Investigation of Mechanical and Thermal Properties of Graphitic System

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UNIVERSITY OF MIAMI

INVESTIGATION OF MECHANICAL AND THERMAL PROPERTIES OF GRAPHITIC SYSTEM

By
Chenxi Zhang

A DISSERTATION

Submitted to the Faculty of the University of Miami in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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the requirements for the degree of
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INVESTIGATION OF MECHANICAL AND THERMAL PROPERTIES OF
GRAPHITIC SYSTEM

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The focus of the doctoral research presented in this dissertation consists of two kinds of graphitic materials, graphene and single walled carbon nanotubes (SWNTs). Owing to its fascinating electrical, thermal, and mechanical properties, graphene and SWNTs have shown great promise for a multitude of applications, ranging from flexible and invisible displays, nanoelectronic components, nanosensors, to energy conversion and storage devices.

The use of graphene/h-BN heterostructure for graphene electronics has attracted much interest from science and engineering communities because graphene/h-BN heterostructures exhibit much higher electron mobility, less intrinsic doping and improved on/off ration than conventional graphene devices on SiO$_2$ substrate. Understanding the mechanical properties of graphene/h-BN, where the interface plays a key role, is crucial in enabling future high-quality graphene applications. A continuum framework is established for the cohesive law due to the van der Waals force for the interface between graphene and h-BN in terms of the area density of carbon atoms on the graphene and those of boron and nitrogen atoms on the h-BN layer, number of h-BN layer and the parameters in van der Waals interaction. Also, the buckling of graphene on
h-BN substrate under equi-biaxial compression with five buckling patterns is studied. Total energy consisting of cohesive energy, graphene membrane energy and graphene bending energy is obtained analytically for each buckling mode. It is found that the total energies are quite same for all buckling modes at a compression slightly larger than the critical strain while the herringbone mode has the lowest total energy at a compression much larger than the critical compression.

SWNTs remain of significant interest in the electronic materials research community due to their excellent electrical properties. However, the heterogeneity of synthesized SWNTs significantly hampers device performance. Recent efforts to remove metallic SWNTs using thermocapillary flow of thin film due to Joule heating yielded purified semiconducting SWNTs. An analytical model, as well as a fully coupled thermo-mechanical-fluid finite element model, is developed to understand the underlying physics associated with the thermocapillary flow. The predicted results agree well with experimental measurements such that the models are reliable for further optimization. It is shown that thermocapillary force due to the high temperature gradient makes the trench. A simple scaling law for the film thickness profile is established in terms of the geometrical (e.g., film thickness), material (e.g., thermal conductivity and viscosity) and loading parameters (e.g., power density). It shows that the normalized thickness profile only depends on three non-dimensional parameters in addition to the normalized position and normalized time. In particular, for the system of MG2OH/Quartz under a low power density, the thickness profile only depends on one non-dimensional parameter. These may serve as design guidelines for system optimization.
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Chapter 1

Introduction

The focus of the doctoral research presented in this dissertation consists of two kinds of graphitic materials, graphene and single walled carbon nanotubes (SWNTs). The scope of this work ranges from fundamental studies of materials properties of graphene, to the cohesive law for the interfaces between graphene and hexagonal boron nitride (h-BN) substrate and the buckling mechanism in the graphene/h-BN heterostructures, from studies of experiment results of thermocapillary enhanced purification of SWNTs, to the development of analytical and finite element models of this system. This introduction shows the background information in these areas and discusses the methodologies in this work.

1.1 General properties of graphitic materials

Carbon is an important and interesting element in the earth not only because it forms millions of organic compounds with other elements, but also due to its allotropes [1]. They play an extremely irreplaceable role in our society. Diamond and graphite, the two well-known three-dimensional (3D) allotropes of carbon, were found from ancient times. Fullerenes, the zero-dimensional (0D) allotrope of carbon [2], were discovered in 1985 and the one-dimensional (1D) form, carbon nanotubes [3], in 1991. Although it was realized in 1991 [3] that carbon nanotubes were formed by rolling a two-dimensional (2D) graphene sheet, which is a single layer from 3D graphitic crystal, the isolation and characterization of graphene was not achieved in experiments until 2004 [4]. Graphene is the building block for carbon materials of all other dimensionalities [5] and therefore is
considered as the mother of all graphitic materials. It can be wrapped up into 0D fullerene, rolled into 1D nanotube or stacked into 3D graphite (shown in Fig. 1.1). They are the bases of many important technologies ranging from pencils, absorbents and metal strengtheners to batteries and many others. Studies in the past few decades have further revealed their optical, electrical and mechanical properties, making it possible to use them in advanced applications. The research interests in this work focus on graphene and SWNTs.

![Figure 1.1 Mother of all graphitic forms. Graphene (upper) can be wrapped up into 0D fullerenes (lower left), rolled into 1D nanotubes (lower middle) or stacked into 3D graphite (lower right). (Reproduced with permission from Ref. [5])](image)

Since its fabrication, identification and characterization in 2004, graphene has been stimulating scientists’ and engineers’ imagination and passion for nanoscience and nanotechnology. Its structure is one-atom-thick planar sheet of carbon atoms that are densely packed in a honeycomb crystal lattice. Graphene appeared to be one of the
strongest materials known with a breaking strength over 100 times greater than a hypothetical steel film of the same thickness [6], and a Young's modulus (stiffness) of 1 TPa [7]. The Nobel announcement illustrated this by saying that a one-square-meter graphene hammock would support a 4 kg cat but would weigh only as much as one of the cat's whiskers, at 0.77 mg (about 0.001% of the weight of one m$^2$ of paper) [6] (see Fig. 1.2). Measurements show that graphene has remarkably high electron mobility at room temperature, and the corresponding resistivity of the graphene sheet is less than the resistivity of silver [8], the lowest known at room temperature. Also it has a high thermal conductivity and it is optically transparent and bendable. So it is regarded as the material for next generation of display technology.

![Figure 1.2](image-url) A cat in the graphene hammock. (Reproduced with permission from Ref. [6].)

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. CNTs have length-to-diameter ratio of up to 132,000,000:1 [9], significantly larger than that of any other materials. Over the past few decades, CNTs have become a common topic of research in the fields of nanotechnology, electronics, optics and many others of materials science and technology owing to their outstanding properties. In particular, their extraordinary thermal conductivity, mechanical and
electrical properties make them core materials or excellent additives to various thermoelectrical or structural applications. The structure of CNTs can be conceptualized by wrapping graphene sheet into seamless cylinders. With different numbers of graphene sheets, single walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) (see Fig. 1.3) differs in methods of synthesis, structures and properties [10, 11]. In this work, only SWNTs are studied.

![Figure 1.3 Schematic representation of SWNT (left) and MWNT (right). (Reproduced with permission from Ref. [10].)](image)

1.2 Mechanics of graphene and h-BN heterostructures

1.2.1 Graphene/h-BN heterostructures

Owing to its fascinating electrical, thermal, and mechanical properties, graphene has shown great promise for a multitude of applications, ranging from flexible and invisible displays, nanoelectronic components, nanosensors, to energy conversion and storage devices. Although the feasibility of constructing free-standing graphene sheet has been demonstrated [12-14], most applications will either require graphene to be grown on [15-17] or transferred [18-20] to a supporting substrate. However, the presence of
substrates leads to a significant reduction in electron mobility [4, 21, 22] from ~100,000 cm$^2$V$^{-1}$s$^{-1}$ to ~1,000 cm$^2$V$^{-1}$s$^{-1}$ due to the charged surface states and impurities [23-26], surface roughness [27, 28] and surface optical phonons [29, 30]. One solution to allow a substrate-supported geometry while retaining the quality achieved with a suspended sample is to use graphene/h-BN heterostructures (as shown in Fig. 1.4), where h-BN serves as a dielectric layer between graphene and substrate to reduce the substrate influences on graphene.

Figure 1.4 Schematic diagram of graphene/h-BN heterostructure.

