^t \), such that \( \tilde{K}_C^t \leq \tilde{K}_C^0 \).

Figure 7.3: a) Schematic of the bilinear interface normal resistance-separation law used in the current work for the coupled electrostatic cohesive zones and b) the bilinear interface normal resistance-separation law for inherently piezoresistive binder. [155]

In addition to the normal and tangential traction-separation laws, electrostatic cohesive zone laws are specified at the explosive grain boundaries in terms of interfacial resistance-normal interface separation laws to allow for current density transfer across the nanocomposite binder interface. The electrostatic cohesive law nominally follows a bilinear response (Fig. 7.3a) for a non-piezoresistive binder e.g. pure polymer binder with no CNTs. The interfacial resistance in the initial linear region of the electrostatic cohesive law is given by

\[
\tilde{R}(\Delta \tilde{u}_n) = \frac{\tilde{\rho}}{\tilde{A}} \Delta \tilde{u}_n \quad \Delta \tilde{u}_n \leq \Delta \tilde{u}_n^{sw} \quad (7.1)
\]

where \( \tilde{A} \) is the effective cross sectional area for the cohesive zone node pair. The normal interface separation (\( \Delta \tilde{u}_n \)) acts as the effective length of the polymer ligament connecting the interface. In effect, the interface resistance increases linearly as the interface normal separation increases with a rate given by \( \tilde{\rho}/\tilde{A} \). It should be noted that the local resistance of the cohesive zone is dependent on the separation distance, thus, every cohesive zone could possibly have a different current resistance for applied displacement boundary conditions on the inhomogeneous microscale RVE. The local resistivity of the polymer medium (\( \tilde{\rho} \)),

\[
G_s^{sc} = 0, G_t^{sc} = 0
\quad \text{Red} \quad G_s^{sc} = G_t^{sc} = 2G
\quad \text{Blue} \quad G_s^{sc} = 5G, G_t^{sc} = 10G
\]
however, remains constant in absence of interfacial damage.

If the normal interface separation becomes larger than \( \Delta \tilde{u}^{sw}_n \), the cohesive zone starts to get progressively damaged up to \( \Delta \tilde{u}_n^{\text{max}} \), where it gets completely damaged, i.e. becomes an open circuit. The rate of change of resistance with increasing interface separation should be larger than the nominal slope with no interfacial damage (\( \frac{\tilde{\rho}}{\tilde{A}} \)) to account for the damage induced increase in local polymer ligament resistivity. For this study, it is assumed that the increase in resistance with cohesive zone damage follows a linear response with a higher rate of \( \gamma \tilde{\rho}/\tilde{A} \) where \( \gamma \geq 1 \). The symbol, \( \gamma \), denotes the increase in rate of change of interfacial resistance with interfacial damage, thus, for an undamaged cohesive zone \( \gamma = 1 \). The interfacial resistance for interface separation larger than \( \Delta \tilde{u}^{sw}_n \) is given by

\[
R(\Delta \tilde{u}_n) = \frac{\rho}{A} \Delta \tilde{u}^{sw}_n + \frac{\gamma \rho}{A} (\Delta \tilde{u}_n - \Delta \tilde{u}^{sw}_n) \quad \Delta \tilde{u}_n \geq \Delta \tilde{u}^{sw}_n \tag{7.2}
\]

The local cohesive zone resistivity on any general point in BD of Fig. 7.3a is given by the slope of the line joining the current position on the interfacial resistance-normal separation curve to the origin, and can be expressed as

\[
\tilde{\rho}(\Delta \tilde{u}_n) = \rho \frac{\Delta \tilde{u}^{sw}_n}{\Delta \tilde{u}_n} + \gamma \tilde{\rho} \left(1 - \frac{\Delta \tilde{u}^{sw}_n}{\Delta \tilde{u}_n}\right) \quad \Delta \tilde{u}_n \geq \Delta \tilde{u}^{sw}_n \tag{7.3}
\]

In the case where the cohesive zone interface is interpenetrating, i.e. \( \Delta \tilde{u}_n < 0 \), the interface resistance is fixed at approximately zero, as shown in Fig. 7.3a. It is to be noted that the bilinear normal traction-separation law shown in Fig. 7.2 and the bilinear interfacial resistance-separation law shown in Fig. 7.3 are coupled through the normal interface separation and represent electromechanical response of the binder medium. It is to be noted that only normal current density is allowed across the cohesive zone node pairs through the normal interfacial resistance-normal interface separation laws, however, the model can be readily extended to allow for tangential current density through an appropriate phenomenological model if required.

The discussion of the electrostatic cohesive zones so far has been restricted to nominal non-
piezoresistive binder medium e.g. pure polymer. Addition of CNTs to the binder results in the interface response to be inherently piezoresistive, representative of CNT-polymer nanocomposites. Thus, the bilinear normal interface resistance-separation law shown in Fig. 7.3 needs to be modified appropriately to account for the inherent piezoresistivity of the nanocomposite binder medium. By extending Eqs. 7.1 and 7.2 for piezoresistive nanocomposite binder, the interface normal resistance-separation can be mathematically expressed as shown in Eqn. 7.4, where $\rho_0$ is the initial unstrained resistivity of the nanocomposite binder and $\delta_n$ is the reference length associated with the normal separation of the cohesive zone which scales normal interface separation into normal interfacial stretch, and thus, relates the normal separation to the local strain in the cohesive zone. The piezoresistive response of CNT-polymer nanocomposite binder is captured (Fig. 7.3b) through the effective nanocomposite gauge factors before and after the initiation of damage in the nanocomposite represented by $G^{NC}_0$ and $G^{NC}_d$, respectively.

$$
\tilde{R}(\Delta \tilde{u}_n) = \begin{cases} 
0 & \Delta \tilde{u}_n(\tilde{x}) \leq 0 \\
\frac{\rho_0}{4} \left[ 1 + \tilde{G}^{NC}_0 \frac{\Delta \tilde{u}_n}{\delta_n} \right] \Delta \tilde{u}_n & 0 \leq \Delta \tilde{u}_n \leq \Delta \tilde{u}_n^{aw} \\
\frac{\rho_0}{4} \left[ 1 + \tilde{G}^{NC}_d \frac{\Delta \tilde{u}_n - \Delta \tilde{u}_n^{aw}}{\delta_n} \right] (\Delta \tilde{u}_n - \Delta \tilde{u}_n^{aw}) & \Delta \tilde{u}_n^{aw} \leq \Delta \tilde{u}_n \leq \Delta \tilde{u}_n^{max} \\
\infty & \Delta \tilde{u}_n^{max} \leq \Delta \tilde{u}_n
\end{cases}
$$

(7.4)

7.1.3 Electromechanical Cohesive Zone Parameter Estimation

The parameters used in construction of the electromechanical cohesive laws determine the response of the nanocomposite binder. While a detailed modeling of the nanocomposite piezoresistive response from the subscales is out of scope of the current work, estimates of the effective properties based on effective properties, reported in the literature and using micromechanics analysis, are used in the current work to construct the electromechanical cohesive laws. As an example, estimates of effective CNT-polymer nanocomposite stiffness components are used to construct the mechanical cohesive law i.e. the initial undamaged cohesive stiffness for normal mode of separation is chosen based on the axial modulus of CNT-polymer nanocomposites while estimates of effective shear modulus is used to find the
initial undamaged stiffness of the cohesive law in tangential mode of separation.

The idealized 10-grain RVE (Fig. 7.1a) is used in the current work for demonstration of effective piezoresistive response in the nanocomposite bound explosives. Furthermore, parametric studies are conducted by varying the elastic modulus and conductivity of the explosive grains in addition to different nanocomposite piezoresistive response in order to provide an initial assessment of different combinations of properties which lead to the largest piezoresistive response for the composite. For the 10-grain RVE, the strain to initiation of damage and complete nanocomposite failure are used to evaluate the interface separation peak traction and the interface separation at complete failure of the cohesive zone through an appropriate reference length of the cohesive zones. The reference length for the interface the is related to the length scale of the microstructure and the binder volume fraction such that integrating over the entire interface with the reference length as cohesive zone thickness provides the volume fraction of the interfacial binder during the averaging process. For the electrostatic cohesive zones, the initial resistivity is assigned using estimates of nanocomposite resistivity [71, 72] with the estimates of nanocomposite effective gauge factors [20, 133] before and after damage initiation are used to allow for the bilinear electrostatic piezoresistive cohesive law to evolve into fully non-linear cohesive zone law (Fig. 7.3b). For the 10-grain RVE, Tab. 7.1 summarizes the parameters used in the construction of nanocomposite binder’s coupled electromechanical cohesive zone laws along with the material parameters used for the explosive grains, where $E$, $\nu$ and $\rho$ are the linear elastic modulus, Poisson’s ratio and resistivity of the explosive grains, respectively. It is to be noted that parametric studies were conducted for some of explosive properties and cohesive zone parameters, and thus, a range is provided for these in Tab. 7.1. It is expected that the parametric studies conducted on the 10-grain RVE will provide insight into the effect of grain and binder properties on the NCBX piezoresistive response.

For the microstructure morphology inspired 31-grain microscale RVE, the properties of the explosive grains are fixed with the grains modeled as linear elastic materials with mechanical properties corresponding to HMX crystals [101] with an elastic modulus of 25GPa and a Poisson’s ratio of 0.25. The electrostatic conductivity of the HMX grains are not readily
Table 7.1: Material properties for the explosive grains and parameters for the electromechanical cohesive zones used in the current work. [155]

<table>
<thead>
<tr>
<th>Type of Property</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Explosive grain properties</td>
<td>E</td>
<td>10-250 GPa</td>
</tr>
<tr>
<td></td>
<td>$\nu$</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>$\rho$</td>
<td>0.01-2.5 $\Omega$m</td>
</tr>
<tr>
<td>Mechanical cohesive law</td>
<td>$\tilde{K}_n$</td>
<td>10 GPa</td>
</tr>
<tr>
<td></td>
<td>$\Delta\tilde{u}_n^{sw}$</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>$\Delta\tilde{u}_n^{max}$</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>$\tilde{K}_t$</td>
<td>1 GPa</td>
</tr>
<tr>
<td></td>
<td>$\Delta\tilde{u}_t^{sw}$</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>$\delta_n$</td>
<td>0.1 $\mu$m</td>
</tr>
<tr>
<td>Electrostatic cohesive law</td>
<td>$\tilde{\rho}_0$</td>
<td>0.1 $\Omega$m</td>
</tr>
<tr>
<td></td>
<td>$\tilde{G}^{NC}_0$</td>
<td>0-5</td>
</tr>
<tr>
<td></td>
<td>$\tilde{G}^{NC}_d$</td>
<td>0-10</td>
</tr>
<tr>
<td></td>
<td>$\gamma$</td>
<td>10</td>
</tr>
</tbody>
</table>

available in the literature, however, PBX conductivity has been reported to be between 300 and 5000S/m [156]. Based on these estimates for PBX conductivity, a grain conductivity of 1000S/m is used in the current work. The effective properties for the construction of electromechanical cohesive zones are obtained using a more rigorous micromechanics based evaluation of nanocomposite effective properties. The key assumption for the microscale RVE is that the nanotube bundles, composed of aligned SWCNTs, are identical, well dispersed and randomly oriented in the polymer matrix. For a given CNT volume fraction within the bundle, in the unstrained state, the mechanical response of the nanoscale bundle are obtained using the Mori-Tanaka method [131] with aligned CNTs in the polymer medium. The CNT volume fraction within the bundle is chosen to be 0.4 based on some experimental estimates in literature [140]. The corresponding unstrained electrostatic conductivity is obtained using a finite element based micromechanical analysis allowing for electron hopping at the nanoscale [139]. Once the bundle properties are obtained, the Mori-Tanaka method is used to allow for random/aligned orientations of the bundles within the polymer matrix. The effective stiffness and electrostatic conductivity for the microscale RVE is obtained by treating each orientation of a given bundle as a different phase, and averaging over all possible orientations in a consistent manner such that the orientations of nanotube bundles
are accounted for [72, 133, 150–152].

As an example, the Mori-Tanaka method for allowing random/aligned orientation of CNT bundles is described here. The effective electrostatic conductivity for the microscale RVE is obtained by treating each orientation of a given bundle as a different phase, and averaging over all possible orientations in a consistent manner such that the orientations of nanotube bundles are accounted for [72, 150–152]. For discrete number of orientations, the effective nanocomposite electrical conductivity can be expressed in terms of summation over all orientations as

\[
\tilde{\Sigma}_{\text{Eff}} = \tilde{\Sigma}^{(\text{m})} + \sum_{J=1}^{P} c_{J}^{B} \left( \tilde{\Sigma}^{(B)}_{J} - \tilde{\Sigma}^{(\text{m})}_{J} \right) \tilde{A}_{J}^{(B)}
\]

(7.5)

where \( P \) is the total number of discrete orientations of the nanotube bundle and \( c_{J}^{B} \) is the volume fraction of nanotube bundles having the \( J \)th orientation such that

\[
\sum_{J=1}^{B} c_{J}^{B} = V_{f}^{B}
\]

(7.6)

where \( V_{f}^{B} \) is the total microscale bundle volume fraction such that \( V_{f}^{B} + V_{f}^{m} = 1 \) in the microscale RVE, where \( V_{f}^{m} \) is the volume fraction of matrix. The quantities \( \tilde{\Sigma}_{J}^{(\text{m})} \) and \( \tilde{\Sigma}_{J}^{(B)} \) are the matrix conductivity and the \( J^{\text{th}} \) orientation nanotube bundle conductivity tensors, respectively, and the quantities \( \tilde{A}_{J}^{(B)} \) denote the \( J \)th orientation electric field concentration tensors. The effective microscale electrical conductivity averaging for the \( P \) discrete orientations of the microscale bundles can then be found using

\[
\tilde{\Sigma}_{\text{Eff}}^{ij} = \tilde{\Sigma}_{ij}^{(\text{m})} + \frac{V_{f}^{B}}{4\pi} \sum_{k=1}^{P_{1}} \sum_{m=1}^{P_{2}} P^{B}(\psi_{k}, \varphi_{m}) \left( \tilde{\Sigma}_{il}^{(B)}(\psi_{k}, \varphi_{m}) - \tilde{\Sigma}_{il}^{(\text{m})} \right) \tilde{A}_{lj}^{B}(\psi_{k}, \varphi_{m}) \sin(\varphi_{m}) \Delta \varphi \Delta \psi
\]

(7.7)

where \( P^{B}(\psi_{k}, \varphi_{m}) \) is the probability of an orientation at a given set of Euler angles, \( \psi_{k} \) and \( \varphi_{m} \), summed over a discrete number \( P_{1} \) and \( P_{2} \) of respective angles. The components of the
electric field concentration tensors, \( \tilde{A}^B_{ij}(\psi_k, \varphi_m) \) can be evaluated using a variety of micromechanics methods. In the present work, they are obtained using the Mori-Tanaka method [131] which is a micromechanics based averaging technique for obtaining concentration tensors that account for interactions among nanotube bundles by modifying the components of the average electric fields in the matrix medium from their dilute approximation values. The components of the electric field concentration tensors can thus be obtained as

\[
\tilde{A}^B_{ij}(\psi_k, \varphi_m) = Q_{im}(\psi_k, \varphi_m) \tilde{T}^B_{mn} Q_{ln}(\psi_k, \varphi_m) \left[ (1 - v_f^B) \delta_{jl} + \frac{v_f^B}{4\pi} \sin(\varphi_m) \sum_{r=1}^{P_1} \sum_{s=1}^{P_2} \left( \tilde{Q}_{jr}(\psi_r, \varphi_s) \tilde{T}^{(B)}_{rs} \tilde{Q}_{ls}(\psi_r, \varphi_s) \right) \right]^{-1}
\]

where \( \delta_{ij} \) is Kronecker delta and \( \tilde{T}^{(B)}_{ij} \) is the dilute electric field concentration tensor obtained using the Eshelby’s tensor for infinitely long cylinders, \( S_{ml} \), as

\[
\tilde{T}^{(B)}_{mn} = \left[ \delta_{mn} + S_{ml} \left( \tilde{\Sigma}_{lr}^{(m)} \right)^{-1} \left( \tilde{\Sigma}^{(B)}_{rn} - \tilde{\Sigma}_{rn}^{(m)} \right) \right]^{-1}
\]

\( Q_{ij}(\psi_r, \varphi_s) \) are the components of the rotation matrix used to transform the microscale coordinate system with the local nanotube bundle coordinate system. To allow for alignment of CNT bundles, with \( x_2 \) direction as the alignment direction, a Poisson’s distribution for the probability of an orientation is used with a variance of 0.1. Similar procedure is used to obtain the unstrained effective stiffness tensor components.

The effective unstrained properties shown in Tab. 7.2 are used to construct the initial linear stiffness for the bilinear normal and tangential traction-separation laws and the initial linear resistance-separation law shown in Fig. 7.2 and Fig. 7.3, respectively. As an example, \( C_{22}^{Eff} \) is used to construct the initial normal traction-separation law stiffness as \( \tilde{K}_n = C_{22}^{Eff} / \delta_n \), where \( \delta_n \) is the reference length associated with the normal mode of separation. For the 31-grain RVE, a reference length of 47\( \mu \)m is calculated based on the nanocomposite binder volume fraction of 30%. Similarly, \( C_{44}^{Eff} \) is used to construct the initial tangential traction-separation law stiffness, \( \tilde{K}_t \), for both the random and the aligned cases. The initial resistivity of the
Table 7.2: Effective electromechanical properties of CNT-polymer nanocomposites calculated using the Mori-Tanaka method allowing for different orientations of CNT bundles. Three different weight concentrations (relative to epoxy polymer) are shown corresponding to the experimental samples. Note that the MWNT concentrations are shown here are relative to epoxy polymer. [155]

<table>
<thead>
<tr>
<th>Property</th>
<th>0.5 wt%</th>
<th>1 wt%</th>
<th>2 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global ( (V_f) )</td>
<td>0.006</td>
<td>0.012</td>
<td>0.024</td>
</tr>
<tr>
<td>Local CNT ( (V_{f}^{CNT_B}) )</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Bundle ( (V_f^B) )</td>
<td>0.015</td>
<td>0.03</td>
<td>0.06</td>
</tr>
<tr>
<td>Random: ( C_{22}^{Eff} = C_{33}^{Eff} ) (GPa)</td>
<td>8.06</td>
<td>9.77</td>
<td>11.34</td>
</tr>
<tr>
<td>Random: ( C_{44}^{Eff} ) (GPa)</td>
<td>4.95</td>
<td>5.93</td>
<td>6.77</td>
</tr>
<tr>
<td>Random: ( \Sigma_{22}^{Eff} = \Sigma_{33}^{Eff} ) (S/m)</td>
<td>61.16</td>
<td>93.68</td>
<td>127.62</td>
</tr>
<tr>
<td>Aligned: ( C_{22}^{Eff} ) (GPa)</td>
<td>9.39</td>
<td>11.74</td>
<td>13.94</td>
</tr>
<tr>
<td>Aligned: ( C_{33}^{Eff} ) (GPa)</td>
<td>7.59</td>
<td>9.27</td>
<td>10.92</td>
</tr>
<tr>
<td>Aligned: ( C_{44}^{Eff} ) (GPa)</td>
<td>5.55</td>
<td>7.29</td>
<td>9.16</td>
</tr>
<tr>
<td>Aligned: ( C_{55}^{Eff} ) (GPa)</td>
<td>4.4</td>
<td>5.51</td>
<td>6.69</td>
</tr>
<tr>
<td>Aligned: ( \Sigma_{22}^{Eff} ) (S/m)</td>
<td>142.97</td>
<td>219.01</td>
<td>298.33</td>
</tr>
<tr>
<td>Aligned: ( \Sigma_{33}^{Eff} ) (S/m)</td>
<td>1.68</td>
<td>2.86</td>
<td>4.40</td>
</tr>
</tbody>
</table>

The cohesive zone used in the normal resistance-separation law is obtained as \( \tilde{\rho} = 1/\Sigma_{22}^{Eff} \) for both the random and aligned cases. In addition to the random and aligned cases, an additional aligned transverse (or tangential) to the interface is considered. The initial properties for this case are obtained by replacing \( C_{22}^{Eff} \), \( C_{44}^{Eff} \) and \( \Sigma_{22}^{Eff} \) by \( C_{33}^{Eff} \), \( C_{55}^{Eff} \) and \( \Sigma_{33}^{Eff} \), respectively, obtained for the aligned case. It is to be noted that the properties shown in Tab. 7.2 are nanocomposite binder properties local to the interface expressed in terms of local cohesive zone coordinate system. In the finite element analysis, the local stiffnesses and conductivities are transformed to the global coordinate system before their influence is added to the global finite element matrices.

In addition to the effective unstrained stiffnesses and conductivities, the initiation and rate of damage for the nanocomposite cohesive zones needs to be estimated in order to evaluate...
\( \Delta \tilde{u}_n^{sw}, \Delta \tilde{u}_n^{sw} \) and \( \Delta \tilde{u}_n^{max} \). These parameters are obtained using fracture toughness estimates for CNT-polymer nanocomposite. It is assumed that the addition of CNTs to the epoxy polymer system does not result in a large change in the fracture toughness such that the polymer fracture toughness \( 3.2 \text{MPa} \) [157], assuming linear elastic brittle material response) can be used. Thereafter, two different cases of bilinear cohesive zone normal traction-separation laws are generated assuming brittle damage and ductile damage of the interface, in absence of direct experimental investigation of damage at the local interface in such composites. For the brittle damage case, fracture toughness is approximated from the given undamaged normal stiffness (chosen to be 10GPa which is nearly representative of each alignment case) by specifying \( \Delta \tilde{u}_n^{sw} = 0.0225 \) and \( \Delta \tilde{u}_n^{max} = 0.0285 \). For the ductile damage case, \( \Delta \tilde{u}_n^{sw} \) and \( \Delta \tilde{u}_n^{max} \) are chosen to be 0.008 and 0.08, respectively, keeping the fracture toughness of the cohesive zones for normal mode of separation constant at 3.2MPa. For the tangential traction separation law, \( \Delta \tilde{u}_n^{sw} \) is assumed to be equal to \( \Delta \tilde{u}_n^{sw} \) for all cases. Finally, typical estimates of nanocomposite effective gauge factors before \( \tilde{G}_{0}^{NC} \) and after \( \tilde{G}_{d}^{NC} \) damage initiation are chosen based on published work in the literature which are typically reported to be in between 1 and 20 [3, 4, 7, 8, 11–13].

### 7.1.4 Micromechanics Based Averaging for Effective Properties

The general relationship for a piezoresistive material relates the strain tensor to the relative change in resistivity, i.e. current strain resistivity minus unstrained resistivity \( \Delta \rho \) normalized by the unstrained resistivity \( \rho_0 \), as

\[
\frac{\Delta \rho_{(i)(j)}}{\rho_{0_{(i)(j)}}} = \Pi_{ijkl} \varepsilon_{kl}
\]  

(7.10)

In the current study, it will be assumed that the explosive crystals are not inherently piezoresistive, i.e. all components of the piezoresistive strain tensor are zero. However, due to the piezoresistive nanocomposite binder and local interfacial separation/damage, the effective macroscale material demonstrates an effective piezoresistive response, i.e. \( \Pi_{ijkl}^{Eff} \) has non-zero components. The changes in volume averaged resistivities needed to determine the
components of the piezoresistive strain tensor are obtained from the averaged representation of Ohm’s law which is expanded as

\[
\begin{align*}
\langle \hat{J}_1 \rangle &= \Sigma_{11}^{Eff} \langle \hat{E}_1 \rangle + \Sigma_{12}^{Eff} \langle \hat{E}_2 \rangle \\
\langle \hat{J}_2 \rangle &= \Sigma_{21}^{Eff} \langle \hat{E}_1 \rangle + \Sigma_{22}^{Eff} \langle \hat{E}_2 \rangle
\end{align*}
\]  

(7.11)

The components of the effective conductivity tensor are obtained by systematically allowing only one component of the applied electric field to be non-zero, e.g. when \( E_1 \) is non-zero, the conductivity components \( \Sigma_{11}^{Eff} \) and \( \Sigma_{21}^{Eff} \) are obtained from Eqn. 7.11. The effective conductivity components obtained are then used to evaluate the effective resistivity components.

The effective piezoresistive response is presented in terms of relative change in resistivity as a function of applied strain in accordance with Eqn. 7.10. For the experimentally obtained microstructure morphology inspired 31-grain RVE, the effective response is presented in terms of relative change in resistance to compare with the experiments. The effective resistance \( (R^{Eff}) \) at a given strain state is evaluated using the effective resistivity as

\[
R^{Eff}_{22}(\varepsilon) = \rho^{Eff}_{22}(\varepsilon) \frac{L^{RVE}}{A^{RVE}}
\]

(7.12)

where \( L^{RVE} \) is the length of the RVE in the direction of applied test electric field, i.e. \( x_2 \) direction, \( A^{RVE} \) is the area transverse to the applied test electric field which is given by the width of the RVE in the \( x_1 \) direction multiplied by the plane strain thickness for the problem.

In order to quantify interfacial damage in the nanoscale RVE, an averaged damage parameter \( (D_{avg}) \) is defined by averaging the local damage in each of the cohesive zone finite element node pairs which constitute the microscale grain boundary interface. The averaged damage parameter is mathematically expressed as

\[
D_{avg} = \frac{1}{\tilde{A}^I} \int_{\tilde{A}^I} D(\tilde{x})d\tilde{A}^I
\]

(7.13)

where \( \tilde{x} \) is any point lying along the interface, \( \tilde{A}^I \) is the total cohesive zone interface area
perpendicular to the direction of normal interface separation, i.e. cohesive zone differential width multiplied by the plane strain thickness, and \( D(\bar{x}) \) is the local damage parameter defined at interface location \( \bar{x} \). \( D(\bar{x}) \) is defined based on the bilinear mechanical cohesive zone law normal to the interface used in the current study as

\[
D(\bar{x}) = \begin{cases} 
1 & \Delta \bar{u}_n(\bar{x}) \leq \Delta \bar{u}^{sw}_n \\
1 - \left[ \frac{\Delta \bar{u}_n(\bar{x}) - \Delta \bar{u}^{sw}_n}{\Delta \bar{u}^{max}_n - \Delta \bar{u}^{sw}_n} \right] & \Delta \bar{u}^{sw}_n \leq \Delta \bar{u}_n(\bar{x}) \leq \Delta \bar{u}^{max}_n \\
0 & \Delta \bar{u}^{max}_n \leq \Delta \bar{u}_n(\bar{x}) 
\end{cases}
\] (7.14)

Integrating the damage state across the entire set of interfaces allows for representation of each cohesive zone in the averaged damage parameter, where every cohesive zone may possibly have a different state of damage depending on the local interface separation.

### 7.2 NCBX Piezoresistive Modeling Using Idealized 10-grain RVE

In order to evaluate the NCBX piezoresistive response, ad-hoc electromechanical cohesive laws are constructed based on known estimates of effective CNT-polymer nanocomposite electromechanical properties as shown in Tab. 7.1. Once the coupled electromechanical cohesive laws are defined from the nanocomposite effective properties, an idealized representative volume element (RVE) for the microscale grain boundary problem is constructed. For the current work, a 10-grain model of the microscale NCBX is constructed using Voronoi Tessellation as shown in the undeformed state in Fig. 7.4a. The grains are meshed using linear triangular finite elements such that the 17 cohesive zone edges have 187 initially coincident node pairs across the interface connected through the electromechanical cohesive laws developed. In addition, Fig. 7.4a shows the deformed mesh after application of 2% tensile strain in the \( x_2 \) direction (with a displacement magnification factor of 5) where the cohesive zones at the grain boundaries are observed to separate. In addition to the properties provided in Tab. 7.1, the Young’s modulus and resistivity of the explosive grains are fixed at 50
GPa and 0.1Ωm, respectively, for the demonstration case presented in Fig. 7.4. The effective nanocomposite gauge factors before ($\tilde{G}^{NC}_0$) and after ($\tilde{G}^{NC}_d$) the initiation of damage are chosen to be 2 and 4, respectively [20,133].

![Image of nanocomposite gauge factors](attachment:nanocomposite_gauge_factors.png)

The electromechanical boundary value problem is solved over the microscale RVE under plane strain assumptions assuming that the grain distribution is sufficiently random so as to result in an effective isotropic response. Local stress component ($\sigma_{22}$) contours and local current density component contours ($J_2$) for the 10-grain problem is shown in Fig. 7.4b in the unstrained state along with 1% and 2% applied tension. In the unstrained state, $\sigma_{22}$ is zero everywhere in the domain because of no applied deformation on the RVE and $J_2$ is uniform over the domain because the applied uniform test electric field in the $x_2$ direction results in uniform current density in absence of material inhomogeneities, i.e. cohesive zone separation. As the applied tensile strains are increased, the distribution of grain boundaries

---

**Figure 7.4:** a) A sample result from the current grain boundary cohesive zone exploration of NCBX showing the undeformed and deformed meshed with a displacement magnification factor of 5. b) Local stress and current density contours are presented at different applied strain states. c) The corresponding effective piezoresistive response and averaged damage index. [155]
leads to localized cohesive zone separation along the edges leading to redistribution of stress and current density pathways. On application of larger strains, some of the current density pathways get completely severed because of cohesive zone damage resulting in smaller current density across the interface. The evolution of the current density pathways in response to separating and damaging interfacial cohesive zones results in an effective piezoresistive response of the microscale RVE shown in Fig. 7.4c obtained using micromechanics based energy equivalence.

It is observed from Fig. 7.4c that the effective stress component \((\sigma_{22}^{Eff})\) increases linearly from zero on application of tensile strains up to an applied tensile strain of about 1.2%. It is to be noted that there is no damage accumulation at the interfaces in the entire RVE up to 1.2% applied strain which signifies that all of the cohesive zones are still in the initial linear elastic region of the normal traction-separation response. Thus, the initial stiffness of the effective microscale RVE is a function of the explosive crystal stiffness, the normal and tangential cohesive zone initial undamaged stiffnesses and the distribution of nanocomposite binder cohesive zone edges in the microscale RVE. The relative change in resistivity for this initial linear elastic region, in absence of cohesive zone damage, is dependent on the initial cohesive zone resistivity and the effective nanocomposite gauge factor before damage initiation, \(\tilde{G}_0^{NC}\). At an applied tensile strain of about 1.2%, a sharp reduction in \(\sigma_{22}^{Eff}\) is observed which can be closely correlated to a sudden increase in the amount of interfacial damage and relative change in effective resistivity \((\Delta \rho_{22}^{Eff} / \rho_{22}^0)\). This process is accompanied by a rearrangement of local stress contours and in local current density contours in the microscale RVE. For the current case, it is observed that the relative change in resistivity is about 8% in response to 2% applied strain with about 5% interfacial damage accumulation in the RVE. Thus, the result demonstrates that applied deformation induced separation and damage of the binding polymer nanocomposite medium in the microscale NCBX RVE leads to an effective piezoresistive response which can distinguish between the linear elastic region and the damage evolution regime. While the results presented in Fig. 7.4 demonstrate a coupled piezoresistive response in CNT-polymer nanocomposite bonded explosives for a chosen given set of properties. The properties of explosive grain crystals and CNT-polymer nanocomposites can vary over a large range depending on their type and microstructural morphology.
Thus, in order to explore the range of piezoresistive response in NCBX materials, parametric studies is conducted over these properties.

Figure 7.5: Comparison of a) averaged damage index, b) relative change in resistivity c) local displacement contours and d) local stress component contours for the NCBX 10-grain microscale RVE with different relative stiffness of grains and cohesive zones. Note that symbol $E_g$ and $E_{cz}$ are used for the elastic modulus and $S_g$ and $S_{cz}$ for the conductivity of the grains and cohesive zone interface, respectively. [155]

The first set of parametric study is conducted by varying the grain stiffness relative to the nanocomposite binder stiffness in order to explore the similarities and differences in cohesive zone separation behavior and associated piezoresistive response. In order to differentiate only between the relative stiffness based piezoresistive response, the resistivity of the explosive grains are set equal to the nanocomposite resistivity provided in Tab. 7.1. In addition, the effective nanocomposite gauge factors before ($\tilde{G}^{NC}_0$) and after ($\tilde{G}^{NC}_d$) the initiation of damage are chosen to be 2 and 4, respectively, for all of the cases. The results obtained from the parametric study are presented in Fig. 7.5. Fig. 7.5a shows the averaged damage index of the cohesive zones obtained using Eqn. 7.13 as a function of applied strain at different ratios of grain stiffness to initial cohesive zone stiffness. For cases where the grains are about the same stiffness as the nanocomposite binder, i.e grain to cohesive zone stiffness ($E_g/E_{cz}$) of 1 and 2, the applied deformation gets distributed between the grains and cohesive zones.
Figure 7.6: Comparison of a) averaged damage index and b) relative change in resistivity c) local electrostatic potential contours and d) local current density contours for the NCBX 10-grain microscale RVE with different relative conductivities of grains and cohesive zones. Note that symbol $E_g$ and $E_{cz}$ are used for the elastic modulus and $S_g$ and $S_{cz}$ for the conductivity of the grains and cohesive zone interface, respectively. [155] such that the interface separation between the grain interfaces is less than $\Delta \tilde{u}_{sw}$. Thus, the averaged damage index for the entire microscale RVE is 1, i.e. no damage accumulation at the interfaces. However, as the relative stiffness of the grains increases, interfacial damage accumulation is observed in the nanoscale RVE because the applied deformations predominantly result in separation of relatively more compliant interface. The local displacement component ($u_2$) contours for the $E_g/E_{cz}$ ratios of 1 and 25 are presented in Fig. 7.5c in both the unstrained and 2% applied strain states. It is observed that for the case with equal stiffnesses, there is insignificant separation in the cohesive zones as compared to the case with $E_g/E_{cz}$ ratio of 25 where the grains act like nearly rigid bodies with minor deformation as the interfacial cohesive zones undergo significantly large normal separation. Fig. 7.5d presents the corresponding local stress component ($\sigma_{22}$) contours. Following from the local displacement and stress component contours, at 2% applied strain, the averaged damage index is observed to be 0.94, 0.92 and 0.90 for cases with $E_g/E_{cz}$ ratio of 5, 10 and 25, respectively, i.e. about 6%, 8% and 10% damage accumulation. The effective piezoresistive
response of NCBX is presented in Fig. 7.5b in terms of relative change in resistivity with applied strain. It is observed that increasing the relative grain stiffness leads to a larger piezoresistive response. For example, the relative change in resistivity at 2% applied strain is observed to be close to zero for the cases with $E_g/E_{cz}$ ratios of 1 and 2 because of small cohesive zone separations. However, the relative change in resistivity is observed to be 0.081, 0.087 and 0.093 for cases where $E_g/E_{cz}$ ratio is 5, 10 and 25, respectively, at 2% applied strain.