The h-BN is the most stable crystalline form of boron nitride. It has a layered structure similar to graphite. Within each layer, boron and nitrogen atoms are bound by strong covalent bonds, whereas the layers are held together by weak van der Waals forces. Also, h-BN layer has structure very similar to graphene. Lattice mismatch between them is only 1.7% [31]. The h-BN’s strong in-plane bonds, large band gap, and planar structure provide an ideal flat, insulating and inert surface, isolating the graphene from the substrate [32-34]. It is shown that graphene/h-BN heterostructure exhibits electron mobility as high as ~60,000 cm$^2$V$^{-1}$s$^{-1}$, which is an order of magnitude higher than the commonly reported substrate-supported graphene [35].
The use of graphene/h-BN heterostructure for graphene electronics has attracted much interest from science and engineering communities. Most of the existing studies on graphene/h-BN heterostructure focus on the electrical [35-42], magnetic [43, 44] and thermal properties [45], as well as its behaviors when applied in field effect transistor [46, 47]. An example is shown in Fig. 1.5. Although interfacial sliding and/or buckling of graphene on polymer substrates have been observed experimentally [48-50], the studies on mechanical modeling for interfaces in graphene/h-BN heterostructure are rarely seen. In order to utilize graphene/h-BN heterostructure in graphene electronics, mechanical properties of this heterostructure are critical because it is to be used as structural and functional components in electronics. Moreover, mechanical properties (or deformations) of graphene/h-BN are strongly tied to its electrical performance. Therefore, understanding the mechanical properties of graphene/h-BN, where the interface plays a key role, is crucial in enabling future high-quality graphene applications such as stretchable electronics.

Figure 1.5 Schematic of the top view (left upper) and the side view (left lower) of the buried-gate graphene transistor. Scanning election microscope graph (right) of the fabricated device with the dashed and the dotted lines showing the location of the graphene channel and buried TiN gates, respectively. (Reproduced with permission from Ref. [46].)
1.2.2 A cohesive law for the interfaces between graphene and h-BN

A continuum framework is established to develop the cohesive law for the interfaces between graphene and h-BN in Ch. 2. Both graphene and h-BN are modeled as homogenized solids and infinitely large in the in-plane directions [51-53]. The interlayer bonding between graphene and h-BN is due to van der Waals interaction [54], which is usually represented by the Lennard-Jones 6-12 potential

\[ V(r) = 4\varepsilon \left( \frac{\sigma^{12}}{r^{12}} - \frac{\sigma^{6}}{r^{6}} \right), \]  

(1.1)

where \( V(r) \) is the energy between a pair of atoms of distance \( r \), \( \sqrt[6]{2}\sigma \) is the equilibrium distance between two atoms and \( \varepsilon \) is the bond energy at the equilibrium distance. As shown in Fig. 1.6, the potential energy reaches a minimum at the equilibrium distance where the interaction force is 0.

Figure 1.6 (a) The van der Waals potential energy versus distance; (b) interaction force versus distance.
Integrating the interaction between carbon atom and nitrogen atom or boron atom over the entire plane gives the cohesive energy of the graphene and h-BN. Then, minimization of the energy gives the equilibrium distance between graphene layer and h-BN. After introducing opening displacement beyond the equilibrium distance, energy minimization leads to the cohesive stress in terms of the area density of carbon atomes on the graphene and those of boron and nitrogen atoms on the h-BN layer, number of h-BN layer and the parameters in van der Waals interaction. It is shown that the cohesive law in the graphene/h-BN is dominated by the first three h-BN layers which are closest to graphene.

1.2.3 Periodic patterns and energy states of buckled graphene on h-BN substrate

Due to the reduced interaction of graphene with h-BN substrate, graphene/h-BN is also an ideal system to study intrinsic physical properties of graphene. Although the electrical, magnetic and thermal properties of graphene/h-BN heterostructure have been extensively explored [34-45], its mechanical properties have been rarely explored thus far. In particular, strain has been used to tune the electrical properties (e.g., band gap) of graphene for graphene electronics [31, 55, 56].

Recently, Yoon et al. [57] realized an equi-biaxial compression in graphene on SiO2 due to their thermal expansion coefficient mismatch although the deformation of graphene was not well understood. Pan et al. [58] studied biaxial compressive strain in graphene/h-BN heterostructures and found that the strain is spatially inhomogeneous with the occurrence of bubbles due to the existence of defects. Some questions still remain unknown for an ideal graphene/h-BN heterostructure under biaxial compression. For example, can the graphene/h-BN heterostructure buckle as the compression increases?
What is the condition for buckling? What is the buckling mode? These questions are very critical since the deformation of graphene is strongly tied to its electrical performance (e.g., electron mobility and band gap) \([31, 55, 56]\).

It is shown that the film bonded to a substrate under equi-biaxial compression may buckle into several intriguing periodic buckling patterns such as one-dimensional, square checkerboard, hexagonal, triangular and herringbone modes as shown schematically in Fig. 1. Many researchers have investigated these periodic buckling modes. For example, Chen and Hutchinson \([59]\) and Song \textit{et al.} \([60]\) developed an energy method with the total energy including the film energy and substrate energy to study one-dimensional, square checkerboard and herringbone mode and they showed that the heringbone mode has the lowest energy in the buckled state while the one-dimensional mode has the greatest. Audoly and Boudaoud \([61]\) explored further details of these modes including the transition from one-dimensional mode to the herringbone mode as the compression is not equi-biaxial. Cai \textit{et al.} \([62]\) established an analytical upper-bond method and performed a full numerical analysis to study the energy of all these periodic patterns in the buckled state. It is found that the square checkerboard mode has lowest energy in small strain state (larger than the critical buckling strain) and the herringbone mode is dominant in relatively large strain state.
Figure 1.7 Schematics of mode shapes: (a) one-dimensional mode; (b) square checkerboard mode; (c) hexagonal mode; (d) equilateral triangular mode; and (e) herringbone mode.
The deformation (or buckling behavior) of graphene/h-BN heterostructure under equi-biaxial compression is studied analytically in Ch. 3. All five possible periodic patterns (i.e., one-dimensional, square checkerboard, hexagonal, triangular and herringbone modes) are considered. An energy method is developed to obtain the total energy of the buckled state of graphene/h-BN heterostructures. Different from the system of a film perfectly bonded to a substrate, where the total energy includes the film energy and substrate energy, the graphene /h-BN has film energy and cohesive energy due to the van der Waals interaction at the interface but not the substrate energy since the substrate could be assumed to be a rigid body [63].

1.3 Modeling of thermocapillary enhanced purification of single walled carbon nanotubes

1.3.1 Variation of SWNTs

SWNTs are hollow cylinders of carbon with diameters on the order of 1 nm, lengths ranging from tens of nanometers to centimeters, and of one-atom thick [64] (see Fig. 1.8). Their excellent electrical properties (high electronic mobility [65, 66] and potential for ballistic transport [67]) make them interesting for applications related to digital [68, 69] and RF analog electronic [70, 71] devices. They have been proposed as potential substitution for Si as advances which follow Moore’s law become limited [72]. Like other nanomaterial, the properties of SWNTs depend on their size and structure.
The structure of a SWNT is typically discussed in terms of graphene, as mentioned in Sec.1.1, it can be made by rolling up graphene to form a cylinder. The electrical properties of a SWNT depend on the direction in which the graphene was rolled up. As shown in Fig. 1.9, this direction is called the chiral vector. Every single atom in graphene sheet can be identified with a pair of integers \((n,m)\) and a pair of unit vectors \((\vec{a}_1, \vec{a}_2)\), leading to the definition of the chiral vector, \(C_h = n\vec{a}_1 + m\vec{a}_2\). SWNTs with \(n = m\) (known as armchair) and those with \(n - m = 3j\), where \(j = 0, 1, 2, 3, \ldots\), are metallic (m-SWNTs) at room temperature (labelled green in Fig. 1.9). SWNTS with \(n - m = 3j + 1\) (labelled pink in Fig. 1.9), and \(n - m = 3j + 2\) (labelled purple in Fig. 1.9), where \(j = 0, 1, 2, 3, \ldots\), are semiconductors (s-SWNTs). And SWNTs with \(m = 0\) are known as zigzag and can be either metallic or semiconducting. Among a random population of SWNTs, approximately 1/3 are metallic and 2/3 are semiconducting at room temperature [64].
1.3.2 Purification of SWNTs

Most applications of SWNTs require perfectly aligned, horizontal arrays of purely semiconducting SWNTs. For example, most digital electronics require high on/off ratio \( \geq 10^3 \sim 10^4 \), necessitating \( > 99.99\% \) pure s-SWNTs. So the isolation of pure s-SWNTs has been of great concern. Figure 1.10 shows the progress in SWNT transistor technology since the first demonstration of a SWNT field-effect transistor in 1998 [73]. The purity of s-SWNTs is plotted in terms of percentage of m-SWNTs impurity. The placement of SWNTs at a certain density is shown for both consistent and inconsistent pitch (distance) between SWNTs, with the target of 125 SWNTs per micrometer specified, along with the maximum of 500 SWNTs per micrometer obtained when the SWNTs are packed together without a gap between them. Trends in both purification and placement over the past decade suggest the ability to meet their targets before 2020, provided the scientific effort continues (dotted-line trajectories).
Because directly selected growth of s-SWNTs remains a topic of continuing study, the synthetic strategies that offer the greatest potential fall into two categories: (1) purify the SWNTs and then assemble them into arrays; and (2) assemble the SWNTs into arrays and then purify them [74]. The advantage of first one is that it can be built on several recently developed techniques for purification (ultracentrifugation [75, 76], chromatography [77-79] and others [80, 81], Fig. 1.11 shows an example). But the resulting SWNT are typically short, chemically coated or in low degree of alignment [82-84]. The second method can overcome these limitations by using chemical vapor deposition on quartz to yield nearly perfect alignment (>99.99% of SWNTs within 0.01°), long arrays (100 μm and up to millimeters) and chemically pristine SWNTs [85-87]. The main difficulty comes with this method includes incomplete removal of m-SWNTs, degradation of s-SWNTs and some uncertain mechanism [88-90]. Furthermore, when considering purification schemes, it is also important that they should be cost-effective, scalable, nondestructive to remaining s-SWNTs and iteratively repeatable [64].
1.3.3 Thermocapillary enhanced purification of SWNTs

Jin et al. [74] introduced a superb purification technique that is combined with a modest density of SWNTs at an inconsistent pitch. Final approaches for achieving both less than 0.0001% of m-SWNTs and a SWNT density of more than 125 SWNTs per micrometer with consistent pitch must be compatible. They developed a method in which the nanoscale thermocapillary flows in thin-film organic coatings followed by reactive ion etching serve as highly efficient means for selectively removing metallic carbon nanotubes from electronically heterogeneous aligned arrays grown on quartz substrates. The low temperatures and unusual physics associated with this process enable robust, scalable operation, with clear potential for practical use.
As shown in Fig. 1.12, in their approach films coated onto aligned arrays of SWNTs undergo flow only at regions of selective current injection, and Joule heating, at the m-SWNT. This process creates openings that allow removal of the m-SWNTs by gas phase etching, in a manner that leaves the semiconducting SWNTs unaltered. To fully understand the underlying physics associated with the process, an analytical thermo-mechanical model as well as the finite element model is developed in Ch. 4.

1.4 In this dissertation

Chapter 1 provides a general overview of properties of graphitic materials, especially for graphene and SWNTs. Furthermore, the graphene/h-BN heterostructure and the purification of SWNTs are introduced as well.

Chapter 2 develops a continuum framework for the cohesive law due to the van der Waals force for the interface between graphene and h-BN.
Chapter 3 discusses the periodic patterns and energy states of buckled graphene on h-BN substrate. Five different buckling modes are studied by comparing the total energies.

Chapter 4 takes a deep view into the thermocapillary enhanced purification of SWNTs. An analytical model, as well as a fully coupled thermo-mechanical-fluid finite element model, is developed to understand the underlying physics associated with the thermocapillary flow.

Chapter 5 provides an overview of this work and discusses the directions for future works.
Chapter 2

A cohesive law for the interfaces in the graphene/hexagonal boron nitride heterostructures

2.1 Introductory remarks

Since its fabrication, identification and characterization in 2004 [4], graphene has been stimulating scientists’ and engineers’ imagination and passion for nanoscience and nanotechnology. Owing to its fascinating electrical, thermal, and mechanical properties, graphene has shown great promise for a multitude of applications, ranging from flexible and invisible displays, nanoelectronic components, nanosensors, to energy conversion and storage devices. Although the feasibility of constructing free-standing graphene sheet has been demonstrated [12-14], most applications will either require graphene to be grown on [15-17] or transferred [18-20] to a supporting substrate. However, the presence of substrates leads to a significant reduction in electron mobility [14, 21, 22] from ~100,000 cm²V⁻¹s⁻¹ to ~1,000 cm²V⁻¹s⁻¹ due to the charged surface states and impurities [23-26], surface roughness [27, 28] and surface optical phonons [29, 30]. One solution to allow a substrate-supported geometry while retaining the quality achieved with a suspended sample is to use graphene/h-BN heterostructure, where h-BN serves as a dielectric layer between graphene and substrate to reduce the substrate influences on graphene. The h-BN’s strong in-plane bonds, large band gap, and planar structure provide an ideal flat, insulating and inert surface, isolating the graphene from the substrate [32-34]. It is shown that graphene/h-BN heterostructure exhibits electron mobility as high as

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1 Significant portions of this chapter were published as “A Cohesive Law for Interfaces in Graphene/Hexagonal Boron Nitride Heterostructure Due to the van der Waals Force,” C. Zhang, J. Luo and J. Song, Journal of Applied Physics 115, 144308 (2014). Reproduced with permission from the journal.
\( \approx 60,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \), which is an order of magnitude higher than the commonly reported substrate-supported graphene [35].

The use of graphene/h-BN heterostructure for graphene electronics has attracted much interest from science and engineering communities. Most of the existing studies on graphene/h-BN heterostructure focus on the electrical [35-42], magnetic [43, 44] and thermal properties [45], as well as its behaviors when applied in field effect transistor [46, 47]. In order to utilize graphene/h-BN heterostructure in graphene electronics, mechanical properties of this heterostructure are critical because it is to be used as structural and functional components in electronics. Moreover, mechanical properties (or deformations) of graphene/h-BN are strongly tied to its electrical performance. Therefore, understanding the mechanical properties of graphene/h-BN, where the interface plays a key role, is crucial in enabling future high-quality graphene applications such as stretchable electronics. Although interfacial sliding and/or buckling of graphene on polymer substrates have been observed experimentally [48-50], the studies on mechanical modeling for interfaces in graphene/h-BN heterostructure are rarely seen. The objective of this chapter is to study graphene/h-BN heterostructure to understand the interaction between graphene and h-BN.

Section 2.2 describes the deriving procedure of the cohesive law for graphene/monolayer h-BN heterostructure. Section 2.3 describes how to extend it to multi-layer h-BN model. After having analytical cohesive law for graphene/multi-layer h-BN heterostructure, an approximate method is given in Sec. 2.4, which has much simpler expression and good approximation. Conclusions are given in Sec. 2.5.
2.2 Cohesive law for graphene/monolayer h-BN

Jiang et al. [51] developed a cohesive zone model directly from the van der Waals interactions for interfaces between SWNTs and polymer–matrix. It gives the relation between the normal (and shear) traction(s) and the opening (and sliding) displacement(s) across the interface in terms of parameters for the van der Waals interactions. Such a cohesive law provides the link between the nanoscale cohesive law and macroscopic properties of composite materials. Lu et al. [52, 53] extended Jiang et al.’s cohesive law to interfaces between graphene sheets in MWNTs and that between MWNTs and polymer–matrix.

Based on the approaches of Jiang et al. and Lu et al. [51-53], both graphene and monolayer h-BN are modeled as homogenized solids and infinitely large in the in-plane directions. The interlayer bonding between graphene and h-BN is due to van der Waals interaction [54], which is usually represented by the Lennard-Jones 6-12 potential

\[ V(r) = 4\varepsilon\left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6}\right), \quad (2.1) \]

where \( V(r) \) is the energy between a pair of atoms of distance \( r \), \( \sqrt[6]{2}\sigma \) is the equilibrium distance between two atoms and \( \varepsilon \) is the bond energy at the equilibrium distance. For a pair of carbon and nitrogen atoms, the bond energy and equilibrium distance are \( \varepsilon_{C-N} = 0.004068 \text{ eV} \) and \( \sigma_{C-N} = 0.3367 \text{ nm} \), respectively. For a pair of carbon and boron atoms, they are \( \varepsilon_{C-B} = 0.003294 \text{ eV} \) and \( \sigma_{C-B} = 0.3411 \text{ nm} \) [91].

To describe van der Waals interactions between graphene and monolayer h-BN, both graphene and monolayer h-BN are modeled as a homogenous layer with
\[ \rho_c = \frac{4}{3\sqrt{3}l_c^2} \] denoting the number of carbon atoms per unit area on graphene and

\[ \rho_N = \rho_B = \frac{2}{3\sqrt{3}l_{h-BN}^2} \] denoting the number of the nitrogen and boron atoms per unit area on h-BN. Here \( l_c \) and \( l_{h-BN} \) are the equilibrium bond length of graphene and h-BN. Let \( h \) denote the equilibrium distance between these two layers. The distance between a carbon atom on graphene and an atom (nitrogen or boron) on h-BN is \( r = \sqrt{h^2 + z^2} \), where \( z \) is the projected distance between the two atoms on each layer (shown in Fig. 2.1).