Figure 7.7: Comparison of a) averaged damage index and b) relative change in resistivity for the NCBX 10-grain microscale RVE with different effective nanocomposite binder gauge factors before ($\tilde{G}^{NC}_0$) and after ($\tilde{G}^{NC}_d$) the initiation of damage. [155]

In addition to studying the effect of relative stiffness on the effective NCBX piezoresistive response, test cases were designed to explore the effect of relative difference in initial grain conductivity and cohesive zone conductivity. For these test cases, the ratio of grain to cohesive zone stiffness ($E_g/E_{cz}$) is fixed at 5 such that the applied deformations lead to an appreciable amount of interface separation in the microscale RVE. The effective nanocomposite gauge factors before ($\tilde{G}^{NC}_0$) and after ($\tilde{G}^{NC}_d$) the initiation of damage are chosen to be 2 and 4, respectively. Fig. 7.6a shows that the averaged damage index for all of these cases follow a similar behavior because the mechanical BVP for all of these cases has the same geometry and mechanical properties. About 6% damage accumulation is observed in the microscale RVEs at 2% applied strain for each of these cases. The effective piezoresistive response for the microscale RVE is presented in Fig. 7.6a in terms of relative change in resistivity for different cases of relative grain conductivity ($S_g/S_{cz}$) as a function of ap-
plied strain. It is observed that the case with the largest relative grain conductivity, i.e. 25 times the cohesive zone conductivity, exhibits the largest effective piezoresistive response. For example, the case with the $S_g/S_{cz}$ of 25 leads to a relative change in resistivity of 0.43 on application of 2% strain. In contrast, the case with $S_g/S_{cz}$ of 0.1 undergoes a relative change in resistivity of 0.01 on application of 2% strain. The reason for such behavior can be observed from the local electrostatic potential and local current density contours presented in Fig. 7.6c and Fig. 7.6d, respectively, in the undeformed state and at 2% applied strain. It is observed from Fig. 7.6c,d that the local electrostatic potential and current density do not undergo significant redistribution for the case with $S_g/S_{cz}$ of 0.1 even when the grain boundary gets separated by a significant amount due to interfacial damage. For this case, the interface is more conductive, hence, it acts like a conductive medium and allows insignificant hindrance to the current density pathways connecting across the interface. However, as the grains become more conductive, the cohesive zone interface acts as the barrier for current density whereas the grains act predominantly as a conductive medium. Thus, a significant amount of redistribution is observed in the local electrostatic potential and current density as the interfaces separate and accumulate damage. For non-conductive grains (e.g. sugar crystals), however, tangential current density in the binder medium (or explicit polymer binder modeling instead of cohesive interface) may lead to current density pathways through the binder without going through the grains significantly. In the current work such tangential current density pathways which allow for current density only through the binder are not captured in absence of tangential electrostatic cohesive zones and explicit polymer binder modeling.

The piezoresistive response of the nanocomposite binder depends on the microstructural morphology of CNTs within the polymer matrix. A range of gauge factors between 1 and 20 [3, 4, 7, 8, 11–13] are typically reported in the literature for CNT-polymer nanocomposites. Hence, a parametric study is conducted in the current work by varying the effective nanocomposite gauge factors before ($\tilde{G}^0_{NC}$) and after ($\tilde{G}^d_{NC}$) the initiation of damage, keeping the relative grain stiffness at 5 times the cohesive zone stiffness and the relative grain conductivity equal to the cohesive zone. The mechanical BVP for all of these cases is the same, hence, all of the cases undergo same amount of interfacial damage accumulation with
applied strain as shown in Fig. 7.7a. About 6% interfacial damage accumulation is observed for all of these cases at 2% applied strain.

The effective piezoresistive response is presented in Fig. 7.7b, where the case with largest nanocomposite binder gauge factors before ($\tilde{G}_{0}^{NC}$) and after ($\tilde{G}_{d}^{NC}$) the initiation of damage exhibits the largest piezoresistive response. For the case with zero gauge factors before ($\tilde{G}_{0}^{NC}$) and after ($\tilde{G}_{d}^{NC}$) the initiation of damage, the effective piezoresistive response is purely governed by the separation and damage of microscale interfaces resulting in a relative change in resistivity of 0.04 at 2% applied strain. In contrast, for the case with $\tilde{G}_{0}^{NC}=5$ and $\tilde{G}_{d}^{NC}=10$, the effective piezoresistive response additionally depends on the piezoresistive response of the local cohesive zone binder resulting in a relative change in resistivity of 0.12 at 2% applied strain. This observation is tied to the interfacial resistance relation with normal interface separation shown in Eqn. 7.4 which specifies that larger gauge factors result in larger change in interfacial resistance.

7.3 NCBX Piezoresistive Modeling Using 31-grain Microstructure Morphology Inspired RVE

In addition to the 10-grain RVE, the experimental microstructure inspired 31-strain RVE, as shown in Fig. 7.1, is subjected to a parametric study to understand the effect of CNT-polymer nanocomposite binder morphology on the effective NCBX piezoresistive response. For the 31-grain RVE, the material properties of the grains are assumed to be constant corresponding to the HMX crystals [101,156] while micromechanics based estimates of effective nanocomposite electromechanical properties (Tab. 7.2) are used to construct the cohesive normal and tangential traction-separation and normal resistance-separation curves. Computational model parameters explored parametrically include the 1) effect of ductile versus brittle interfacial damage response at different damage rates, 2) effect of CNT alignment at the interface i.e. normal to the interface, tangential to the interface or randomly aligned, 3) effect of local CNT volume fraction within the nanocomposite, 4) effect of nanocomposite
piezoresistivity.

The mechanical response of the microscale RVE is presented first, as shown in Fig. 7.8. Fig. 7.8a shows the effective stress in the microscale RVE as a function of applied strain for different types of applied strains. As an example, the effective stress-strain response when the deformation is applied in the $x_1$ direction is represented as $(\sigma_{11}^{Eff}, \varepsilon_{11}^{App})$. Fig. 7.8b shows the corresponding average damage index for each of the cases shown in Fig. 7.8a. It is observed from Fig. 7.8a that initial stiffness for applied axial deformations in the $x_1$ and $x_2$ directions ($C_{11}^{Eff}$ and $C_{22}^{Eff}$, respectively) is around 10.1GPa. The initial stiffness ($C_{44}^{Eff}$) for the cases with applied positive and negative shear strains is observed to be 6.47GPa, i.e. around 36% smaller than the axial stiffnesses. The reason for the observed difference in the initial stiffness lies in the local deformation of the cohesive zones. For the axial deformation cases, the interface separation of the cohesive interfaces is predominantly normal to the interface in the direction of applied deformation. For applied shear strains, the interface separation is predominantly tangential, i.e. more compliant as shown in Tab. 7.2.

Along with the initial stiffnesses, the peak stress component along the applied deformation is observed to be similar for the cases with applied axial deformation in the $x_1$ and $x_2$ directions i.e. around 200MPa. The strain to failure, however, is observed to be much larger when the
deformations are applied in the $x_2$ direction ($\sim 4\%$) as compared to the case with applied axial deformation in the $x_1$ direction ($\sim 2.5\%$). For the cases with applied shear deformation, the peak shear stress is much smaller than the axial deformation cases at around 100GPa, with a strain to failure close to 2\%. In the current work, strain to failure is defined as the applied deformation at which the stiffness or conductivity matrices become ill-conditioned due to progressive damage. The averaged damage index is observed to be at an initial value of 1 which signifies that none of the cohesive zones are damaged in the nanoscale RVE. After about 1\% applied strain, all of the applied deformation cases start to undergo interfacial cohesive zone damage. It is observed that the at about 2\% applied strain, around 10\% damage is accumulated in the cohesive zones for all deformation cases. However, the final failure occurs at different strain states and at different values of the damage index with the axial deformation in the $x_2$ direction accumulating the largest amount of interfacial cohesive zone damage (around 25\%) before final failure.

Figure 7.9: The local current density component ($J_1$) in the $x_1$ direction shown in a) unstrained state and at strain to failure for b) axial tension in $x_1$ direction c) axial tension in $x_2$ direction d) positive in-plane shear and e) d) negative in-plane shear, shown over the deformed configuration of the microscale RVE. [155]

In addition to exploring the mechanical response of NCBX material, the effective electrostatic properties of the microscale RVE are investigated by applying electrostatic boundary conditions corresponding to uniform applied electric fields in the $x_1$ and $x_2$ directions, independently, for each of the deformation modes. Using the averaged representation of Ohm’s
law, shown in 7.11, the effective conductivity components $\Sigma_{11}^{Eff}$ and $\Sigma_{22}^{Eff}$ are evaluated for each boundary value problem. The local current density contours in the $x_1$ and $x_2$ directions is shown in Fig. 7.9 and Fig. 7.10, respectively, in the unstrained state and at strain to failure.

In addition to the local current density contours, Fig. 7.9 and Fig. 7.10 present the deformed configuration for each of the applied deformation types. As an example, Fig. 7.9a shows the microscale RVE in the undeformed state and Fig. 7.9b-e present the microscale RVE at strain to failure for the uniaxial tension in the $x_1$ and $x_2$ and positive and negative in-plane shear deformations. It is observed that for the tensile deformation cases, the interfacial cohesive zones separate predominantly in the direction of applied deformation leading to microcracks running predominantly along interface edges normal to the applied deformations. For the applied shear strains, a few interfaces are observed to separate with microcracks running predominantly along edges at $\pm 45^\circ$ to the $x_1$ direction.

Figure 7.10: The local current density component ($J_2$) in the $x_2$ direction shown in a) unstrained state and at strain to failure for b) axial tension in $x_1$ direction c) axial tension in $x_2$ direction d) positive in-plane shear and e) d) negative in-plane shear, shown over the deformed configuration of the microscale RVE. [155]

It is observed from Fig. 7.9 and Fig. 7.10 that for the uniaxial tensile deformation modes, the evolving interfacial separation and damage disrupts the local flow of current density in the microscale RVE leading to complex rearrangement of the current carrying pathways. In general, the case with applied axial strain in the $x_2$ direction leads to largest rearrangement in local current density pathways since it undergoes a larger amount of interfacial damage.
The applied in-plane shear deformation cases lead to smaller disruption and rearrangements in the current density pathways indicating a smaller change in electrostatic properties.

The local current density contours are used to construct volume averages of the current density and electric field to evaluate the effective conductivity components at each of the applied strain states for different deformation modes. The evolution of the effective conductivity components as a function of applied strain for each of the deformation modes is presented in Fig. 7.11. It is observed that the microscale RVE is initially isotropic with equal values of conductivity components $\Sigma_{11}^{\text{Eff}}$ and $\Sigma_{22}^{\text{Eff}}$ for each deformation mode. However, as the cohesive interfaces start to separate, the effective conductivity components start to decrease from their unstrained state value of 1000 S/m. At 1% applied strain, the effective conductivity component $\Sigma_{11}^{\text{Eff}}$ is observed to be about 20%, 12%, 6% and 5% smaller for the axial tension in $x_1$ and $x_2$ directions, positive shear and negative shear deformation, respectively. Similarly, at 1% applied strain, the effective conductivity component $\Sigma_{22}^{\text{Eff}}$ is observed to be about 16%, 25%, 6% and 7% smaller for the axial tension in $x_1$ and $x_2$ directions, positive shear and negative shear deformation, respectively. The effective conductivity components undergo a larger amount of reduction in effective conductivity from their unstrained state for the applied axial tension cases as compared to the shear deformation cases following from the larger disruption and rearrangement of current density contours. Additionally, a larger change in effective conductivity components is observed for cases where the applied electric field and applied deformation are in the same direction, e.g. $\Sigma_{11}^{\text{Eff}}$ undergoes largest change with the axial tension in $x_1$ direction and $\Sigma_{22}^{\text{Eff}}$ undergoes largest change with the axial tension in $x_2$ direction.

In order to quantify the piezoresistive response of the microscale RVE, the evolution of effective conductivity components with applied deformation is further converted to the relative change in resistivity components ($\Delta \rho_{11}^{\text{Eff}}/\rho_{11}^{0}$ and $\Delta \rho_{22}^{\text{Eff}}/\rho_{22}^{0}$) with applied deformations. It is to be noted that the piezoresistive strain tensor coefficients ($\Pi_{ijkl}^{\text{Eff}}$) can be directly evaluated form the variation of $\Delta \rho_{11}^{\text{Eff}}/\rho_{11}^{0}$ and $\Delta \rho_{22}^{\text{Eff}}/\rho_{22}^{0}$ with applied strain as shown in Fig. 7.12. The evolution of relative change in resistivity components follows from the evolution of effective conductivity such that a large piezoresistive response is obtained for cases...
where the applied electric field and applied deformation are in the same direction. As an example, for the case where axial tension is applied in the $x_2$ direction leads to around 400% change in resistivity at about 4% applied strain. Similarly, the applied shear deformation lead to smaller piezoresistive response with the relative change in resistivity under 50% for each case.

At 1% applied strain state, the piezoresistive strain tensor components $\Pi^{Eff}_{1111}$ and $\Pi^{Eff}_{2211}$ components are evaluated using the relative change in resistivity components with applied axial deformation in the $x_1$ direction to be 25.9 and 19.6, respectively. A larger value of $\Pi^{Eff}_{1111}$ over $\Pi^{Eff}_{2211}$ indicates that an applied strain in the $x_1$ direction leads to a larger change in the $\Sigma^{Eff}_{11}$ conductivity component, where positive sign is reserved for decrease in conductivity with applied strain for the current work. Similarly, at 1% applied strain state, the piezoresistive strain tensor components $\Pi^{Eff}_{1122}$ and $\Pi^{Eff}_{2222}$ are observed to be 14.6 and 33.3, respectively. The piezoresistive strain components $\Pi^{Eff}_{1112}$ and $\Pi^{Eff}_{2212}$ for 1% positive applied shear strain are observed to be 6.4 and 7.1, respectively, much smaller than the coefficients corresponding to applied deformations in the axial directions. Similarly, the piezoresistive strain components $\Pi^{Eff}_{1112}$ and $\Pi^{Eff}_{2212}$ for 1% negative applied shear strain are observed to be 4.8 and 8.0, respectively. The variation in the effective piezoresistive strain tensor coefficients
indicates that the effective piezoresistive response of the microscale RVE is largely driven by the type of applied deformation and the magnitude of applied strain.