![Figure 2.1 Schematic diagram of graphene/monolayer h-BN.](image)

The cohesive energy \( \Phi \) is the energy per unit area and is given by

\[ \Phi_{\text{graphene/h-BN}} = \Phi_{C-N} + \Phi_{C-B}, \]  
(2.2)

where \( \Phi_{C-N} \) and \( \Phi_{C-B} \) are the energy due to the interaction between carbon and nitrogen atoms, and carbon and boron atoms, respectively, and they are given by

\[ \Phi_{C-N} = 2\pi \rho_c \rho_N \int_0^\infty \tilde{V}_{C-N}(r) \, dz = 2\pi \rho_c \rho_N \sigma_{C-N}^2 \left( \frac{2\sigma_{C-N}^{10}}{5h^{10}} - \frac{\sigma_{C-N}^4}{h^4} \right), \]  
(2.3)

and

\[ \Phi_{C-B} = 2\pi \rho_c \rho_B \int_0^\infty \tilde{V}_{C-B}(r) \, dz = 2\pi \rho_c \rho_B \sigma_{C-B}^2 \left( \frac{2\sigma_{C-B}^{10}}{5h^{10}} - \frac{\sigma_{C-B}^4}{h^4} \right). \]  
(2.4)
Minimization of the total cohesive energy, $\frac{\partial \Phi_{\text{graphene/h-BN}}}{\partial h} = 0$, gives the equilibrium distance $h_e$ as

$$h_e = \left( \frac{\varepsilon_{C-N} \sigma_{C-N}^{12} + \varepsilon_{C-B} \sigma_{C-B}^{12}}{\varepsilon_{C-N} \sigma_{C-N}^{6} + \varepsilon_{C-B} \sigma_{C-B}^{6}} \right)^{\frac{1}{5}}. \quad (2.5)$$

Figure 2.2 The monolayer h-BN is subjected to the opening displacement $v$ and sliding displacement $u$.

For the opening displacement $v$ and sliding displacement $u$ beyond the equilibrium distance $h_e$, as shown in Fig. 2.2, the cohesive energy can be similarly obtained as

$$\Phi_{\text{graphene/h-BN}}(u, v) = 2\pi \rho_C \rho_N \varepsilon_{C-N} \sigma_{C-N}^{2} \left( \frac{2\sigma_{C-N}^{10}}{5(h_e + v)^{10}} - \frac{\sigma_{C-N}^{4}}{(h_e + v)^{4}} \right) + 2\pi \rho_C \rho_B \varepsilon_{C-B} \sigma_{C-B}^{2} \left( \frac{2\sigma_{C-B}^{10}}{5(h_e + v)^{10}} - \frac{\sigma_{C-B}^{4}}{(h_e + v)^{4}} \right). \quad (2.6)$$

This leads to a vanishing shear cohesive stress

$$\tau_{\text{cohesive}} = \frac{\partial \Phi_{\text{graphene/h-BN}}(u, v)}{\partial u} = 0 \quad (2.7)$$

and a tensile cohesive stress
Given the bond length of graphene prior to deformation, $l_c = 0.1408 \text{ nm}$ and h-BN, $l_{h-BN} = 0.1440 \text{ nm}$ [92], the densities are obtained as $\rho_c = 38.80 \text{ nm}^{-2}$ and $\rho_B = 18.56 \text{ nm}^{-2}$. The equilibrium distance between graphene and monolayer h-BN is given by Eq. (2.5) as $h_{G/hBN}^{e} \approx 0.3388 \text{ nm}$. Figure 2.3 shows the cohesive stress versus the opening displacement for graphene and monolayer h-BN. The critical separation $\delta_{G/hBN} \approx 0.0476 \text{ nm}$ at which the cohesive strength (maximum cohesive stress) is reached as $\sigma_{G/hBN} \approx 2.04 \text{ GPa}$. The total cohesive energy (area underneath the $\sigma_{\text{cohesive}} - \nu$ curve) is $\Phi_{G/hBN} \approx 0.367 \text{ J/m}^2$. 

Figure 2.3 The cohesive stress $\sigma_{\text{cohesive}}$ versus the opening displacement $\nu$ for graphene/monolayer h-BN.
2.3 Cohesive law for graphene/multi-layer h-BN

The cohesive energy for graphene/multi-layer h-BN consists of the van der Waals interactions among h-BN layers and that between graphene and h-BN layers. Figure 2.4 shows the schematic diagram of graphene/multi-layer h-BN with $h_i$ denoting the equilibrium distance between graphene and the $i^{th}$ layer h-BN, $u_i$ and $v_i$ denoting the sliding and opening displacements of $i^{th}$ h-BN layer beyond the equilibrium distance. And $i = 1$ corresponds to the h-BN layer closest to graphene and $i = n$ corresponds to the outmost layer.

![Figure 2.4 Schematic diagram of graphene/multi-layer h-BN.](image)

Similar to the cohesive energy between graphene and monolayer h-BN, the cohesive energy between the $i^{th}$ and $j^{th}$ h-BN ($i < j$) is

\[
\Phi_{i-h-BN/j-h-BN} = 2\pi\rho_N^2 \varepsilon_{N-N}\sigma_{N-N}^2 \left( \frac{2\sigma_{N-N}^{10}}{5(h_j - h_i)^{10}} - \frac{\sigma_{N-N}^4}{(h_j - h_i)^4} \right) + 4\pi\rho_N\rho_B \varepsilon_{N-B}\sigma_{N-B}^2 \left( \frac{2\sigma_{N-B}^{10}}{5(h_j - h_i)^{10}} - \frac{\sigma_{N-B}^4}{(h_j - h_i)^4} \right) + 2\pi\rho_B^2 \varepsilon_{B-B}\sigma_{B-B}^2 \left( \frac{2\sigma_{B-B}^{10}}{5(h_j - h_i)^{10}} - \frac{\sigma_{B-B}^4}{(h_j - h_i)^4} \right) \]  

(2.9)
where \( \varepsilon_{N-N} = 0.006283 \text{ eV} \) and \( \sigma_{N-N} = 0.3365 \text{ nm} \) are the bond energy and equilibrium distance for a pair of nitrogen atoms, \( \varepsilon_{N-B} = 0.005084 \text{ eV} \) and \( \sigma_{N-B} = 0.3409 \text{ nm} \) for a pair of nitrogen and boron atoms, and \( \varepsilon_{B-B} = 0.004117 \text{ eV} \) and \( \sigma_{B-B} = 0.3453 \text{ nm} \) for a pair of boron atoms [91]. For monolayer h-BN and monolayer h-BN, the equilibrium distance can be obtained by minimizing the above energy as \( h_{h\text{BN}/h\text{BN}}^{(e)} \approx 0.3407 \text{ nm} \). The total cohesive energy among all h-BN layers is then obtained by

\[
\Phi_{\text{total } h-BN} = \sum \Phi_{i-h-BN/ j-h-BN} .
\tag{2.10}
\]

Replacing \( h \) in Eq. (2.2) by \( h_i \) gives the cohesive energy between the graphene and \( i^{th} \) h-BN layers

\[
\Phi_{\text{graphene}/i-h-BN} = 2\pi \rho_c \rho_N \varepsilon_{C-N} \sigma_{C-N}^2 \left( \frac{2\sigma_{C-N}^2}{5h_i^{10}} - \frac{\sigma_{C-N}^4}{h_i^2} \right) + 2\pi \rho_c \rho_B \varepsilon_{C-B} \sigma_{C-B}^2 \left( \frac{2\sigma_{C-B}^2}{5h_i^{10}} - \frac{\sigma_{C-B}^4}{h_i^2} \right).
\tag{2.11}
\]

The total cohesive energy between the graphene and all h-BN layers is then obtained as

\[
\Phi_{\text{graphene/all h-BN}} = \sum \Phi_{\text{graphene}/i-h-BN} .
\tag{2.12}
\]

The total cohesive energy in graphene/multi-layer h-BN is summation of energy among all h-BN layers in Eq. (2.10) and energy between graphene and all h-BN layers in Eq. (2.12), i.e.,

\[
\Phi_{\text{total}} = \Phi_{\text{graphene/all h-BN}} + \Phi_{\text{total } h-BN} .
\tag{2.13}
\]