In order to study the effect of different types of damage, i.e. ductile vs. brittle, electromechanical cohesive laws are constructed for 0.15% wt random CNT alignment at the interface with the gauge factors before ($\tilde{G}^{NC}_0$) and after ($\tilde{G}^{NC}_d$) the initiation of damage to be 2 and 4, respectively. The effective initial undamaged electromechanical properties $C^{Eff}_{22}$, $C^{Eff}_{44}$ and $\Sigma^{Eff}_{22}$ for the nanocomposite are presented in Tab. 7.2 and are used as estimates for the random alignment case, are used as estimates of initial slopes of the normal and tangential traction-separation and the normal resistance-separation laws respectively. Finally, the brittle and ductile damage cases are approximated by specifying $\Delta\tilde{u}^{sw}_{n}=0.0225$, $\Delta\tilde{u}^{max}_{n}=0.0285$ and $\Delta\tilde{u}^{sw}_{n}=0.008$, $\Delta\tilde{u}^{max}_{n}=0.08$, respectively, keeping the separation energy (i.e. fracture toughness) constant as described in Sec. 7.1.3. The comparison of the brittle vs ductile response is presented in Fig. 7.13 in terms of the effective stress-strain behavior (Fig. 7.13a) and relative change in effective resistance (Fig. 7.13b) where the resistance of the RVE is calculated using Eqn 7.12. In addition, local stress and current density contours are provided in the direction of applied strains/test electric fields, i.e. $x_2$ direction, in Fig. 7.13c,d.
Figure 7.13: Comparison of ductile and brittle interfacial damage on the effective piezoresistive response with 0.15% wt random CNT alignment at the interface with the gauge factors before ($G^{NC}_0$) and after ($G^{NC}_d$) the initiation of damage to be 2 and 4, respectively. a) Effective stress-strain response along with the evolution of averaged damage index, b) Relative change in effective resistance along with the effective stress-strain response for comparison, c) the local stress component ($\sigma_{22}$) contours in the 31-grain RVE for the ductile and brittle damage cases in the unstrained state, at 1% and 2% applied tensile strain, and d) local current density contours show a difference in the evolution of current density ($J_2$) carrying pathways for the two cases in the unstrained state, at 1% and 2% applied tensile strain. [155]

The effective stress-strain response for the ductile and brittle damage cases presented in Fig. 7.13a undergoes an initial linear increase in effective stress for both the ductile and brittle damage cases while the local cohesive interface follows a linear elastic response everywhere in the RVE. At about 0.5% applied tensile strain, the ductile damage case starts to deviate from the linear elastic behavior because of initiation of local damage and reduction in local stiffness in some of the cohesive zones as indicated by the averaged damage index which starts to decrease from its initial value of 1. The local strain associated with damage initiation of the nanocomposite binder interface is much smaller for the ductile cohesive zones ($\Delta \tilde{u}_{sw} = 0.008$) as compared to the brittle cohesive zones ($\Delta \tilde{u}_{sw} = 0.0225$) which leads to a faster damage
initiation in the local cohesive zones. Similarly, the effective stress-strain response for the brittle case deviates from the linear elastic behavior at about 1% strain along with a reduction in the corresponding averaged damage index. Once damage initiates in the local cohesive zones, the effective stress-strain response for the ductile and brittle damage cases evolves with significantly different effective stress states for a given applied strain state. For example, at 2% applied strain state, the effective stress for the brittle and ductile damage cases is observed to be 36MPa and 135MPa, respectively, with about 20% damage accumulation for both cases. The differences observed in the effective stress at a given strain state can also be observed in Fig. 7.13c which shows the local stress component ($\sigma_{22}$) contours in the 31-grain RVE for the ductile and brittle damage cases in the unstrained state and at 1% and 2% applied tensile strain. It is observed that the local interface separation and damage paths are slightly different for the two cases because of differences in local interface damage behaviors. In addition, at 2% applied strain state, the stress carrying columns for the ductile case are weaker as compared to the brittle damage case leading to the observed difference in effective stress. It is noted that the effective stress-strain response for the brittle damage case follows a more ductile behavior because of while the local damage is brittle the effective response is dependent on collective behavior of grains and interfaces.

It is worth noting that the relative change in effective resistance for the ductile and brittle cases, shown in Fig. 7.13b, starts to increase from zero (in the unstrained state) much before an observed deviation from the linear elastic mechanical behavior. It is observed that the deviation the relative change in resistance starts to capture the local interfacial damage faster than the stress-strain response, especially for the brittle damage case, where the stress-strain response is linear up to 1% applied strain whereas the relative change in resistance starts to increase significantly at around 0.5% applied strain. The rate of increase of relative change in effective resistance is observed to be sensitive to the initiation and evolution of damage in the local cohesive zones such that the ductile case has a larger change in resistance at an applied strain of 1% because of larger damage accumulation. At 1% applied strain, while the brittle damage case undergoes about 7.4% increase in resistance, the ductile damage case undergoes about 37% increase with about 12% and 3% averaged interfacial damage for the ductile and brittle damage cases, respectively. Fig. 7.13d shows the local current density
contours demonstrate a difference in the evolution of current density ($J_2$) carrying pathways for the two cases in the unstrained state and at 1% and 2% applied tensile strain.

The ductile damage case was further studied by changing the local orientation of the CNTs in the nanocomposite binder interface at a volume fraction of 0.15% wt and with the gauge factors before ($\tilde{G}_{0}^{NC}$) and after ($\tilde{G}_{d}^{NC}$) the initiation of damage to be 2 and 4, respectively. Three different local orientation cases are considered in the current work i.e. randomly oriented, aligned normal to the interface and aligned tangential/parallel to the interface. The local orientation distribution of CNTs leads to differences in effective undamaged nanocomposite electromechanical properties used to construct the cohesive laws. These effective electromechanical properties are obtained using the micromechanics based Mori-Tanaka method as illustrated in Sec. 7.1.3 with properties for the aligned and randomly oriented CNTs are listed in Tab. 7.2. The aligned (normal to interface) properties are transformed by replacing $C_{22}^{Eff}$, $C_{44}^{Eff}$ and $\Sigma_{22}^{Eff}$ by $C_{33}^{Eff}$, $C_{55}^{Eff}$ and $\Sigma_{33}^{Eff}$, respectively, to identify the electromechanical properties for the transverse alignment case.

The effective stress-strain response for the three alignment cases is shown in Fig. 7.14 along with the evolution of averaged damage index. The initial linear elastic stiffness for the three cases is observed to be different as the local interfaces have different initial stiffness such that
the aligned case has the largest stiffness (9.39GPa), followed by the random case (8.06GPa) and transverse alignment case (7.39GPa). As such, the effective composite stiffnesses for the aligned, random and transverse cases are observed to be 18.0GPa, 17.1GPa and 16.5GPa, respectively, i.e. largest for larger degree of alignment normal to the interface. Following from the initial stiffness, the peak stress is largest for the aligned case and is observed to be around 1% applied strain for each of the three cases. The averaged damage index is observed to follow a similar evolution for the three cases with about 22% damage observed at 2.3% applied strain.

The relative change in effective resistance for the three alignment cases is presented in Fig. 7.14b. A larger difference is observed in the relative change in resistance with applied strain for the three cases in comparison to the corresponding stress-strain response because while the different orientations cause a slight differences in the effective undamaged interface stiffnesses, they lead to a much larger difference in undamaged effective conductivities, as observed from Tab. 7.2. The unstrained interface conductivity is larger with a larger degree of alignment normal to the interface i.e. the aligned case (142.97S/m) is most conductive followed by random (61.16S/m) and transverse (1.68S/m) cases. However, the small undamaged conductivity for the transverse case leads to a larger relative difference between the grain (1000S/m) and interface conductivities. In addition, the more compliant transverse alignment (in comparison to the grains) leads to larger interface separation. Thus, following from the discussion of Fig. 7.6 in Sec. 7.2, the largest change in effective resistance is observed for the transverse alignment case followed by the random and aligned cases. For example, at 2.3% applied strain, the relative change in resistance is observed to be 244%, 435% and 566% for the aligned, random and transverse cases, respectively. The results indicate that while a larger degree of alignment normal to the interface may improve the mechanical stiffness if the material, transverse alignment leads to a larger piezoresistive response for strain and damage sensing.

The random local CNT orientation case with ductile damage was further studied with different weight concentrations (volume fractions) of CNTs in the nanocomposite binder having the gauge factors before \((\tilde{G}_0^{NC})\) and after \((\tilde{G}_d^{NC})\) the initiation of damage to be 2 and 4,
respectively. The effective undamaged electromechanical properties for each weight concentration, i.e. 0.5%, 1% and 2%, are listed in Tab. 7.2 along with the corresponding volume fractions. The effective stress-strain response for the three cases is shown in Fig. 7.15a along with the corresponding evolution of averaged damage index. The effective unstrained interface stiffness is larger for larger weight concentration of CNTs in the nanocomposite resulting in a larger initial effective composite stiffness for the 0.6%wt case. The evolution of stress-strain curve follows a similar behavior for the three cases with larger observed stresses in the 0.6%wt case for a given strain state followed by 0.3%wt and 0.15%wt. The averaged damage index starts to deviate from its initial value of 1 around 0.5% strain and about 22% average damage is observed at 2.3% applied strain for all three cases.

![Figure 7.15](image)

Figure 7.15: Effect of local weight concentration of the randomly oriented CNTs in the nanocomposite binder interface undergoing ductile damage with the gauge factors before ($\tilde{G}_{0}^{NC}$) and after ($\tilde{G}_{d}^{NC}$) the initiation of damage to be 2 and 4, respectively. a) Effective stress-strain response along with the evolution of averaged damage index, b) Relative change in effective resistance along with the effective stress-strain response for comparison. [155]

The corresponding relative change in resistance for the three cases with different weight concentrations are shown in Fig. 7.15b. The local conductivity of the unstrained interface obtained from Mori-Tanaka methods is smallest for the 0.15%wt (61.16S/m, 0.5%wt relative to epoxy) case followed by 0.3%wt (93.68S/m, 1%wt relative to epoxy) and 0.6%wt (127.62S/m, 2%wt relative to epoxy) cases. The 0.15%wt case undergoes the largest change in effective resistance with applied strains because the relative difference between the grain (1000S/m) and interface conductivities is highest for this case. At 2.3% applied strain, a 435%, 300% 250% increase in resistance is observed for the 0.15%wt, 0.3%wt and 0.6%wt,
respectively. Thus, a larger weight concentration of CNTs leads to a larger initial effective stiffness, but a smaller weight concentration may produce a larger effective piezoresistive response for NCBX materials.

In the discussion so far, the gauge factors before and after the initiation of damage have been chosen to be 2 and 4, respectively, based on some typical values in the literature. These values were kept constant even when the orientation and volume fraction of CNTs was varied to explore the difference in response by varying one set of microstructural features/response. However, a typical nanocomposite will exhibit different effective piezoresistive response as the volume fractions and orientations of CNTs is changed. In particular, the effective piezoresistive response of nanocomposite with transverse alignment of CNTs has been observed to be more piezoresistive than the random and aligned cases [22,133]. Thus, the transverse case for 0.15%wt with ductile damage is further studied by increasing \((\tilde{G}^{NC}_0, \tilde{G}^{NC}_d)\) from (2,4) to (5,10) and (20,40) along with a baseline case with no nanocomposite piezoresistivity (0,0), i.e. the purely geometric and damage dependent case. The effective stress-strain response, shown in Fig. 7.16a, is observed to be the same for all of these cases as the mechanical problem has the same properties. Local interfacial damage is observed to initiate at about 0.5% applied strain with approximately 22% average interfacial damage observed at 2.3% applied strain.

Figure 7.16: Effect of nanocomposite binder gauge factors before \((\tilde{G}^{NC}_0)\) and after \((\tilde{G}^{NC}_d)\) the initiation of damage for 0.15%wt transversely oriented CNTs in the nanocomposite binder interface undergoing ductile damage. a) Effective stress-strain response along with the evolution of averaged damage index, b) Relative change in effective resistance along with the effective stress-strain response for comparison. [155]
The relative change in effective resistance increases as the nanocomposite effective gauge factors are increased as shown in Fig. 7.16b. At 1% applied strain, the relative in resistance is observed to be 1.83%, 2.46% and 6.06% larger for the (2,4), (5,10) and (20,40) cases, respectively, as compared to the baseline (0,0) case. The observed increase in resistance, however, is much smaller than that observed for the 10-grain RVE presented in Fig. 7.7b. For the 10-grain RVE, there were only 2 grains \((x_1)\) across the width of the sample. A change in local interface resistance was reflected better in the effective response. For the 31-grain RVE there are several additional pathways that the current density can travel through. Thus, the effect of local interface piezoresistive response does not lead to as large a change in effective piezoresistive response. It is to be noted that at about 1% applied strain, the relative change in resistance is observed to decrease slightly because local damage of the cohesive zone leads to rearrangement of current carrying pathways through the 31-grain RVE.

Figure 7.17: Comparison of damage rate going from ductile to brittle interfacial damage (with constant fracture toughness) on the effective piezoresistive response with 0.15% wt (relative to epoxy) random CNT alignment at the interface with the gauge factors before \(\tilde{G}_{NC}^0\) and after \(\tilde{G}_{NC}^d\) the initiation of damage to be 2 and 4, respectively. a) Effective stress-strain response along with the evolution of averaged damage index, b) Relative change in effective resistance along with the effective stress-strain response for comparison. [155]

Finally, the surface treatment of the grains during processing could be affected the interfacial separation and damage between the grains and the polymer interface similar to how functionalized CNT interfaces lead to different interfacial response in CNT-polymer nanocomposites [158]. Thus, a damage rate comparison is presented in Fig. 7.17 with three other interfacial damage rates in addition to the ductile and brittle damage discussed earlier. The
separation energy for each of these cases is kept constant equal to the polymer fracture toughness (3.2MPa) assuming that the CNTs do not change it significantly. For each of these cases, the interface nanocomposite binder has the 0.15%wt randomly oriented CNTs with an undamaged and damaged effective gauge factors of 2 and 4, respectively. The effective stress-strain response for each of these cases is presented in Fig. 7.17a along with the evolution of averaged damage index. It is observed that the cases with faster damage initiation deviate from the initial linear elastic response and the corresponding averaged damage index deviates faster from the initial value of 1 at smaller applied strain, i.e. going from more ductile to more brittle like damage. The evolution of damage index does not necessarily follow the order for all strain states because of localized rearrangements in microstructure as damage develops at the local interfaces as was similarly illustrated in the discussion for Fig. 7.13 where a comparison of brittle vs. ductile damage was presented. The evolution of relative change in resistance follows from the evolution of averaged damage index such that faster damage initiation leads to larger relative change in resistance, in general. However, some deviations from this trend are observed at different states of applied strain which can be closely correlated to the evolution of averaged damage index. In conclusion, while the more brittle like damage leads to larger values of peak stress, the effective piezoresistive response of ductile damage cases capture the effect of local interfacial damage better.

7.4 Comparison of Computational Modeling and Experimental Investigation

While the experimentally observed [155] and computationally obtained effective behavior is similar in terms of regions of deviation from linear elastic response with damage progression and larger damage sensitivity of the relative change in resistivity, some differences between the two are observed such as 1) smaller experimentally obtained NCBX initial stiffness 2) smaller peak stresses observed experimentally, and 3) smaller relative change in resistivity observed experimentally for a given strain state and weight concentration of CNTs. For example, the peak stress observed in the experimental results [155] was between 3 and 5
MPa, whereas those computationally obtained from the 31-grain RVE were observed to be between 75 and 150 MPa (Sec. 7.1). Similarly, the experimentally observed relative change in resistance was observed to be typically smaller than 1 at 2% applied strain in comparison to the computationally obtained range between 2 and 6 for 2% strain for the 31-grain RVE. Some of these differences could possibly be reduced by lifting some of the modeling idealizations which include 1) allowing for tangential current density through the interface, 2) modeling of the polymer binder region explicitly and 3) more accurate microstructure characterization of the CNT-polymer nanocomposite to build RVEs for the nanocomposite interface. On the other hand, there remains a large degree of uncertainty regarding the identification of accurate material properties for NCBX under the processing conditions employed in preparing the surrogate samples [155], such as uncertainty regarding 1) degree of uncured matrix pockets due to constrained curing of the polymer matrix, 2) voids in nanocomposite binder which may require degassing, and 3) interfacial bonding strength between the polymer nanocomposite and sugar crystals. Thus, in order to explore possible reasons for these differences in further detail, the model inputs are treated as tunable parameters in an effort to better reproduce experimental results using the 31-grain RVE.

In tuning the material properties, some of the properties were fixed initially, e.g. the mechanical properties of the grains were fixed at the properties obtained for HMX from the literature as indicated in Sec. 7.1.3. The remaining model input parameters were varied. For example, the electrostatic conductivity of the grains was reduced from the nominal value of 1000S/m estimated for HMX grains (as indicated in Sec 7.1.3) as the sugar particles are believed to be less conductive. In absence of estimates of sugar grain conductivity a smaller grain conductivity of 1E-3S/m is used herein. The mechanical properties of the effective nanocomposite binder were reduced significantly to reduce the large initial stiffness and the peak stress obtained from the computational model. The nanocomposite axial stiffness was chosen to be 0.3GPa in comparison to ~10GPa used earlier for the 31-grain model, while the shear modulus was chosen to be 0.15GPa. The conductivity of the nanocomposite binder medium was fixed at the derived value (61.16 S/m) for the case where randomly aligned 0.5% weight concentrations of CNTs were used. A ductile mode of damage was assumed
with rates of damage adjusted such that a $\Delta \tilde{u}_{sw}^{n}$ of 0.007 and a $\Delta \tilde{u}_{max}^{n}$ of 0.013 was used in order to match the applied strain at which the peak stress would occur. The choice of initial stiffness and damage rates significantly reduces the fracture toughness of the interface from 3.2MPa to 0.0136MPa. Finally, the bilinear electrostatic cohesive law damage rate parameter ($\gamma$) was reduced from its nominal value of 10 to 2, while the nanocomposite binder gauge factors before and after the initiation of damage were fixed at their nominal value of 2 and 4.

![Figure 7.18: Comparison of the stress-strain and relative change in resistance response with applied strain obtained from the experimental investigation (0.3%wt) and the calibrated 31-grain computational model. [155]](image)

Figure 7.18: Comparison of the stress-strain and relative change in resistance response with applied strain obtained from the experimental investigation (0.3%wt) and the calibrated 31-grain computational model. [155]

The effective stress-strain and relative change in resistance generated after calibrating the model are shown in Fig. 7.18 along with the experimentally obtained results for the 0.3%wt MWNT concentration results. An initial stiffness of 1.46GPa is obtained from the model, which is significantly smaller than the initial stiffnesses for cases presented in Sec 7.3 before calibration, as compared to 2.59GPa obtained experimentally. A peak stress of 3.8MPa was obtained computationally which compares well to the 3.80MPa obtained experimentally. The relative change in resistance obtained computationally undergoes and initial linear increase, however the rate of increase is much smaller for the model as compared to the experiment. The relative change in resistance at a strain state of 1.1%, however, is close to 0.5 for both cases. Overall, while exact replication of the experimental results is difficult given the complex interdependence of the effective response on the material properties as illustrated
in Sec 7.3, the calibrated model is much closer to the experimentally observed behavior. Some key conclusions which can be made based on this calibration exercise include 1) the interface stiffness and fracture toughness of the nanocomposite binder is significantly smaller as compared to estimated values indicating weak interfacial bonding between the polymer and grains and/or initial voids/cracks in the polymer binder, and 2) the sugar grains are non-conductive which does not compare well with estimates of HMX conductivity indicating that while sugar grains may be a good mechanical surrogate for HMX, they may be less suitable as a surrogate electrically.
Chapter 8

Interfacial Modeling in Material Point Method

The computational modeling of nanocomposites presented so far has been based on the finite element framework where modeling of large displacement problems with local damage could result in mesh distortion, entanglement and singular matrices. The Material Point method allows for large deformation of materials using and Eulerian-Lagrangian solution scheme presented in Chapter 2. Figure 8.1 shows the solution for the mechanical plane strain uniform tension BVP using MPM for the hexagonal nanoscale RVE introduced in Chapter 3. Figure 8.1a, 8.1b and 8.1c show the local contours of displacement, strain and stress components, respectively, in the $x_2$ direction for the nanoscale RVE when subjected to 50% applied tension.

Contours of electron hopping modified local conductivity are presented in Fig. 8.2. Figure 8.2a shows the local conductivity component ($\Sigma_{22}$) for the hexagonal RVE in the unstrained state as discussed in Chapter 3 and Fig. 8.2b shows the local conductivity component when subjected to 50% applied tension in the $x_2$ direction.

Finally, Fig. 8.3 shows the solution for the electrostatic BVP for the nanoscale RVE with electron hopping at 50% applied tension in the $x_2$ direction. The local contours of electrostatic potential, electric field and current density components in the $x_2$ direction are presented in
Figure 8.1: The solution for the mechanical plane-strain constrained tension BVP for the hexagonal RVE subjected to 50% applied tension using MPM showing local contours of a) displacement component $u_2$, b) strain component $\varepsilon_{22}$ and c) stress component $\sigma_{22}$.

Figure 8.2: The contours of local conductivity for the hexagonal RVE with conductive pathways based on electron hopping a) in the unstrained state and b) at 50% applied tension.
Fig. 8.3a, 8.3b and 8.3c, respectively.

Figure 8.3: The solution for the electrostatic plane-strain constrained tension BVP for the hexagonal RVE subjected to 50% applied tension using MPM showing local contours of a) electrostatic potential $\phi$, b) electric field component $E_2$ and c) current density component $J_2$.

In general, the local contours obtained from the electromechanical BVP using MPM exhibit features similar to those observed form the FEM solutions presented earlier. However, the effective properties calculated from the MPM solution has significant errors as compared to the FEM solution. The primary reason for these errors lies in the inability of the traditional MPM implementation (as discussed in Chapter 2) to capture the interfaces accurately since the interface gets homogenized over the background mesh in the solution scheme. Thus, in the current work, an implementation of MPM is proposed using concepts borrowed from cohesive zone modeling to allow for interfacial modeling in MPM.

One of the issues with the MPM solution scheme arises when the continuum body is composed of more than one material phases e.g. composite materials. In this case, one background mesh element may contain material particles of both material phases. The effective behavior of this mesh element, then, is dependent on the properties of both of the materials. However, in computing the effective stiffness of the background mesh, the information about the specific geometry of the interface is lost and the interface instead acts as a diffused boundary. In other words, the jump conditions in secondary variables across the interfaces are not satisfies exactly which are important for composite problems. A similar problem arises in
treatment of material interfaces in other meshless methods with discontinuous derivatives at
the material interfaces [159–162]. These issues are typically alleviated by special treatment of
the interface conditions by introducing Lagrange multipliers to satisfy interfacial conditions,
by introducing a special jump functions which exist near the interface or by modifying the
variational formulation of the problem. In the current work, a new MPM algorithm is pro-
posed where the material interfaces are resolved using a cohesive zone [163] type framework
across the interface. Each phase of the continuum body described using a different set of
basis functions on the background mesh such that the two bodies are non-interacting until
the cohesive terms are appropriately introduced in the formulation to couple the interfaces
of each phase.

8.1 Model Description

Handling material interfaces in MPM requires special attention [117, 118, 118] similar to
other meshless methods [159–161]. In each of these meshless methods, the discontinuous
secondary variables at the interface are approximated using continuous functions resulting in
errors in resolution of the function at the interface. More specifically for MPM, the interface
lies within the background mesh element which has a set of continuous and differentiable
active basis functions used to approximate the weak discontinuity resulting in large errors
at the interface. Moreover, the background element sharing the particles from both material
phases homogenizes the interface, thus, losing an accurate resolution and representation of
the interface. In order to alleviate the homogenization of interface and the non-physical
errors related to continuous approximation of discontinuous functions, here we propose an
MPM solution scheme using ideas borrowed from cohesive zone modeling in finite elements.

In MPM, the foreground particles interact with each other through the background mesh
elements and the associated basis functions. Thus, if an interfacial node pair was to lie
within the same element, MPM does not recognize an interface between the two parts and
thus the components shown in Eqn. 2.69 become nonphysical if included in the stiffness
matrix or the force vector description. In other words, as long as the foreground particles
are interacting with the same set of background mesh elements which have continuous basis functions associated with them, the MPM framework does not allow for interfaces within the elements. In the current work, it is proposed that more than one background meshes should be used for multimaterial problem with interfaces in MPM. Each background mesh has its own set of continuous basis functions which interpolates the primary and secondary variables for each material phase. For the current work, a two phase MPM model is developed by assuming that the two phases are two distinct bodies represented by $\Omega_1$ and $\Omega_2$. However, the methodology can be extended to problems with more than two phases.

An illustration of the proposed solution scheme is presented in Fig. 8.4 in the form of a BVP where a rectangular domain with two distinct phases separated by an interface is subjected to uniform tension (Fig. 8.4a). A discretized version of the 2-block problem shown in Fig. 8.4a is presented in Fig. 8.4b, where the material domains are discretized using a set of material points which are overlaid on a larger background mesh with rectangular elements. In the traditional form of MPM, Fig. 8.4b is the graphical representation of the final form of the problem setup for analysis. However, in the current work, the BVP in Fig. 8.4b is further split into two separate problems for graphical representation (Fig. 8.4c and Fig. 8.4d) in order to resolve the composite interfaces. It is to be noted that the background mesh nodes in Fig. 8.4c and Fig. 8.4d are coincident on an x-y plane, i.e. they are identical. Each material phase has its own associated background mesh, or in other words, the primary and secondary field variables for each phase are approximated using a different set of basis functions. This implies that the two problems shown in Fig. 8.4c and Fig. 8.4d are decoupled in their mathematical MPM formulation. Each of these problems have a set of background mesh element containing some material points which belong to the material interface. These elements which contain these special interface points are coupled between problems shown in Fig. 8.4c and Fig. 8.4d using a cohesive zone type evaluation of the coupling terms and appropriately added to the existing stiffness matrices for the two problems.

Say a set of basis functions $\psi_i$ are used to over the background mesh associated with body $\Omega_1$ and a different set of basis functions $\phi_i$ are used to over the background mesh associated with body $\Omega_2$. In the cohesive zone formulation, for one set of initially coincident node pairs,
Figure 8.4: a) Rectangular domain with two material phases and a composite interface separating the two phases. b) The domain is discretized using material points which are overlaid on a background rectangular computational mesh. The problem domain is composed of material points which belong to the two phases and overlapping interfacial material points. c) The first part of the problem presented in (b) where only the material particles which belong to phase I are retained along with the corresponding set of interface particles. d) The second part of the problem presented in (b) where only the material particles which belong to phase II are retained along with the corresponding set of interface particles. The background mesh in (c) and (d) is chosen to be identically the same as that in (b), such that a superposition of the two problems presented in (c) and (d) result in (b).
one node lies in $\Omega_1$ and the other lies in $\Omega_2$. Thus, the primary and secondary variables for the two cohesive zone node pairs are interpolated by $\psi_i$ and $\phi_i$ as

$$
\begin{align*}
  u^+_x &= \sum_{j=1}^{N} \psi_j(x^+, y^+) \hat{u}_x^j \\
  u^+_y &= \sum_{j=1}^{N} \psi_j(x^+, y^+) \hat{u}_y^j \\
  u^-_x &= \sum_{j=1}^{N} \phi_j(x^-, y^-) \hat{u}_x^j \\
  u^-_y &= \sum_{j=1}^{N} \phi_j(x^-, y^-) \hat{u}_y^j
\end{align*}
$$

(8.1)

where $\hat{u}$ and $\hat{u}$ are the displacement components of the background mesh nodes corresponding to bodies $\Omega_1$ and $\Omega_2$, respectively, $(x^+, y^+)$ and $(x^-, y^-)$ are the coordinates of the two nodes in the cohesive zone node pair. Substituting the definitions for the displacement components of the cohesive zone node pairs in Eqn. 8.1, the finite element formulation for one set of cohesive zone node pairs shown in Eqn. 2.69 can be expanded as

$$
\begin{align*}
  \tilde{K}^{11} \psi_j^+ \hat{u}_x^j + \tilde{K}^{12} \psi_j^+ \hat{u}_y^j + \tilde{K}^{13} \phi_j^- \hat{u}_x^j + \tilde{K}^{14} \phi_j^- \hat{u}_y^j &= 0 \\
  \tilde{K}^{21} \psi_j^+ \hat{u}_x^j + \tilde{K}^{22} \psi_j^+ \hat{u}_y^j + \tilde{K}^{23} \phi_j^- \hat{u}_x^j + \tilde{K}^{24} \phi_j^- \hat{u}_y^j &= 0 \\
  \tilde{K}^{31} \psi_j^+ \hat{u}_x^j + \tilde{K}^{32} \psi_j^+ \hat{u}_y^j + \tilde{K}^{33} \phi_j^- \hat{u}_x^j + \tilde{K}^{34} \phi_j^- \hat{u}_y^j &= 0 \\
  \tilde{K}^{41} \psi_j^+ \hat{u}_x^j + \tilde{K}^{42} \psi_j^+ \hat{u}_y^j + \tilde{K}^{43} \phi_j^- \hat{u}_x^j + \tilde{K}^{44} \phi_j^- \hat{u}_y^j &= 0
\end{align*}
$$

(8.2)

where a sum on index $j$ is implied, $\psi_j^+ = \psi_j(x^+, y^+)$ and $\phi_j^- = \phi_j(x^-, y^-)$. In assembling Eqn. 8.2, it is assumed that there are no external tractions applied at the interface cohesive zone node pair. However, the extension can be made to allow for external tractions at the cohesive zone node pairs by extrapolating cohesive zone node tractions to the respective background mesh tractions as was done in development of weak form for MPM shown in Eqn. 2.87. The four equations presented in Eqn. 8.2 need to be satisfied for each of the cohesive interfaces to couple the the two BVPs shown in Fig. 8.4c and Fig. 8.4d through the cohesive law. These, equations however can only be satisfied in a weak sense such that the value of the equation over the interface is zero in an integrated sense. As an example, let us consider the first equation in Eqn. 8.2 and satisfy it in a weak sense over the interface. The weak form of the equation over the composite interface can be expressed as
\[
\int_{\Gamma^I} w_2 \left\{ \tilde{K}_{ij}^1 \psi_i^+ \dot{u}_j^I + \tilde{K}_{ij}^2 \psi_j^+ \dot{u}_i^I + \tilde{K}_{ij}^{13} \phi_j^- \dot{u}_i^I + \tilde{K}_{ij}^{14} \phi_i^- \dot{u}_j^I \right\} d\Gamma^I = 0 \quad (8.3)
\]

where \( w_2 \) is the weight function associated with the interface coordinates, and \( \Gamma^I \) is the composite interface. The weight function can be approximated using the same set of finite element basis functions which were used for the two phases during their MPM discretization i.e \( \psi_i \) and \( \phi_i \). Remembering that the first two equations in Eqn. 8.2 were for the material point associated with \( \psi_i \) and the last two equations were for the material point associated with \( \phi_i \), Eqn. 8.3 can then be rewritten as

\[
\begin{bmatrix}
\tilde{K}_{ij}^1 \int_{\Gamma^I} \psi_i^+ \psi_j^+ d\Gamma^I & \tilde{K}_{ij}^2 \int_{\Gamma^I} \psi_i^+ \psi_j^- d\Gamma^I & \tilde{K}_{ij}^{13} \int_{\Gamma^I} \psi_i^+ \phi_j^+ d\Gamma^I & \tilde{K}_{ij}^{14} \int_{\Gamma^I} \psi_i^+ \phi_j^- d\Gamma^I \\
\tilde{K}_{ij}^{21} \int_{\Gamma^I} \psi_i^+ \psi_j^+ d\Gamma^I & \tilde{K}_{ij}^{22} \int_{\Gamma^I} \psi_i^+ \psi_j^- d\Gamma^I & \tilde{K}_{ij}^{23} \int_{\Gamma^I} \psi_i^+ \phi_j^+ d\Gamma^I & \tilde{K}_{ij}^{24} \int_{\Gamma^I} \psi_i^+ \phi_j^- d\Gamma^I \\
\tilde{K}_{ij}^{31} \int_{\Gamma^I} \phi_i^- \psi_j^- d\Gamma^I & \tilde{K}_{ij}^{32} \int_{\Gamma^I} \phi_i^- \psi_j^+ d\Gamma^I & \tilde{K}_{ij}^{33} \int_{\Gamma^I} \phi_i^- \phi_j^+ d\Gamma^I & \tilde{K}_{ij}^{34} \int_{\Gamma^I} \phi_i^- \phi_j^- d\Gamma^I \\
\tilde{K}_{ij}^{41} \int_{\Gamma^I} \phi_i^- \psi_j^- d\Gamma^I & \tilde{K}_{ij}^{42} \int_{\Gamma^I} \phi_i^- \psi_j^+ d\Gamma^I & \tilde{K}_{ij}^{43} \int_{\Gamma^I} \phi_i^- \phi_j^+ d\Gamma^I & \tilde{K}_{ij}^{44} \int_{\Gamma^I} \phi_i^- \phi_j^- d\Gamma^I
\end{bmatrix}
\begin{bmatrix}
\dot{u}_i^I \\
\dot{u}_j^I \\
\dot{u}_i^I \\
\dot{u}_j^I
\end{bmatrix} =
\begin{bmatrix}
0 \\
0 \\
0 \\
0
\end{bmatrix} \quad (8.4)
\]

where each of the rows shown in Eqn. 8.4 represent \( R \) number of equations where \( R \) is equal to the number of nodes per elements with finite element approximation. The numerical integration of the terms like \( \int_{\Gamma^I} \psi_i^+ \psi_j^+ d\Gamma^I \) are performed numerically using the normalized local area associated with each cohesive zone node pair as the weighing function such that

\[
\int_{\Gamma^I} \psi_i^+ \psi_j^+ d\Gamma^I = \sum_{k=1}^{p_I} \psi_i^+(x_k^+, y_k^+) \psi_j^+(x_k^+, y_k^+) \left( \frac{l_k}{L} \right) \quad (8.5)
\]

where \( (x_k^+, y_k^+) \) are the coordinates of the \( k^{th} \) cohesive zone node pair, \( l_k \) is the length associated with the \( k^{th} \) cohesive zone node pair, and \( L \) is the total length of the composite interface. The stiffness matrix components in Eqn. 8.4 couple the boundary value problems associated with bodies \( \Omega_1 \) and \( \Omega_2 \) which were initially independent of each other. In other words, the stiffness matrix components in Eqn. 8.4 account for the interaction between the two material phases though cohesive zone based interface. It is to be noted that in the algorithm outlined here the cohesive zone pairs within an element get homogenized along
with the material points resulting in an effective background element stiffness. The effective stiffness matrix obtained at the end of the procedure outlined here may not be symmetric or banded which will require use of asymmetric solvers for a non-banded system of linear equations.