The equilibrium distances can be determined by minimizing the energy, \( \partial \Phi_{\text{total}} / \partial h_i = 0 \), which gives
\[ 8\pi\rho_c \rho_n \sigma_{C-NA} \left( \frac{\sigma_{C-N}^5}{h_k^5} - \frac{\sigma_{C-N}^{11}}{h_k^{11}} \right) + 8\pi\rho_c \rho_b \sigma_{C-B} \left( \frac{\sigma_{C-B}^5}{h_k^5} - \frac{\sigma_{C-B}^{11}}{h_k^{11}} \right) \]

\[ + 8\pi\rho_n^2 \sigma_{N-N} \sum_{1 \leq k \leq n} \left( \frac{\sigma_{N-N}^5}{(h_j - h_k)^5} - \frac{\sigma_{N-N}^{11}}{(h_j - h_k)^{11}} \right) \]

\[ - 8\pi\rho_n^2 \sigma_{N-N} \sum_{k < j \leq n} \left( \frac{\sigma_{N-N}^5}{(h_j - h_k)^5} - \frac{\sigma_{N-N}^{11}}{(h_j - h_k)^{11}} \right) \]

\[ + 16\pi\rho_n \rho_b \sigma_{N-B} \sum_{1 \leq k \leq n} \left( \frac{\sigma_{N-B}^5}{(h_k - h_j)^5} - \frac{\sigma_{N-B}^{11}}{(h_k - h_j)^{11}} \right) \]

\[ + 8\pi\rho_B^2 \sigma_{B-B} \sum_{1 \leq k \leq n} \left( \frac{\sigma_{B-B}^5}{(h_k - h_j)^5} - \frac{\sigma_{B-B}^{11}}{(h_k - h_j)^{11}} \right) \]

\[ - 16\pi\rho_n \rho_B \sigma_{N-B} \sum_{k < j \leq n} \left( \frac{\sigma_{N-B}^5}{(h_j - h_k)^5} - \frac{\sigma_{N-B}^{11}}{(h_j - h_k)^{11}} \right) \]

\[ - 8\pi\rho_B^2 \sigma_{B-B} \sum_{k < j \leq n} \left( \frac{\sigma_{B-B}^5}{(h_j - h_k)^5} - \frac{\sigma_{B-B}^{11}}{(h_j - h_k)^{11}} \right) \]

\[ = 0 \quad (2.14) \]

for \( 1 \leq k \leq n \), where the terms with \((h_k - h_j)\) and the terms with \((h_j - h_k)\) disappear for the layer next to the graphene \((k = 1)\) and the outmost layer \((k = n)\) respectively.

The numerical solution of the above equations gives the equilibrium distance \(h_1\) between the h-BN and graphene and those between h-BN layers \((h_2 - h_1), (h_3 - h_2), \ldots, (h_n - h_{n-1})\) as

- \( n = 1: h_1 = h_{G/hBN}^{(e)} \);
- \( n = 2: h_1 = 0.995h_{G/hBN}^{(e)}, h_2 - h_1 = 0.996h_{ABN/hBN}^{(e)} \);
- \( n = 3: h_1 = 0.994h_{G/hBN}^{(e)}, h_2 - h_1 = 0.991h_{ABN/hBN}^{(e)}, h_3 - h_2 = 0.994h_{ABN/hBN}^{(e)} \);
- \( \vdots \)
It is observed that the equilibrium distance $h_i$ between the h-BN and graphene is very close to $h_{G/hBN}^{(e)}$ and the equilibrium distances between h-BN layers $(h_2 - h_1)$, $(h_3 - h_2)$, …, $(h_n - h_{n-1})$ are very close to $h_{ABN/hBN}^{(e)}$. As $n$ increases, these distances decrease due to the van der Waals interaction from more h-BN layers. This effect becomes negligible once $n$ is larger than 3, which may suggest that the cohesive law is dominated by the first three h-BN layers.

For the opening displacement $v_i$ and sliding displacement $u_i$ beyond the equilibrium distance $h_i$ $(i = 1, 2, 3, \ldots, n)$, as shown in Figure 3, the cohesive energy can be obtained by replacing $h_i$ with $(h_i + v_i)$ as

$$\Phi_{total}(v) = 2\pi \rho_c \rho_n \sigma_{C-N} \sigma_{C-N}^2 \sum_{1 \leq i < n} \left( \frac{2\sigma_{C-N}^{10}}{5(h_i + v_i)^{10}} - \frac{\sigma_{C-N}^4}{(h_i + v_i)^4} \right)$$

$$+ 2\pi \rho_c \rho_B \sigma_{C-B} \sigma_{C-B}^2 \sum_{1 \leq i < n} \left( \frac{2\sigma_{C-B}^{10}}{5(h_i + v_i)^{10}} - \frac{\sigma_{C-B}^4}{(h_i + v_i)^4} \right)$$

$$+ 2\pi \rho_n \sigma_{N-N} \sigma_{N-N}^2 \sum_{1 \leq i < j \leq n} \left( \frac{2\sigma_{N-N}^{10}}{5(h_j + v_j - h_i - v_i)^{10}} - \frac{\sigma_{N-N}^4}{(h_j + v_j - h_i - v_i)^4} \right)$$

$$+ 4\pi \rho_n \rho_B \sigma_{N-B} \sigma_{N-B}^2 \sum_{1 \leq i < j \leq n} \left( \frac{2\sigma_{N-B}^{10}}{5(h_j + v_j - h_i - v_i)^{10}} - \frac{\sigma_{N-B}^4}{(h_j + v_j - h_i - v_i)^4} \right)$$

$$+ 2\pi \rho_B \sigma_{B-B} \sigma_{B-B}^2 \sum_{1 \leq i < j \leq n} \left( \frac{2\sigma_{B-B}^{10}}{5(h_j + v_j - h_i - v_i)^{10}} - \frac{\sigma_{B-B}^4}{(h_j + v_j - h_i - v_i)^4} \right)$$

(2.15)

$v_i$ for $i = 2, 3, \ldots, n$ can be determined in terms of $v_i$ by energy minimization $\frac{\partial \Phi_{total}(v)}{\partial v_i} = 0$, that is, $v_i = v_i(v_i)$. The cohesive shear stress, $\frac{\partial \Phi_{total}}{\partial u_i}$, is zero since the total cohesive energy does not depend on the sliding displacement. The cohesive tensile stress is given by
\[ \sigma_{\text{cohesive}} = \frac{\partial \Phi_{\text{total}}(v)}{\partial v_1} \]

\[ = 8\pi \rho_N^2 \epsilon_{N-N} \sigma_{N-N} \sum_{1<j,N,h} \left( \frac{\sigma_{N-N}^{11}}{(h_j + v_j - h_i - v_i)^{11}} - \frac{\sigma_N^{5}}{(h_j + v_j - h_i - v_i)^{5}} \right) + 16\pi \rho_N \rho_B \epsilon_{N-B} \sigma_{N-B} \sum_{1<j,B,N,h} \left( \frac{\sigma_{N-B}^{11}}{(h_j + v_j - h_i - v_i)^{11}} - \frac{\sigma_{N-B}^{5}}{(h_j + v_j - h_i - v_i)^{5}} \right) + 8\pi \rho_B^2 \epsilon_{B-B} \sigma_{B-B} \sum_{1<j,B,N,h} \left( \frac{\sigma_{B-B}^{11}}{(h_j + v_j - h_i - v_i)^{11}} - \frac{\sigma_{B-B}^{5}}{(h_j + v_j - h_i - v_i)^{5}} \right) - 8\pi \rho_C \rho_N \epsilon_{C-N} \sigma_{C-N} \left( \frac{\sigma_{C-N}^{11}}{(h_i + v_i)^{11}} - \frac{\sigma_{C-N}^{5}}{(h_i + v_i)^{5}} \right) - 8\pi \rho_C \rho_B \epsilon_{C-B} \sigma_{C-B} \left( \frac{\sigma_{C-B}^{11}}{(h_i + v_i)^{11}} - \frac{\sigma_{C-B}^{5}}{(h_i + v_i)^{5}} \right). \] (2.16)

This is the cohesive law for graphene/multi-layer h-BN due to the van der Waals force.

### 2.4 Approximate solutions of cohesive law for graphene/multi-layer h-BN

Figure 2.5 shows the cohesive stress \( \sigma_{\text{cohesive}} \) versus the opening displacement \( v_1 \) for graphene/multi-layer h-BN with 1, 2, 3 and 10 h-BN layers. It is noted that the result for \( n=10 \) is almost equal to that for \( n=3 \) (error < 0.5%), which suggests that the cohesive law is dominated by the first three h-BN layers closest to the graphene. The maximum cohesive stress and total cohesive energy are 2.04 GPa and 0.367 J/m\(^2\) for one h-BN layer, 2.20 GPa and 0.405 J/m\(^2\) for two h-BN layers and converge to 2.23 GPa and 0.416 J/m\(^2\) for three or more h-BN layers.
Figure 2.5 (a) The cohesive stress $\sigma_{\text{cohesive}}$ versus the opening displacement $v_1$ for graphene/multi-layer h-BN with 1, 2, 3, and 10 h-BN layers; (b) illustration of the dashed area in (a).

The cohesive law in Eq. (2.16) can be simplified by introducing the following three assumptions:
• \( v_i = v_i \) where \( i = 2, 3, \ldots, n \);

• \( h_i = \tilde{h}_{G/hBN} = \frac{\sigma_{C-N} + \sigma_{C-B}}{2} \) (error < 0.7%);

• \( h_i - h_{i-1} = \tilde{h}_{hBN/hBN} = \frac{\sigma_{N-N} + \sigma_{N-B} + \sigma_{B-B}}{3} \) (error < 1.4%) where \( i = 2, 3, \ldots, n \).

The cohesive stress then becomes

\[
\sigma_{\text{cohesive}} \approx -8\pi \rho_c \rho_N \varepsilon_{C-N} \sigma_{C-N} \sum_{1 \leq i \leq n} \left\{ \frac{\sigma_{C-N}^{11}}{\tilde{h}_{G/hBN} + (i-1)\tilde{h}_{hBN/hBN} + v_i} \right\} - \frac{\sigma_{C-B}^{5}}{\tilde{h}_{G/hBN} + (i-1)\tilde{h}_{hBN/hBN} + v_i} \left[ \tilde{h}_{G/hBN} + (i-1)\tilde{h}_{hBN/hBN} + v_i \right]^{11}
\]

\[
-8\pi \rho_c \rho_B \varepsilon_{C-B} \sigma_{C-B} \sum_{1 \leq i \leq n} \left\{ \frac{\sigma_{C-B}^{11}}{\tilde{h}_{G/hBN} + (i-1)\tilde{h}_{hBN/hBN} + v_i} \right\} - \frac{\sigma_{C-B}^{5}}{\tilde{h}_{G/hBN} + (i-1)\tilde{h}_{hBN/hBN} + v_i} \left[ \tilde{h}_{G/hBN} + (i-1)\tilde{h}_{hBN/hBN} + v_i \right]^{11}.
\]

Expressed (2.17).

Figure 2.6 shows the cohesive law of graphene/multi-layer h-BN for \( n = 2 \) and 3 from the exact solution in Eq. (2.16) and the approximate solution in Eq. (2.17). The approximate solution has a good agreement with the accurate solution.
2.5 Conclusive discussions

In summary, we have established the cohesive law for interfaces between graphene and monolayer or multi-layer h-BN based on the van der Waals force. The cohesive law is obtained in terms of the area density of carbon atoms on the graphene and those of boron and nitrogen atoms on the h-BN layer, number of h-BN layer and the parameters in van der Waals interaction. It is shown that the cohesive law in the graphene/multi-layer h-BN model is dominated by the first three h-BN layers which are closest to graphene. An approximate solution for the cohesive law is also obtained to give simpler expression. For graphene/h-BN heterostructure with more than three layers of h-BN, only the summation for $i = 1, 2$ and 3 are needed since the contribution of further layers can be neglected.
Chapter 3

Periodic patterns and energy states of buckled graphene on hexagonal boron nitride substrate

3.1 Introductory remarks

Since its discovery, Graphene has attracted wide attention for both fundamental physics and potential applications ranging from flexible and invisible displays, nanoelectronic components and nanosensors to energy conversion and storage devices due to its fascinating electrical, thermal and mechanical properties [4, 12-14]. Most graphene applications require a supporting substrate (e.g., SiC and SiO\textsubscript{2}) [15-20], which leads to a significant reduction in electron mobility due to the charged surface states and impurities, surface roughness and surface optical phonons [23-30]. Recently, hexagonal boron nitride (h-BN) has been proposed as an ideal substrate for graphene devices due to h-BN’s atomically flat structure with little dangling bonds and charge traps [35]. It is shown that graphene/h-BN heterostructures exhibit much higher electron mobility, less intrinsic doping and improved on/off ratio than conventional graphene devices on SiO\textsubscript{2} substrate [93-97]. Due to the reduced interaction of graphene with h-BN substrate, graphene/h-BN is also an ideal system to study intrinsic physical properties of graphene. Although the electrical, magnetic and thermal properties of graphene/h-BN heterostructure have been extensively explored [35, 36-45], its mechanical properties have been rarely explored thus far. In particular, strain has been used to tune the electrical properties (e.g., band gap) of graphene for graphene electronics [98-104]. Recently, Yoon

\[ \text{Significant portions of this chapter have been submitted as “Periodic Buckling Patterns of Graphene/Hexagonal Boron Nitride Heterostructure,” C. Zhang, J. Song and Q. Yang, Nanotechnology before this dissertation is submitted.} \]
et al. [57] realized an equi-biaxial compression in graphene on SiO$_2$ due to their thermal expansion coefficient mismatch although the deformation of graphene was not well understood. Pan et al. [58] studied biaxial compressive strain in graphene/h-BN heterostructures and found that the strain is spatially inhomogeneous with the occurrence of bubbles due to the existence of defects. Some questions still remain unknown for an ideal graphene/h-BN heterostructure under biaxial compression. For example, can the graphene/h-BN heterostructure buckle as the compression increases? What is the condition for buckling? What is the buckling mode? etc. These questions are very critical since the deformation of graphene is strongly tied to its electrical performance (e.g., electron mobility and band gap) [31, 55, 56].

It is shown that the film bonded to a substrate under equi-biaxial compression may buckle into several intriguing periodic buckling patterns such as one-dimensional, square checkerboard, hexagonal, triangular and herringbone modes as shown schematically in Fig. 3.1. Many researchers have investigated these periodic buckling modes. For example, Chen and Hutchinson [59] and Song et al. [60] developed an energy method with the total energy including the film energy and substrate energy to study one-dimensional, square checkerboard and herringbone mode and they showed that the herringbone mode has the lowest energy in the buckled state while the one-dimensional mode has the greatest. Audoly and Boudaoud [61] explored further details of these modes including the transition from one-dimensional mode to the herringbone mode as the compression is not equi-biaxial. Cai et al. [62] established an analytical upper-bond method and performed a full numerical analysis to study the energy of all these periodic patterns in the buckled state. It is found that the square checkerboard mode has lowest
energy in small strain state (larger than the critical buckling strain) and the herringbone mode is dominant in relatively large strain state. However, experimental observations have apparent conflicts with the theoretical results [62]. The hexagonal mode was observed in small strain state other than checkerboard. And the triangular mode had not been observed, which has precisely the same energy as the hexagonal mode. They suggested that mode selection based on minimum energy considerations has its limitations: initial imperfections may play a role in mode selection given the small difference in energy between the modes when the strain is small. They also explained that once a periodic mode pattern develops, there is a barrier to its evolving to another mode even if the other mode has lower energy.

The objective of this chapter is to study the deformation (or buckling behavior) of graphene/h-BN heterostructure under equi-biaxial compression analytically. All five possible periodic patterns (i.e., one-dimensional, square checkerboard, hexagonal, triangular and herringbone modes) are considered. This chapter is outlined as follows. An energy method is developed in Sec. 3.2 to obtain the total energy of the buckled state of graphene/h-BN heterostructures. Different from the system of a film perfectly bonded to a substrate, where the total energy includes the film energy and substrate energy, the graphene/h-BN has film energy and cohesive energy due to the van der Waals interaction at the interface but not the substrate energy since the substrate could be assumed to be a rigid body [63, 105]. The analytical solutions for the five periodic buckling modes are presented in Sec. 3.3. Section 3.4 describes the results and discussions.
Figure 3.1 Schematics of mode shapes: (a) one-dimensional mode; (b) square checkerboard mode; (c) hexagonal mode; (d) equilateral triangular mode; and (e) herringbone mode.
3.2 An energy method for buckling analysis

We develop an energy method to determine the buckling geometry in this section. The total energy of the graphene/h-BN heterostructure consists of the strain energy of graphene and cohesive energy at the interface (or graphene-substrate interaction energy) [63, 105]. Minimization of total energy yields the buckling geometry.

3.2.1 The strain energy density of graphene

The graphene is subjected to an equi-biaxial compressive strain \( \varepsilon_{11} = \varepsilon_{22} = \varepsilon_0 \) due to the thermal expansion coefficient mismatch between graphene and substrate, and it buckles once \( \varepsilon_0 \) exceeds a critical value. The graphene is modeled as an elastic Von Karman plate with finite rotation [106]. The strain energy density of graphene consists of the membrane energy density and the bending energy density.