In the current work, the MPM algorithm is implemented in an in-house MPM code written in FORTRAN 90. The algorithm is implemented to solve quasi-static plane elasticity boundary value problems as discussed earlier. For the current work, the primary boundary conditions are applied using a penalty function approach over the material points on the boundary. The background mesh elements are chosen to be 8-noded quadratic elements. The finite element basis functions for 8-noded quadratic elements are also used to pass the information back and forth between the background mesh and the foreground material particles. The weights associated with each material point, which are equal to the volume of the material points in absence of inertial forces, are set equal to the area occupied by each material point multiplied by the plane elasticity thickness. The problem domain is first discretized using a triangular mesh and each nodal coordinate is seeded with a material point. For each of these material points, the area occupied is calculated by adding a third of the area of each adjoining element. These weights are calculated only once at the beginning of the first time step and are kept constant throughout the course of the simulation. Before each time step, each background mesh element is marked as active or inactive based on whether or not they contain any material particles. For the inactive background mesh elements, trivial elemental stiffness matrices and force vectors are initialized which results in zero displacement of the nodes. The elemental stiffness matrices and force vectors for the active background mesh elements are calculated using the MPM algorithm described in Section 2.5.

For problems with composite interfaces, the background finite element mesh is chosen to have the same geometry for the meshes associated with each phase. The MPM stiffness matrices and force vectors are assembled for each part together in one matrix which has twice the number of degrees of freedom. These matrices represent the discretized version of the entire problem with the two phases, but with no interfacial coupling in between the two phases. The interfacial coupling is established using the algorithm presented in Section 8.1.
The number of degrees of freedom in the problem remain unchanged during this procedure. Finally, the solution to the system of equations is evaluated using a non-banded asymmetric solver which used LU decomposition algorithm available through the LAPACK library for linear algebra.

Figure 8.5: Schematic of the two quasi-static boundary value problems studied in the current work, a) Two-block problem with inclined composite interface separating two different material phases and b) Single fiber in matrix medium with the composite interface separating the fiber and matrix. The figure also shows the material properties for each phase in the two problems. The boundary conditions applied on the two problems are detailed in Table 8.1.

The mathematical framework of quasi-static MPM with appropriate resolution of interface discontinuities through cohesive zone type framework is subjected to verification tests with problems which have an established analytical or numerical solution. These verification tests are aimed at understanding the effects of introducing the interface algorithm presented in the current work against the regular implementation of MPM without any special interface handling. Fig. 8.5 shows the schematic of the two quasi-static boundary value problems studied in the current work. Fig. 8.5a shows a two-block rectangular domain (ABCD) with an inclined composite interface (EF), similar to the one presented in Fig. 8.4a. The parts of the domain above and below the composite interface have different linear elastic mechanical properties which leads to non-uniform field variables when uniform deformations are applied. In the proposed MPM model, parts CDEF has and ABFE have different sets of basis functions associated with them and the two parts are coupled through cohesive coupled
nature of the two parts at the edge EF. Similarly, Fig. 8.5b shows a BVP with a single fiber (Phase I) within the polymer matrix (Phase II). The problem studied here is the upper plane of the single-fiber in matrix problem which can be recovered if a mirror image is taken across the x axis. A detailed description of the boundary conditions applied on these two problems for the verification tests are presented in Table 8.1.

Table 8.1: Boundary conditions applied on the quasi-static verification problems presented in Fig. 8.5.

<table>
<thead>
<tr>
<th>Problem</th>
<th>Boundary Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-block uniform tension</td>
<td>Edge AB: ( u_2 = -\varepsilon_0 L )</td>
</tr>
<tr>
<td></td>
<td>Edge BFC: ( u_1 = 0 )</td>
</tr>
<tr>
<td></td>
<td>Edge CD: ( u_2 = +\varepsilon_0 L )</td>
</tr>
<tr>
<td></td>
<td>Edge DEA: ( u_1 = 0 )</td>
</tr>
<tr>
<td></td>
<td>Edge EF: ( u_1^+ = u_1^- \quad u_2^+ = u_2^- )</td>
</tr>
<tr>
<td></td>
<td>( T_n^+ = -T_n^- = -k_n(\Delta u_n)\Delta u_n )</td>
</tr>
<tr>
<td></td>
<td>( T_t^+ = -T_t^- = -k_t(\Delta u_t)\Delta u_t )</td>
</tr>
<tr>
<td>Single fiber uniform tension</td>
<td>Edge AEGB: ( u_2 = 0 )</td>
</tr>
<tr>
<td></td>
<td>Edge BC: ( u_1 = 0 )</td>
</tr>
<tr>
<td></td>
<td>Edge CD: ( u_2 = +\varepsilon_0 L )</td>
</tr>
<tr>
<td></td>
<td>Edge DA: ( u_1 = 0 )</td>
</tr>
<tr>
<td></td>
<td>Edge EFG: ( u_1^+ = u_1^- \quad u_2^+ = u_2^- )</td>
</tr>
<tr>
<td></td>
<td>( T_n^+ = -T_n^- = -k_n(\Delta u_n)\Delta u_n )</td>
</tr>
<tr>
<td></td>
<td>( T_t^+ = -T_t^- = -k_t(\Delta u_t)\Delta u_t )</td>
</tr>
</tbody>
</table>

For both of these problems, the computational domain is subjected to boundary conditions which will lead to a constrained uniform tension in the y-direction for a homogeneous medium of length L in y-direction. The displacements are applied incrementally on the domain with a maximum applied strain of \( \varepsilon_0 \). However, two different material phases along with the composite interface leads to non-uniform field variables. The composite interfaces (EF and EFG in Fig. 8.5a and Fig. 8.5b, respectively) are coupled through a cohesive law as shown in Table 8.1 which is numerically implemented using the procedure described in Section 8.1. It is to be noted that for the current work cases with perfect bonding of the composite interface are presented in addition to cases with weak cohesive interfaces. In order to simulate perfect bonding at the composite interface, the cohesive law is assumed to be linear elastic and the normal and tangential stiffnesses are considered to be much larger than the material properties of the either phases, i.e. \( k_n(\Delta u_n) = k \), where k is a constant such that \( |k| >> E_{(1,2)} \),
where $E_{(1,2)}$ are the linear elastic moduli for the two phases.

### 8.2 Perfect Interfacial Bonding

#### 8.2.1 Two-block Problem with Inclined Interface

The two-block problem with a composite interface shown in Fig. 8.5a is discretized into approximately 25000 randomly placed material points within the domain. The domain is initially discretized into triangular finite element mesh where the nodal coordinates are chosen to be the material particles having an area equal to one-third of the sum of adjoining element areas. A background computational mesh is constructed with a geometry larger than the initial problem domain such that the deformed problem domain is contained within the background mesh for all applied strain states. For this problem, the background mesh is discretized into 15 quadratic rectangular elements with about 1500 material particles per element. A maximum strain of 5% tension is applied on the domain in the y-direction over 50 displacement steps.

The local contours for displacements ($u_2$), strains component ($\varepsilon_{22}$) and the stress component ($\sigma_{22}$) in the y-direction are shown in Fig. 8.6 using finite element modeling, traditional MPM modeling and the proposed cohesive zone based MPM (CZMPM) modeling. For each of these field variables, comparisons are made between the MPM and CZMPM results with the finite element solution as the benchmark solution. As an example, Fig. 8.6a, 8.6b, and 8.6c present the displacement component ($u_2$) solutions for the finite element, MPM and CZMPM, respectively. The displacement contours are observed to have a sharper contour near the interface for the CZMPM model which represents the FEM solutions more accurately as compared to the traditional MPM model. Similarly, the local strain component ($\varepsilon_{22}$), presented in Fig. 8.6d, 8.6e and 8.6f, shows fluctuations near the composite interface for the MPM solution whereas the CZMPM solution results in a prominent sharp interface boundary comparing well with the FEM solution. Finally, the stress component ($\sigma_{22}$) contours, presented in Fig. 8.6g, 8.6h and 8.6i, show the breakdown of interface conditions
for the traditional MPM model with large fluctuations in the local contour near the interface. The proposed CZMPM model performs considerably better in satisfying the interfacial conditions and compares well with the finite element results.

The difference between results obtained from the MPM model and the CZMPM model can be studied quantitatively in terms of local error contours. The local error in the field variables is calculated by evaluating the difference in field variables obtained from MPM or CZMPM models from the FEM model at a given coordinate and normalizing the difference by the span of the contour level. As an example, the local error in $u_2$ for the MPM model at a point $P$ is calculated as $\varepsilon_{(u_2)}|_P = \frac{\text{abs}(u_2^{(M)}|_P - u_2^{(F)}|_P)}{\Delta u_2}$, where $u_2^{(M)}|_P$ and $u_2^{(F)}|_P$ are the MPM and FEM solutions, respectively, at point $P$ and $\Delta u_2$ is the span of $u_2$ which for the two-block problem is set to 0.1 (refer colorbar for Fig. 8.6a, 8.6b, 8.6c). In addition, volume averaged error is calculated for each field variable by integrating the local error in the field variable over the entire problem domain, e.g. $\langle \varepsilon_{(u_2)} \rangle = \frac{1}{A} \int_{\Omega} \varepsilon_{(u_2)}^P \Delta A^P d\Omega$, where $\Delta A^P$ is the area associated with each point $P$ at which local error $\varepsilon_{(u_2)}^P$ is calculated within the domain. In the current work, since the number of material points is much larger than the number of nodes in finite element modeling, the local error is calculated at the nodes of the finite element solution. The local field variables from the MPM model are interpolated to the coordinates of the finite element nodes using a nearest neighbor interpolation. Since the number of material points is $\sim 25000$ as compared to $\sim 4700$ nodes for the finite element solution over the same problem domain, the nearest neighbor interpolation works well. This is observed from the averaged error in local coordinates, $x_1$ and $x_2$, of the particles which are observed to be 0.14% and 0.15%, respectively.

The local error contours for the MPM and CZMPM solutions relative to the FEM solution are presented in Fig. 8.7. Fig. 8.7a, 8.7b and 8.7c show the local error in the displacement, strain and stress component for the MPM solution, respectively. Similarly, Fig. 8.7d, 8.7e and 8.7f show the local error in the displacement, strain and stress component for the CZMPM solution, respectively. The local error contours for the displacement component $\langle \varepsilon_{(u_2)} \rangle$ are observed to have larger local errors for the MPM solutions as compared to CZMPM especially near and along the interface. The averaged error for the displacement component, $\langle \varepsilon_{(u_2)} \rangle$,.
Figure 8.6: Local contours of solutions obtained from the FEM, MPM and CZMPM modeling of the 2-block problem with 5% tensile strain with the coarse background mesh (15 background mesh elements). Contours of a) local displacement component ($u_2$), b) local strain component ($\varepsilon_{22}$) and c) local stress component ($\sigma_{22}$) from the FEM solution. Contours of d) local displacement component ($u_2$), e) local strain component ($\varepsilon_{22}$) and f) local stress component ($\sigma_{22}$) from the MPM solution. Contours of g) local displacement component ($u_2$), h) local strain component ($\varepsilon_{22}$) and i) local stress component ($\sigma_{22}$) from the CZMPM solution.
Figure 8.7: Contours of local errors in solutions obtained from the MPM and CZMPM modeling of the 2-block problem with the coarse background mesh (15 background mesh elements) as compared to the benchmark FEM solution. Error contours for a) local displacement component, b) local strain component and c) local stress component from the MPM solution. Contours of d) local displacement component, e) local strain component and f) local stress component from the CZMPM solution.
is observed to be 3.45% for the MPM solution and 1.30% for the CZMPM solution i.e. significantly smaller in comparison. Similarly, the error in local strain and stress components is observed to be larger in the MPM solution near the interface in comparison to the CZMPM model. The averaged error in the strain component is observed to be 4.50% for the MPM model and 2.97% for the CZMPM model. The averaged error in stress component \( \langle \| \varepsilon_{(22)} \| \rangle \), is observed to be 6.9% for the MPM model and 6.15% for the CZMPM model, i.e. slightly smaller for the CZMPM model. While the CZMPM model reduces the fluctuations near the interface, the interior regions of the domain have a relatively larger local error as observed from Fig. 8.7d and 8.7f.

In order to explore how the number of background mesh elements affect the MPM and CZMPM solutions, the 2-block problem was solved with 96 background mesh elements keeping the number of material particles at 25000 i.e. around 250 material particles per element. A maximum strain of 5% tension is applied on the domain in the y-direction over 50 displacement steps as was done earlier with smaller number of background mesh elements. The local contours for displacements \( u_2 \), strains component \( \varepsilon_{22} \) and the stress component \( \sigma_{22} \) in the y-direction are shown in Fig. 8.8 using finite element modeling, traditional MPM modeling and the proposed cohesive zone based CZMPM modeling. It is observed that the traditional MPM results are closer to the FEM results because larger number of background mesh elements can resolve the interface better. However, the CZMPM results still match the FEM results more closely. The field variables with derivatives, e.g. strains component \( \varepsilon_{22} \) and the stress component \( \sigma_{22} \), shown in Fig. 8.8b and 8.8c still show large fluctuations near the interface for the traditional MPM model.

In order to understand the results with larger number of background mesh elements quantitatively, local and averaged errors in field variables are evaluated. Fig. 8.9a, 8.9b and 8.9c show the local error in the displacement, strain and stress component for the MPM solution, respectively. Similarly, Fig. 8.9d, 8.9e and 8.9f show the local error in the displacement, strain and stress component for the CZMPM solution, respectively. The local errors in the traditional MPM solutions are observed to be larger as compared to the CZMPM solutions, especially close to the interface. For the errors in local strain and stress components, the
Figure 8.8: Local contours of solutions obtained from the FEM, MPM and CZMPM modeling of the 2-block problem with 5% tensile strain with the fine background mesh (96 background mesh elements). Contours of a) local displacement component (ε_{u_2}), b) local strain component (ε_{22}) and c) local stress component (σ_{22}) from the FEM solution. Contours of d) local displacement component (ε_{u_2}), e) local strain component (ε_{22}) and f) local stress component (σ_{22}) from the MPM solution. Contours of g) local displacement component (ε_{u_2}), h) local strain component (ε_{22}) and i) local stress component (σ_{22}) from the CZMPM solution.
MPM solutions exhibit larger errors because of fluctuations near the interface which is sensitive to the edges of the background mesh elements. The CZMPM solution exhibits smaller local errors near the interface as compared to the MPM solutions, however it still shows large (∼10%) errors in the interior regions, especially in phase I. The local errors near the interface and the regions with large local errors are further observed to be smaller than those observed with smaller number of background meshes in Fig. 8.7.

![Figure 8.9](image_url)

**Figure 8.9:** Contours of local errors in solutions obtained from the MPM and CZMPM modeling of the 2-block problem with the fine background mesh (96 background mesh elements) as compared to the benchmark FEM solution. Error contours for a) local displacement component, b) local strain component and c) local stress component from the MPM solution. Contours of d) local displacement component, e) local strain component and f) local stress component from the CZMPM solution.

The local errors presented in Fig. 8.9 are further used to calculate the averaged errors in field variables by integrating over the entire solution domain. It is observed that the averaged error in local displacements (⟨ε(u₂)⟩) reduced from 3.45% for the solution with 15 background mesh elements to 2.22% for the solution with 96 background mesh elements. The averaged errors in strain and stress components reduced from 4.5% and 6.9% with 15 background elements to 3.36% and 6.44%, respectively, for the traditional MPM solutions. For the CZMPM model, the averaged errors in displacement, strain and stress components changed from 1.30%, 2.97% and 6.15% with 15 background elements to 1.27%, 3.13% and 6.56% with
96 background elements, respectively. While some of the averaged errors increased slightly because of errors in the bulk of the two phases, the CZMPM solution still outperforms the traditional MPM solutions specially in terms of interface resolution.

In the results presented so far, local errors in field variables around the interface have been observed to be sensitive to the edges of the background mesh elements. Since, the background rectangular mesh is chosen to be rectangular the orientation of the composite interface can lead to differences in the local errors in the solution. In order to explore this effect of composite interface orientation with respect to the background mesh, the background mesh is rotated by $30^\circ$ and $60^\circ$ to observe the changes in local errors for the CZMPM model. Fig. 8.10a, 8.10b and 8.10c present the local errors in displacement, strain and stress components for the background mesh at $0^\circ$, respectively. In comparison, Fig. 8.10d, 8.10e and 8.10f present the local errors in displacement, strain and stress components for the background mesh at $30^\circ$ and Fig. 8.10g, 8.10h and 8.10i present the local errors in displacement, strain and stress components for the background mesh at $60^\circ$, respectively. It is observed that the magnitudes of local error are similar for the three cases with different background mesh orientation for the three field variables. However, the local error shows sensitivity to the orientation of the background mesh, especially near the interface. This is especially observed for the errors in the field variable with derivatives involved e.g. local strain and stress components where the local errors are more prominent. In terms of averaged errors in field variables, all three cases with different orientation of background meshes are similar. For example, the averaged errors in local displacement, strain and stress components are observed to be 1.30%, 3.10% and 6.42%, respectively, for the case with the background mesh at $0^\circ$. In comparison, averaged errors in local displacement, strain and stress components are observed to be 1.21%, 2.99% and 6.51%, respectively, for the $30^\circ$ case and 1.24%, 2.99% and 6.31%, respectively, for the $60^\circ$ case.