The membrane strain \( \varepsilon_{ij} \) (where \( i, j = 1, 2 \)) is related to the in-plane displacements \( u_i(x_1, x_2) \) and \( u_j(x_1, x_2) \) and out-of-plane displacement \( w(x_1, x_2) \) given by

\[
\varepsilon_{ij} = \varepsilon_{ij}^0 + \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) + \frac{1}{2} \left( \frac{\partial w}{\partial x_i} \right) \partial_x^j \partial_x^j,
\]

where \( \varepsilon_{ij}^0 \) is the initial strain and \( i, j = 1, 2 \). The Hooke’s law gives the membrane force in the graphene as

\[
N_{ij} = E t \left[ (1 - \nu) \varepsilon_{ij} + \nu \left( \varepsilon_{11} + \varepsilon_{22} \right) \delta_{ij} \right],
\]

where \( E = \frac{E}{(1 - \nu^2)} \) is the plane-strain modulus of graphene, \( \nu \) is the Poisson's ration of graphene, \( t \) is the thickness of graphene and \( \delta_{ij} \) is the Kronecker delta (\( i, j = 1, 2 \)).
The shear tractions at the graphene/h-BN interface are obtained from the force equilibrium as

$$T_i = \frac{\partial N_{yj}}{\partial x_j} = \frac{\partial N_{n_1}}{\partial x_1} + \frac{\partial N_{n_2}}{\partial x_2}. \quad (3.3)$$

It has been shown that the shear stress at the graphene/h-BN interface has a negligible effect on the buckling geometry [107]. The vanishing shear, i.e., $T_1 = 0$ and $T_2 = 0$, yields two governing equations for the in-plane displacements $u_1(x_1, x_2)$ and $u_2(x_1, x_2)$ given the out-of-plane displacement $w(x_1, x_2)$,

$$\left\{ \frac{\partial^2 u_1}{\partial x_1^2} + \frac{1}{2} (1-\nu) \frac{\partial^2 u_1}{\partial x_2^2} + \frac{1}{2} (1+\nu) \frac{\partial^2 u_2}{\partial x_1 \partial x_2} \right\}$$

$$+ \left\{ \frac{\partial w}{\partial x_1} \left[ \left( \frac{\partial^2 w}{\partial x_1^2} \right) + \frac{1}{2} (1-\nu) \left( \frac{\partial^2 w}{\partial x_2^2} \right) \right] + \frac{1}{2} (1+\nu) \left( \frac{\partial w}{\partial x_2} \right) \left( \frac{\partial^2 w}{\partial x_1 \partial x_2} \right) \right\} = 0, \quad (3.4)$$

and

$$\left\{ \frac{\partial^2 u_2}{\partial x_1^2} + \frac{1}{2} (1-\nu) \frac{\partial^2 u_2}{\partial x_2^2} + \frac{1}{2} (1+\nu) \frac{\partial^2 u_1}{\partial x_1 \partial x_2} \right\}$$

$$+ \left\{ \frac{\partial w}{\partial x_2} \left[ \left( \frac{\partial^2 w}{\partial x_1^2} \right) + \frac{1}{2} (1-\nu) \left( \frac{\partial^2 w}{\partial x_2^2} \right) \right] + \frac{1}{2} (1+\nu) \left( \frac{\partial w}{\partial x_1} \right) \left( \frac{\partial^2 w}{\partial x_1 \partial x_2} \right) \right\} = 0. \quad (3.5)$$

Once $u_1(x_1, x_2)$ and $u_2(x_1, x_2)$ are solved, membrane force and membrane strain can be easily obtained by Eq. (3.1) and (3.2). The membrane energy density is then given by

$$\Phi_m = \frac{1}{2} \left( N_{11} \varepsilon_{11} + 2N_{12} \varepsilon_{12} + N_{22} \varepsilon_{22} \right). \quad (3.6)$$

The bending energy density only depends on the out-of-plane displacement and is given by
\[
\Phi_h = \frac{Et^3}{24} \left[ \left( \frac{\partial^2 w}{\partial x_1^2} \right)^2 + \left( \frac{\partial^2 w}{\partial x_2^2} \right)^2 + 2\nu \left( \frac{\partial^2 w}{\partial x_1^2} \right) \left( \frac{\partial^2 w}{\partial x_2^2} \right) + 2(1-\nu) \left( \frac{\partial^2 w}{\partial x_1 \partial x_2} \right)^2 \right].
\] (3.7)

### 3.2.2 The cohesive energy density

The interlayer bonding between graphene and h-BN is due to van der Waals interaction, which is usually represented by the Lennard-Jones 6-12 potential

\[
V(r) = 4\epsilon \left( \frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right),
\] (3.8)

where \( V(r) \) is the energy between a pair of atoms of distance \( r \), \( \xi \sqrt{2} \sigma \) is the equilibrium distance between two atoms and \( \epsilon \) is the bond energy at the equilibrium distance. For a pair of carbon and nitrogen atoms, the bond energy and equilibrium distance are \( \epsilon_{C-N} = 0.004068 \text{ eV} \) and \( \sigma_{C-N} = 0.3367 \text{ nm} \) and \( \epsilon_{C-B} = 0.003294 \text{ eV} \) and \( \sigma_{C-B} = 0.3411 \text{ nm} \) for a pair of carbon and boron atoms [91].

To describe van der Waals interactions between graphene monolayer and h-BN substrate, graphene and h-BN are modeled as homogenous and infinitely large layer and solid (as shown in Fig. 3.2), respectively, with \( \rho_C = \frac{4}{3\sqrt{3}l_C^2} \) denoting the number of carbon atoms per unit area on graphene and \( \rho_N = \rho_B = \frac{2}{3\sqrt{3}l_{h-BN}^2} \frac{l_{h-BN}}{h_{h-BN}} \) denoting the number of the nitrogen and boron atoms per unit volume in h-BN [108]. Here \( l_C = 0.1408 \text{ nm} \) and \( l_{h-BN} = 0.1440 \text{ nm} \) are the equilibrium bond length of graphene and h-BN [92], \( h_{h-BN} = 0.3406 \text{ nm} \) is the inter-layer distance in h-BN. Then we have \( \rho_C = 38.80 \text{ atoms/nm}^2 \) and \( \rho_N = \rho_B = 54.48 \text{ atoms/nm}^3 \).
As shown in Fig. 3.2, the graphene is parallel to the h-BN with $h$ denoting the equilibrium distance. The distance between a carbon atom on graphene and a nitrogen (or boron) atom on h-BN is $r = \sqrt{x^2 + z^2}$, where $z$ is the projected distance between two atoms. The cohesive energy per unit area is then given by

$$\Phi_{\text{graphene}/h\text{-BN}} = \Phi_{C-N} + \Phi_{C-B},$$

where $\Phi_{C-N}$ and $\Phi_{C-B}$ are the energy due to the interaction between carbon and nitrogen atoms, and carbon and boron atoms, respectively, and they are obtained by

$$\Phi_{C-N} = 2\pi \rho_c \rho_N dA \int_{-\infty}^{h} dx \int_{0}^{\infty} V(r) z dz = \frac{2}{3} \pi \rho_c \rho_N \varepsilon_{C-N} \sigma_{C-N}^3 \left( \frac{2\sigma_{C-N}^9}{15h^9} - \frac{\sigma_{C-N}^3}{h^3} \right),$$

and

$$\Phi_{C-B} = 2\pi \rho_c \rho_B dA \int_{-\infty}^{h} dx \int_{0}^{\infty} V(r) z dz = \frac{2}{3} \pi \rho_c \rho_B \varepsilon_{C-B} \sigma_{C-B}^3 \left( \frac{2\sigma_{C-B}^9}{15h^9} - \frac{\sigma_{C-B}^3}{h^3} \right).$$

The equilibrium distance $h_e$ is determined by minimizing the total cohesive energy,

$$\frac{\partial \Phi_{\text{graphene}/h\text{-BN}}}{\partial h} = 0,$$

and is then given by
\[ h_e = \left[ \frac{2}{5} \frac{e_{C-N} \sigma_{C-N}^{12} + e_{C-B} \sigma_{C-B}^{12}}{e_{C-N} \sigma_{C-N}^6 + e_{C-B} \sigma_{C-B}^6} \right]^{\frac{1}{7}}, \]  

which is about 0.2908 nm.

Figure 3.3 The graphene layer is subjected to the out-of-plane displacement \( w \).