### 8.2.2 Single Fiber in Matrix

For the second verification test, the problem with single fiber in the polymer domain is discretized into about 42000 material particles which are overlaid a background computational
Figure 8.10: Contours of local errors in solutions obtained from the CZMPM modeling of the 2-block problem as compared to the benchmark FEM solution comparing different orientations of the background mesh. Error contours for a) local displacement component, b) local strain component and c) local stress component from the CZMPM solution for the background mesh at 0°. Error contours for d) local displacement component, e) local strain component and f) local stress component from the CZMPM solution for the background mesh at 30°. Error contours for g) local displacement component, h) local strain component and i) local stress component from the CZMPM solution for the background mesh at 60°.
mesh composed of 48 rectangular quadratic elements i.e. about 800 particles per element. A maximum tensile strain of 5% is applied incrementally over 50 displacement steps following the boundary conditions shown in Table 8.1. The contours of local displacement, strain and stresses in the $x_2$ direction are shown in Fig. 8.11 for the solutions obtained from FEM, MPM and CZMPM. The local displacement contours presented in Fig. 8.11a, 8.11b and 8.11c show that the CZMPM solution is closer to the FEM solution, but the difference between the MPM and CZMPM solutions are not significant. However, the differences near the interface start to get more prominent when gradients of the field variables are calculated, as was observed in Section 8.2.1. Fig. 8.11d, 8.11e and 8.11f present local strain component ($\varepsilon_{22}$) from FEM, MPM and CZMPM solutions, respectively. The local strains in the stiffer fiber phase are much smaller in comparison to the more compliant matrix phase as would be expected. The MPM solution is observed to exhibit a significant breakdown in the accuracy of the solution, especially near the composite interface, to the extent where the fiber geometry is lost. On the other hand, the CZMPM solution agrees well with the finite element solution. Similarly, for the local stress component presented in Fig. 8.11g, 8.11h and 8.11i, the MPM solution undergoes significant fluctuation near the interface whereas the CZMPM solution compares well with FEM solution.

In order to understand the differences in a quantitative sense, the local error contours, using the methodology described in Section 8.2.1, for the solution obtained from the MPM and CZMPM models are shown in Fig. 8.12 for the fiber matrix problem. Fig. 8.12a and 8.12d present the local error contours in the local displacement components from the MPM and CZMPM solutions, respectively. The CZMPM solution is observed to have smaller local errors in the displacement component ($x_2$) with a volume averaged error ($\varepsilon_{(u_2)}$) of 0.75%. On the other hand, the MPM solution for local displacements leads to an averaged error of 1.58%, i.e. significantly larger than the CZMPM solution. Similarly, the error in local strain component is observed to be significantly larger in the MPM solution, especially near the interface. The averaged error in local strains ($\langle \varepsilon_{22} \rangle$) is observed to be 4.6% for the CZMPM model as compared to a much larger 7.5% for the MPM solution. Finally, local error in the stress component ($\varepsilon_{(\sigma_{22})}$) is presented in Fig. 8.12c and Fig. 8.12f, respectively, and the errors in local stress are likewise observed have large magnitudes near the interface.
Figure 8.11: Local contours of solutions obtained from the FEM, MPM and CZMPM modeling of the fiber-matrix problem with 5% tensile strain. Contours of a) local displacement component ($\varepsilon_{(u_2)}$), b) local strain component ($\varepsilon_{22}$) and c) local stress component ($\sigma_{22}$) from the FEM solution. Contours of d) local displacement component ($\varepsilon_{(u_2)}$), e) local strain component ($\varepsilon_{22}$) and f) local stress component ($\sigma_{22}$) from the MPM solution. Contours of g) local displacement component ($\varepsilon_{(u_2)}$), h) local strain component ($\varepsilon_{22}$) and i) local stress component ($\sigma_{22}$) from the CZMPM solution.
for the MPM model in comparison to the CZMPM model. The averaged error in stress over the problem domain is observed to be 13.73% for the CZMPM model and a larger 17.73% for the CZMPM model.

![Figure 8.12](image)

The results obtained from the two verification tests presented here show that the proposed CZMPM model results in solutions which are closer to the finite element solutions. Furthermore, the CZMPM model does not exhibit fluctuation in the local field variables near the composite interface as is observed in MPM. The volume averaged local errors in the primary and secondary field variables are observed to be significantly smaller for the CZMPM model in comparison to the MPM model.

In order to explore how the number of background mesh elements affect the MPM and CZMPM solutions for the single fiber in matrix problem, it was solved with 108 background mesh elements keeping the number of material particles at 42000 i.e. around 388 material particles per element. The local contours for displacements ($u_2$), strain component ($\varepsilon_{22}$) and the stress component ($\sigma_{22}$) in the y-direction are shown in Fig. 8.13 using finite element modeling, traditional MPM modeling and the proposed cohesive zone based CZMPM modeling. It is observed that the traditional MPM solution represents the FEM solution more closely.
as compared to solution with smaller number of background elements for all the three field variables. However, the fluctuations in local field variables are still observed for the strain and the stress components near the interface even though they are restricted to a smaller region around the interface. The CZMPM solution is close to the solution observed with CZMPM with smaller number of background meshes and still represents the FEM solution more closely.

Figure 8.13: Local contours of solutions obtained from the FEM, MPM and CZMPM modeling of the fiber-matrix problem with 5% tensile strain. Contours of a) local displacement component \( (\varepsilon u_2) \), b) local strain component \( (\varepsilon_{22}) \) and c) local stress component \( (\sigma_{22}) \) from the FEM solution. Contours of d) local displacement component \( (\varepsilon u_2) \), e) local strain component \( (\varepsilon_{22}) \) and f) local stress component \( (\sigma_{22}) \) from the MPM solution. Contours of g) local displacement component \( (\varepsilon u_2) \), h) local strain component \( (\varepsilon_{22}) \) and i) local stress component \( (\sigma_{22}) \) from the CZMPM solution.

Local and averaged errors in the field variables was calculated in order to quantify the differences between FEM, MPM and CZMPM solutions quantitatively with larger background mesh elements. Fig. 8.14a, 8.14b and 8.14c show the local error in the displacement, strain and stress component for the MPM solution, respectively. Similarly, Fig. 8.14d, 8.14e and 8.14f show the local error in the displacement, strain and stress component for the CZMPM
The local errors in the field variables are observed to be smaller for both MPM and CZMPM solutions in comparison to the solutions with smaller number of background mesh elements for all the three field variables.

![Error Contours](image)

**Figure 8.14:** Contours of local errors in solutions obtained from the MPM and CZMPM modeling of the fiber-matrix problem as compared to the benchmark FEM solution. Error contours for a) local displacement component, b) local strain component and c) local stress component from the MPM solution. Contours of d) local displacement component, e) local strain component and f) local stress component from the CZMPM solution.

### 8.3 Imperfect Interfacial Bonding

In addition to the perfect bonding cases, the proposed CZMPM model is capable of allowing for imperfect interfaces with a specified interfacial traction-separation response. The traditional MPM model does not allow for such imperfect interfaces since the material particles are homogenized over the background mesh which implicitly restricts presence of perfectly bonded or imperfectly bonded interfaces. The two verification boundary value problems are solved with an imperfect interface and the results are compared to a finite element model with cohesive interface.
8.3.1 Two-Block Problem with Inclined Interface

The two-block problem with a composite interface shown in Fig. 8.5a is solved using cohesive zone finite element method (CZFEM) and the proposed CZMPM model with imperfectly bonded interface. Unlike the perfectly bonded cases where the interface stiffnesses was chosen to be several orders of magnitude larger as compared to the elastic moduli of the two composite phases, the normal ($K_n^r$) and tangential ($K_t^r$) interface stiffness is chosen to be 100MPa for the imperfectly bonded case i.e. equal to the modulus of the stiffer phase. For the current work, a linear traction-separation law with constant interface stiffnesses is assumed for verification although the proposed framework can be extended more complex cohesive laws. For the comparison between CZFEM and CZMPM models with imperfect interfaces, local strain component, ($\varepsilon_{22}$), is compared since the field variables involving derivatives of the basis functions were observed to have larger errors for the perfect bonded cases. Fig. 8.16a shows the CZFEM solution for the two-block problem with an imperfect interface at an applied tensile strain of 5%. The CZFEM solution is observed to have similar local strain contours as compared to the perfect bonding case, however, the magnitude of local strains is smaller. Smaller local strains is observed because the weaker imperfect interface absorbs some of the applied deformation and separates as displacement boundary conditions are applied.

The corresponding local strain component contour obtained form the CZMPM model are shown in Fig. 8.16b. It is observed that the interface separation for the CZMPM solution is much larger as compared to the CZFEM solution and the local strains are significantly smaller in magnitude indicating that the imperfect interface is weaker for the CZMPM solution. Similarly, Fig. 8.16c-8.16f show the local strain contours for $\alpha$ of 10, 20, 30 and 40, respectively. The weaker interface for CZMPM is a result of interpolating the interface particles to the background mesh using the quadratic basis functions as presented in Section 8.1.

It is then anticipated that a correction factor will need to be applied to the interfacial stiffness for the CZMPM solution to match the CZFEM solution. Say the interfacial stiffness for the CZFEM solution is $K_0$, then a multiplicative factor $\alpha$ is introduced where $\alpha > 1$ and the updated interface stiffnesses in the normal and tangential directions are given by
Figure 8.15: Local strain contours for the two-block problem with an imperfect composite interface obtained from a) CZFEM and b)-f) CZMPM with $\alpha$ of 1, 10, 20, 30 and 40, respectively. g)-k) Contours of local error in strain for the CZMPM model with $\alpha$ of 1, 10, 20, 30 and 40, respectively.

$$\tilde{K}_n^r = \tilde{K}_n^t = \alpha \tilde{K}_0.$$

The CZMPM solutions with larger interface stiffnesses are presented in 8.16c-f with interface stiffness multiplicative factor ($\alpha$) of 10, 20, 30 and 40, respectively. It is observed that as $\alpha$ increases the CZMPM local strain contours start to resemble the CZFEM solutions more closely. In order to quantify the quality of CZMPM solution, local error contours for the strain component are shown in 8.16g-8.16k for $\alpha$ of 1, 10, 20, 30 and 40, respectively. The local error for the case with $\alpha = 1$ is observed to be large as would be expected based on the differences in the local strain contours. The volume averaged error ($\langle \varepsilon_{(22)} \rangle$) for the case with $\alpha = 1$ is observed to be 25%. In comparison, the local errors are observed to be get smaller as the interface stiffness increases with a volume averaged error of 12%, 7% and 3% for $\alpha$ of 1, 10, 20 and 30, respectively. However, for an $\alpha$ of 40, the volume averaged error in local strains is observe to increase to 5% indicating that a finite value of $\alpha$ may exist which leads to the CZMPM solution close to the CZFEM solution.
8.3.2 Single Fiber in Matrix

The boundary value problem with single fiber in polymer matrix shown in Fig. 8.5b is solved using cohesive zone finite element method (CZFEM) and the proposed CZMPM model with imperfectly bonded interface. The normal ($\tilde{K}_n^r$) and tangential ($\tilde{K}_t^r$) interface stiffness is chosen to be 10MPa for the imperfectly bonded case i.e. equal to the modulus of the more compliant phase. Fig. 8.16a shows the local strain component contour obtained from the CZFEM modeling. Unlike the perfectly bonded interface case, the CZMPM solution shows interface separation caused by a weaker interface. Fig. 8.16b shows the solution obtained from the CZMPM with an $\alpha$ of 1. The local strains are observed to be smaller for the CZMPM solution as was observed for the two-block problem because of reduced interface stiffness in CZMPM. Similarly, Fig. 8.16c-8.16f show the solution obtained from the CZMPM with an $\alpha$ of 10, 20, 30 and 40, respectively.

In addition, local contours of error in strain component are shown in Fig. 8.16g-8.16k for an $\alpha$ of 1, 10, 20, 30 and 40, respectively. It is observed that the local errors are larger for the case with small values of $\alpha$. The volume averaged error is observed to be around 10% for case with $\alpha$ of 1 and 10. However, as $\alpha$ is increased smaller magnitudes local error are observed with a volume averaged error of 8% and 6.7% observed with $\alpha$ of 20 and 30. Finally, the averaged error increases for the case with $\alpha$ of 40 to 8% showing that the multiplicative factor can be calibrated to result in close CZFEM ad CZMPM solutions. It is noted that the most appropriate multiplicative factor for interface stiffness ($\alpha$) is 30 for both of the boundary value problems presented in the current work. While the number of material points, number of background mesh elements, background mesh element size and material point density is different for the two problems, the number of cohesive zone node pairs per element was fixed around 10 on average. It is hypothesized that the multiplicative factors can be calibrated with FEM results and correlated to the number of interface material points per element, however a rigorous mathematical exploration of the factor is out of the scope of the current work.
Figure 8.16: Local strain contours for the single fiber in polymer matrix problem with an imperfect composite interface obtained from a) CZFEM and b)-f) CZMPM with α of 1, 10, 20, 30 and 40, respectively. g)-k) Contours of local error in strain for the CZMPM model with α of 1, 10, 20, 30 and 40, respectively.
Chapter 9

Conclusions

In the current work, computational multiscale analysis of the damage and deformation sensing is presented in polymer nanocomposites and polycrystalline energetic materials using finite elements, computational micromechanics and cohesive zone modeling techniques. In Chapter 3, a continuum micromechanics based computational approach has been proposed to incorporate the electron hopping phenomenon at the nanoscale within a continuum micromechanics based multiscale framework. Further, the effect of applied strains on the changing conductive paths is investigated through the electron hopping mechanism leading to macroscale piezo-resistivity. Some of the key observations based on results presented in Chapter 3 are

- An asymmetry in the conductive/piezo-resistive response for tension and compression modeling results is observed consistent with experimental observations in the literature.

- The effective piezo-resistive strain coefficients and macroscale effective gauge factors are observed to be nonlinear and highly dependent on the applied strains.

- The effective piezo-resistive strain coefficients and macroscale effective gauge factors depend on the type of boundary condition for nanoscale RVEs i.e. are dependent on the local macroscale strain state.

- Smaller maximum electron hopping range and smaller volume fractions yield higher...
effective piezoresistive strain tensor coefficients and macroscale effective gauge factors for initially percolated systems.

- The modeling results were observed to yield higher gauge factors near the percolation threshold for tension/compression tests, which is consistent with experimental observations reported in the literature.

- The modeling results were observed to yield gauge factors of magnitude comparable with experimental observations reported in the literature.

- The results indicate towards a dominant role of electron hopping in determining the macroscale effective piezoresistive response.

It is anticipated that the results will be useful in understanding the origins of the observed macroscale piezoresistive response of CNT-polymer nanocomposites. Moreover, the observations made herein will help in obtaining controllable macroscale effective piezoresistive properties which is essential for accurate correlation of strain state to the observed macroscale response, and thus, can contribute to better nanocomposite piezoresistive sensor design and interpretation.

In Chapter 4, a multiscale continuum micromechanics based approach is proposed to model the electron hopping induced conductive pathways at the nanoscale. Further, a multiscale modeling framework is proposed to transition the effect of evolving nanoscale electrostatic morphology through the microscale to macroscale effective piezoresistive response of CNT polymer nanocomposites. Some of the key observations based on the results presented in Chapter 4 are

- An asymmetry in the conductive/piezoresistive response for tension and compression modeling results is observed consistent with experimental observations in the literature.

- The effective piezoresistive strain coefficients and macroscale effective gauge factors are observed to be nonlinear and highly dependent on the applied strains.
• The effective electrostatic and piezoresistive properties of microscale CNT bundles are more sensitive to applied strains in the transverse direction as compared to the axial direction.

• Smaller macroscale effective gauge factors observed as the degree of alignment of nanotubes in the direction of applied strain is increased.

• Smaller maximum electron hopping range and smaller CNT volume fractions yield higher effective piezoresistive strain tensor coefficients and macroscale effective gauge factors for a CNT-polymer nanocomposite with uniformly dispersed aligned CNTs.

• Longer maximum electron hopping range and larger CNT volume fractions in microscale yield higher effective piezoresistive strain tensor coefficients, and macroscale effective gauge factors for a CNT-polymer nanocomposite with uniformly dispersed randomly oriented/aligned microscale CNT bundles.

• The uniformly dispersed aligned CNT case resulted in significantly higher macroscale effective gauge factors as compared to the aligned/randomly oriented microscale bundle cases.

• The modeling results were observed to yield gauge factors of magnitude comparable with experimental observations reported in the literature.

• The results indicate towards a dominant role of electron hopping in determining the macroscale effective piezoresistive response.

It is anticipated that the multiscale modeling procedure developed in this chapter can be extended to study the effective macroscale multifunctional response originating from several subscales. In addition, the results presented herein are expected to help in further understanding the origins of macroscale piezoresistive response for CNT-polymer nanocomposites which will help in building strain sensing devices with effective control over the macroscale response.
In Chapter 5, a multiscale continuum micromechanics based approach is used to model the electron hopping induced conductive pathways at the nanoscale. The nanoscale CNT-polymer interface is modeled through electromechanical cohesive zones in order to allow for interfacial damage on application of strains. The electromechanical cohesive zone allows for electron hopping based current density across the separated cohesive zone interface. The impact of strain dependent formation/disruption of nanoscale electron hopping pathways and interfacial damage on the effective electrostatic and piezoresistive properties of CNT-polymer nanocomposites is studied using micromechanics based electrostatic energy equivalence. Further, macroscale effective gauge factors for the case with perfectly bonded CNT-polymer interface and for cases with nanoscale interfacial separation/damage are compared. Some of the key observations based on the results presented in Chapter 5 are

- The effective electrostatic and piezoresistive response is observed to be highly sensitive to nanoscale electron hopping, interface separation, initiation and evolution interfacial damage.

- Larger piezoresistive response and higher macroscale effective gauge factors are observed with interfacial separation/damage at the nanoscale as compared to perfectly bonded interface.

- The results indicate that the effective electrostatic/piezoresistive response of CNT-polymer nanocomposites is sensitive to specific the specific traction-separation and interfacial resistance-separation curves which are in turn dependent on temperature, CNT-polymer material system, CNT functionalization, degree of cross linking in the polymer and the nanocomposite processing conditions.

- The macroscale effective gauge factors are observed to be of comparable magnitude (i.e. between 1 and 20 [3, 4, 7, 8, 11–13]) to the experimentally observed gauge factors published in the literature based on uniform tension tests. However, a direct correlation with the experimental results cannot be established because of the idealized microstructure, piezoresistive investigation in the transverse direction and exclusion of microscale microstructure as indicated in [139]. Despite the differences, the results
presented in the current work qualitatively capture some of the elements observed from experimental studies e.g. tension/compression asymmetry, higher gauge factors with interface nanoscale separation/damage indicating that the proposed multiscale computational micromechanics model captures the physics of macroscale nanocomposite piezoresistive response because of nanoscale electron hopping and interfacial separation/damage.

In Chapter 6, a computational micromechanics based model is used to study the effect of interfacial damage initiation, evolution and accumulation at the nanoscale CNT-polymer interface on the effective piezoresistive response of the nanocomposites. The effect of damage accumulation is observed in terms of difference in the loading and unloading pathways of effective property evolution. Some of the key observations made based on the results presented in Chapter 6 include

- The effective piezoresistive response and the effect of interfacial damage accumulation is significantly dependent on the nanoscale local microstructure. A larger volume fraction results in larger differences in the loading/unloading curves because of interfacial damage accumulation.

- The effective piezoresistive response and effect of interfacial damage accumulation is significantly dependent on the electron hopping barrier potential such that a smaller barrier potential (or longer maximum electron hopping range) results in larger differences in the loading/unloading curves.

- The rate of electrostatic damage at the nanoscale CNT-polymer interface affects the difference in loading/unloading response such that a faster electrostatic damage leads to larger damage accumulation effect.

- Over multiple loading cycles, if the maximum amplitude of applied strains is constant, then effective properties cycle along the unloading path of the first cycle.

- Over multiple loading cycles, if the maximum amplitude of applied strains increases every cycle, the effective response is closely governed by the amount of interfacial
damage accumulated in every subsequent cycle.

The results presented in the current work indicate that the nanoscale interfacial damage accumulation under cyclic loading can significantly affect the effective piezoresistive response of CNT-polymer nanocomposites. The correlation between the interfacial damage accumulation and the effective macroscale piezoresistive response can be further utilized for calibrating strain sensors and sensing system that have been in service for significant number of applied load cycles. For scenarios where CNT-polymer nanocomposites as used structural members or are dispersed in the matrix medium of fiber reinforced composites, this correlation can provide basis for quantifying the loading history and prognosticating the remaining fatigue life under dynamic loading conditions. Thus, the observations presented herein are expected to help in development of CNT-polymer based sensor and sensing system design for damage detection and prognostication especially under dynamic loading conditions.

In Chapter 7, a 2-scale hierarchal computational micromechanics based modeling framework was developed to assess the variations in effective piezoresistive response based on differences in material parameters and properties to explore the design space for NCBX materials. The key experimental observation from the current exploration of NCBX piezoresistivity include

- Effective NCBX piezoresistive response is largely dependent on the relative difference in the explosive grains and nanocomposite interface properties,
- A larger relative grain stiffness and conductivity as compared to the nanocomposite binder results in a larger NCBX piezoresistive response,
- Ductile mode of interfacial damage leads to smaller peak stresses and larger relative change in resistance as compared to brittle interfacial damage,
- Alignment of CNTs transverse (tangential) to the interface and smaller CNT volume fractions lead to smaller mechanical stiffness but a larger piezoresistive response, and
- A larger inherent piezoresistivity of the nanocomposite binder results in a larger effective NCBX piezoresistivity.
The initial piezoresistive testing of surrogate MWNT-sugar-epoxy hybrid nanocomposites indicates that addition of CNTs to the polymer binder can lead to piezoresistive response based deformation and damage sensing. In addition, the current work computationally explores the microstructure design space of NCBX materials which is expected to be help in material design with optimized piezoresistive response.

In Chapter 8, a mathematical formulation is proposed to allow for modeling of discontinuities in field secondary variables across a perfectly and imperfectly bonded composite interface in the material point method. This is achieved by using two different set of basis functions over the background mesh associated with each phase for a bi-material composite problem. The two phases are coupled using a mathematical formulation which is based on cohesive zone modeling approach typically applied in finite element problems. The cohesive traction-separation law for each interfacial node pair is satisfied in a weak sense which results in the coupled system of linear equations for the two phases. The proposed mathematical framework is tested in two quasi-static boundary value problems with a perfectly and imperfectly bonded composite interface. The solutions for the two problems is generated using the FEM, the traditional MPM and the proposed CZMPM method. The local contours of primary and secondary variables obtained form each of the models are compared against each other. In addition, the local error contours are generated form the MPM and CZMPM models are presented for each boundary value problem. It is observed that the proposed CZMPM model significantly reduces the fluctuations across the interface, especially observed in the secondary variables, in comparison to the traditional MPM model. Furthermore, the local and averaged errors in the primary and secondary variables is observed to be smaller for the CZMPM model. It is expected that the mathematical framework for CZMPM presented herein will help in advancing the state of the art in MPM and expand its application to a larger array of problems which require appropriate representation of material discontinuity across interfaces.
Bibliography


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Appendix A

Comparison of the two different electron hopping implementations

Two different implementation of the electron hopping model are implemented in the current work. In Chapter 3 the first implementation of electron hopping is introduced where the local conductivity of the intertube region is allowed to evolve isotropically depending on the intertube distance of the CNTs. The intertube conductivity follows an exponential relationship with the intertube distance as

$$
\hat{\Sigma}(\text{CNT})_{ij} \left\{ \begin{array}{ll}
\hat{\Sigma}(\text{poly})_{ij} & d_{\text{CNT-CNT}} < \delta_{\text{max}}^E \\
\hat{\Sigma}(\text{CNT})_{ij} & d_{\text{CNT-CNT}} \geq \delta_{\text{max}}^E
\end{array} \right.
$$

(A.1)

where $\hat{\Sigma}_{ij}^{(\text{CNT})}$ and $\hat{\Sigma}_{ij}^{(\text{poly})}$ are components of the conductivity tensors for the CNT and pure polymer (no electron hopping) in its unstrained state, respectively, and () on the subscripts signifies no summation on the index. Fig. A.1a shows the schematic of local conductivity in the hexagonal RVE with electron hopping pathways in the intertube region for an RVE with 10% CNT volume fraction. As an example, point $P_1$ and $P_2$ lie within the intertube region of the diagonally and vertically adjacent CNTs and has their conductivity modified based on the intertube distance between diagonally and vertically adjacent CNTs, respectively.
On the other hand, point \( P_3 \) lies within the intertube region of both the vertically and diagonally adjacent CNTs. In this case, the local conductivity is modified to be the larger of the two local conductivities based on the vertically and diagonally adjacent CNTs. Finally, point \( P_4 \) does not lie within the intertube region of any of the nanotubes and thus the local conductivity does not get modified. Fig. A.1c shows the evolution of local conductivity within the electron hopping pathways when a tensile and compressive strain of 5% is applied on the nanoscale RVE in the \( x_2 \) direction. As was discussed in Chapter 3, on application of compressive strains vertical pathways of electron hopping augmented conductive pathways are observed and on application of compressive strains, and local pockets of low conductivity between the vertically adjacent CNTs on application of tensile strains.

Figure A.1: Schematic of local conductivity in the hexagonal RVE with electron hopping pathways in the intertube region for an RVE with 10% CNT volume fraction obtained form a) the first electron hopping implementation and b) the second electron hopping implementation. Schematic of local conductivity contours under applied tensile and compressive strains for the c) the first electron hopping implementation and d) the second electron hopping implementation.
Similarly, Fig. A.1b shows a schematic of the local conductivity contours obtained using the second implementation of electron hopping introduced in Chapter 6. In this case, the local conductivity of the polymer matrix in the nanoscale RVEs is modified based on the intertube resistance relation. For a material point \( \hat{x}_i^p \) in the polymer medium, the intertube distance \( (d) \) is approximated [147] as the sum of the distance to the two nearest CNTs from \( \hat{x}_i^p \), accounting for the periodicity of nanoscale microstructure. The electron hopping barrier potential \( (\lambda) \) depends on the type of CNT and the polymer matrix medium, with values typically between 0.05eV and 2.5eV for Epoxy [12]. Once the electron hopping barrier potential for a given CNT-polymer pair is chosen and the distance \( (d) \) is determined, the local conductivity of the polymer medium at any material point \( \hat{x}_i^p \) is given by

\[
\hat{\Sigma}^\text{EH} = \left( \frac{\hat{R}^\text{EH} A}{d} \right)^{-1} = \left[ \frac{h^2}{e^2 \sqrt{2m\lambda}} \exp \left( \frac{4\pi d}{h \sqrt{2m\lambda}} \right) \right]^{-1}
\]  

(A.2)

where \( \hat{\Sigma}^\text{EH} \) is the electron hopping augmented local polymer conductivity in the nanoscale RVE. The local conductivity of electron hopping augmented polymer medium evolves with applied strains as the positions of CNTs and the intertube distances change.

The local conductivity contours at 5% tension and compression obtained from the first electron hopping model are shown in Fig. A.1a and A.1b, respectively, for an RVE with 10% CNT volume fraction. Similarly, Fig. A.1c and A.1d show the local conductivity contours at 5% tension and compression obtained from the second electron hopping model.

The local conductivity component contours at 5% tension and compression obtained from the first electron hopping model are shown in Fig. A.2a and A.2b, respectively, for an RVE with 10% CNT volume fraction. Similarly, Fig. A.2c and A.2d show the local conductivity contours at 5% tension and compression obtained from the second electron hopping model.

The local current density component contours at 5% tension and compression obtained from the first electron hopping model are shown in Fig. A.3a and A.3b, respectively, for an RVE with 10% CNT volume fraction. Similarly, Fig. A.3c and A.3d show the local conductivity contours at 5% tension and compression obtained from the second electron hopping model.
Figure A.2: Comparison of local conductivity contours for a) first EH implementation at 5% tension, b) first EH implementation at 5% at compression, c) second EH implementation at 5% tension and b) second EH implementation at 5% at compression.

Figure A.3: Comparison of local current density contours for a) first EH implementation at 5% tension, b) first EH implementation at 5% at compression, c) second EH implementation at 5% tension and b) second EH implementation at 5% at compression.
A comparison of evolution in effective conductivity for the two electron hopping implementations is presented in Fig. A.4 for the perfect bonding case and with an imperfect interface. It is observed that the evolution of effective conductivities obtained from both electron hopping implementations have differences in the magnitude of effective conductivity at a given strain with the exponential EH model showing a larger effective conductivity. This is because in the implementation of the exponential EH model a larger intertube region undergoes electron hopping based augmentation as compared to the second implementation based on the direct intertube resistance based EH model. The corresponding comparison of relative change in resistivity is presented in Fig. A.5. Finally, Fig. A.6 shows the comparison of gauge factors for these cases. In conclusion, it is observed that there are slight differences in the effective properties obtained from the two implementation of the intertube electron hopping, however the general observations made in the current work hold for either of these implementations.
Figure A.5: Comparison of the relative change in resistivity component for two electron hopping implementations with perfectly bonded interface and with imperfect interface.

Figure A.6: Comparison of the effective gauge factors for two electron hopping implementations with perfectly bonded interface and with imperfect interface.
Appendix B

Verification of electromechanical cohesive zone model

In order to understand the behavior of the interface, a test case is developed for the CNT-polymer interface undergoing purely normal mode of separation. A schematic of the interface model is shown in Fig. 8.4 as a zoomed in version of the CNT-polymer interface in the full nanoscale RVE. Displacements in the \( \hat{x}_2 \) direction are fixed for the bottom surface, while at the top surface displacement boundary conditions \( (\hat{u}^{\text{top}}_{2}) \) are applied in the \( \hat{x}_2 \) direction i.e. normal to the interface. The displacement boundary conditions are applied incrementally at the top surface up to a maximum of 5nm. Electrostatic boundary conditions are applied as electrostatic potentials at the top and bottom surfaces, keeping the bottom surface at -1V and the top surface at +1V. An electric field in -\( \hat{x}_2 \) direction is thus setup to study the effective current density through the interface as the separation distance increases.

The mechanical response of the two-block model is presented in Fig. B.2. It is observed that as the displacement boundary conditions are applied on the top edge in the \( \hat{x}_2 \) direction, the interface starts to separate. The more compliant top block undergoes larger deformation as compared to the stiffer bottom block. As larger displacements are applied to the top block, the the cohesive interface starts to get damaged and a relaxation of deformation in the top block is observed. Fig. B.2 also presents the local traction-separation response of
Figure B.1: The CNT-polymer interface test case as a zoomed version of the full nanoscale RVE indicating displacement and potential boundary conditions.

the cohesive zones and the averaged stress over the two blocks and cohesive zones in the two block model. Since the current problem is similar to a spring in series, the stresses in the two blocks and traction in the cohesive zones are expected to be the same as is observed from the results presented in Fig. B.2. The cohesive zones are observed to follow the bilinear traction-separation law specified and as the cohesive zones get damaged relaxation of stress is observed in the local stress contours.

Fig. B.3 shows the contours of local potentials at different displacement steps. When the CNT polymer interface is in contact ($u_{top}^2 = 0$), the cohesive element has very high conductivity, thus there is negligible potential drop in the cohesive element and the potential contour is continuous across the interface. As the separation distance increases, the conductance of the cohesive element reduces and the potential drop across the interface increases resulting in a discontinuous potential distribution across the interface. The CNT, being highly conductive, retains the potential of -1V applied at the bottom surface. Thus, even when the CNT-polymer are in contact and there is no potential drop at the interface, all of the potential variation is in the polymer. Finally, at complete separation of surfaces, the conductance of the interface becomes zero, and thus all the potential drop happens at the interface which assumes infinite resistance at complete separation. The CNT and polymer matrix retain the applied potentials at the lower and top edge, respectively.

Fig. B.3 also shows the local cohesive zone normal resistance-separation along with the cohesive zone normal current density and averaged current density through the two blocks and
Figure B.2: The mechanical response of the two block problem under monotonic loading with contours of local stresses in the two blocks along with the local cohesive zone traction-separation response and the evolution of averaged stress.

Figure B.3: The electrostatic response of the two block problem under monotonic loading with contours of local potential in the two blocks along with the local cohesive zone resistance-separation response and the evolution of cohesive zone and averaged current density.
the cohesive zones. The interfacial normal resistance-separation is observed to follow the bilinear response with the resistance increasing as the interface gets separated. The current density in the cohesive zones on the other hand decreases as the interface separation increases finally going to zero as the cohesive zone gets completely damaged and the resistance increases to infinity. A similar behavior is observed for the averaged current density since the current case is similar to resistances in series.

In addition to the monotonic loading case, the relaxation and reloading of the cohesive interface is studied by applying acyclic displacement boundary conditions on the top block of the 2-block test case. The local stress contours for this test case are presented in Fig. B.4 at various stages of the loading and unloading along with the local cohesive zone normal traction-separation and averages stress response. It is observed that the normal traction separation response of the cohesive zones follow the bilinear response specified with unloading and reloading preserving the current damaged stiffness.

Figure B.4: The mechanical response of the two block problem with loading and unloading of cohesive zones with contours the of local stresses in the two blocks along with the local cohesive zone traction-separation response and the evolution of averaged stress.

The electrostatic response with unloading and reloading of the cohesive zones is presented
in Fig. B.5. Similar to the mechanical interfacial response, the interface normal resistance follows the bilinear normal resistance-separation response specified and unloads and reloads preserving the current damaged resistivity of the cohesive zones. The corresponding local current density and averaged current density contours are presented in Fig. B.5 as well.

Figure B.5: The electrostatic response of the two block problem with loading and unloading of cohesive zones with contours of the local current density in the two blocks along with the local cohesive zone normal resistance-separation response and the evolution of cohesive zone current density and the averaged current density.