For the out-of-plane displacement \( w(x_1, x_2) \) beyond the equilibrium distance \( h_e \), as shown in Fig. 3.3, the cohesive energy density can be similarly obtained as

\[ \Phi_e(w) = \frac{2}{3} \pi \rho_c \rho_b \varepsilon_{C-N} \sigma_{C-N}^3 \left[ \frac{2\sigma_{C-N}^6}{15(h_e + w)^9} - \frac{\sigma_{C-N}^3}{(h_e + w)^3} \right] + \frac{2}{3} \pi \rho_c \rho_b \varepsilon_{C-B} \sigma_{C-B}^3 \left[ \frac{2\sigma_{C-B}^9}{15(h_e + w)^9} - \frac{\sigma_{C-B}^3}{(h_e + w)^3} \right]. \]  

Equation (3.13) can be rewritten as

\[ \Phi_e = \left( C_{C-N}^1 + C_{C-B}^1 \right) \left( \frac{2}{15} \right) \left( \frac{1}{1 + \frac{w}{h_e}} \right)^9 - \left( C_{C-N}^2 + C_{C-B}^2 \right) \left( \frac{1}{1 + \frac{w}{h_e}} \right)^3, \]  

where

\[ C_{C-N}^1 = \frac{2}{3} \pi \rho_c \rho_b \varepsilon_{C-N} \sigma_{C-N}^{12} / h_e^9, \]  

\[ C_{C-N}^2 = \frac{2}{3} \pi \rho_c \rho_b \varepsilon_{C-N} \sigma_{C-N}^6 / h_e^3, \]  

\[ C_{C-B}^1 = \frac{2}{3} \pi \rho_c \rho_b \varepsilon_{C-B} \sigma_{C-B}^{12} / h_e^9, \]  

\[ C_{C-B}^2 = \frac{2}{3} \pi \rho_c \rho_b \varepsilon_{C-B} \sigma_{C-B}^6 / h_e^3. \]
\[
C_{C-B}^2 = \frac{2}{3} \pi \rho C \rho_B \varepsilon_{C-B} \sigma_{C-B}^6 / h_e^3
\] (3.18)

are all constants. For a small \( w / h_e \), the cohesive energy density could be approximate by the Taylor series ignoring the higher order terms, i.e.,

\[
\Phi_c \approx \left( C_{C-N} + C_{C-B} \right) \left[ \frac{2}{15} \left( \frac{w}{h_e} \right)^4 - \frac{1}{3} \left( \frac{w}{h_e} \right)^3 + 6 \left( \frac{w}{h_e} \right)^2 - 10 \left( \frac{w}{h_e} \right) + 15 \right]
\] (3.19)

### 3.2.3 The total energy

The total energy \( U_{total} \) consists of the membrane energy \( U_m \) and bending energy \( U_b \) in graphene and cohesive energy \( U_c \), which can be obtained from the integration of the corresponding energy densities \( \Phi_m \), \( \Phi_b \), and \( \Phi_c \). Minimization of the total energy with respect to the buckling geometry yields solutions for different buckling patterns in Sec. 3.4.

### 3.3 Energies of the buckling modes

The one-dimensional mode, square checkerboard mode, hexagonal mode, equilateral triangular mode and herringbone mode are considered in this section.

#### 3.3.1 One-dimensional mode

The out-of-plane displacement of one-dimensional mode is given by

\[
w = \xi t \cos(kx),
\] (3.20)
where $k$ is the wave number along the $x_1$ direction, $\xi$ is a dimensionless coefficient of amplitude, $t$ is the thickness of graphene monolayer. Therefore $\xi t$ denotes the amplitude.

Substituting $w$ to the governing equations [Eq. (3.4) and (3.5)] of in-plane displacements $u_1(x_1,x_2)$ and $u_2(x_1,x_2)$ yields

$$u_1 = \frac{1}{8} t^2 \xi^2 k \sin(2kx_1), \quad (3.21)$$

$$u_2 = 0. \quad (3.22)$$

The membrane strain can be obtained by Eq. (3.1) as $\varepsilon_{11} = \varepsilon_0 + \xi^2 t^2 k^2 / 4$ and $\varepsilon_{12} = \varepsilon_{21} = \varepsilon_{22} = 0$. The membrane energy, bending energy and cohesive energy per unit area in one-dimensional mode are then obtained analytically by

$$U_m = \frac{1}{2\pi} \int_0^{2\pi} k_x \Phi_{m} dx_1 = \bar{E} t \left[ (1+\nu)\varepsilon_0^2 + \frac{1}{4} \xi^2 t^2 k^2 (1+\nu) \varepsilon_0 + \frac{1}{32} \xi^4 t^4 k^4 \right], \quad (3.23)$$

$$U_b = \frac{1}{2\pi} \int_0^{2\pi} k_x \Phi_{b} dx_1 = \frac{\bar{E} \xi^2 t^5 k^4}{48}, \quad (3.24)$$

$$U_c = \frac{1}{2\pi} \int_0^{2\pi} k_x \Phi_{c} dx_1 = \left( C_{c-N}^1 + C_{c-B}^1 \right) \left( \frac{2}{15} \right) \left[ 1 + \frac{45}{2} \left( \frac{\xi t}{h_c} \right)^2 + \frac{1485}{8} \left( \frac{\xi t}{h_c} \right)^4 \right]$$

$$- \left( C_{c-N}^2 + C_{c-B}^2 \right) \left[ 1 + \frac{6}{2} \left( \frac{\xi t}{h_c} \right)^2 + \frac{45}{8} \left( \frac{\xi t}{h_c} \right)^4 \right]. \quad (3.25)$$

### 3.3.2 Square checkerboard mode

The out-of-plane displacement of generalized square checkerboard mode is given by [62]

$$w = \xi t \cos \left( \frac{1}{\sqrt{2}} kx_1 \right) \cos \left( \frac{1}{\sqrt{2}} kx_2 \right), \quad (3.26)$$
where in both \( x_1 \) and \( x_2 \) directions, wave number is identical as \( \frac{1}{\sqrt{2}} k \). The in-plane displacements \( u_1(x_1, x_2) \) and \( u_2(x_1, x_2) \) can be solved by Eq. (3.4) and (3.5) as

\[
\begin{align*}
  u_1 & = \frac{1}{32\sqrt{2}} \xi^2 t^2 k \sin(\sqrt{2}kx_1 + \sqrt{2}kx_2) + \frac{1}{32\sqrt{2}} \xi^2 t^2 k \sin(\sqrt{2}kx_1 - \sqrt{2}kx_2) \\
  & \quad + \frac{1}{16\sqrt{2}} \xi^2 t^2 k(1 - \nu_f) \sin(\sqrt{2}kx_1), \\
  u_2 & = \frac{1}{32\sqrt{2}} \xi^2 t^2 k \sin(\sqrt{2}kx_1 + \sqrt{2}kx_2) - \frac{1}{32\sqrt{2}} \xi^2 t^2 k \sin(\sqrt{2}kx_1 - \sqrt{2}kx_2) \\
  & \quad + \frac{1}{16\sqrt{2}} \xi^2 t^2 k(1 - \nu_f) \sin(\sqrt{2}kx_2).
\end{align*}
\] (3.27)

The membrane energy, bending energy and cohesive energy per unit area in square checkerboard mode are then given analytically by

\[
\begin{align*}
  U_m & = \frac{1}{8\pi^2} \int_{k=0}^{2\pi} \int_{x_1=0}^{2\pi} \Phi_m dx_1 dx_2 \\
  & = \bar{E} t \left[ (1 + \nu)\varepsilon_0^2 + \frac{1}{8}(1 + \nu)\xi^2 t^2 k^2 \varepsilon_0 + \frac{1}{512}(1 + \nu)(3 - \nu)\xi^4 t^4 k^4 \right],
\end{align*}
\] (3.29)

\[
\begin{align*}
  U_b & = \frac{1}{8\pi^2} \int_{k=0}^{2\pi} \int_{x_1=0}^{2\pi} \Phi_b dx_1 dx_2 \\
  & = \frac{\bar{E} t^2 k^4}{96}.
\end{align*}
\] (3.30)

\[
\begin{align*}
  U_c & = \frac{1}{8\pi^2} \int_{k=0}^{2\pi} \int_{x_1=0}^{2\pi} \Phi_c dx_1 dx_2 \\
  & = \left( C_{C-N}^l + C_{C-B}^l \right) \left( \frac{2}{15} \right) \left[ 1 + \frac{45}{4} \left( \frac{\xi t}{h_c} \right)^2 + \frac{4455}{64} \left( \frac{\xi t}{h_c} \right)^4 \right] \\
  & \quad - \left( C_{C-N}^l + C_{C-B}^l \right) \left[ 1 + \frac{3}{2} \left( \frac{\xi t}{h_c} \right)^2 + \frac{135}{64} \left( \frac{\xi t}{h_c} \right)^4 \right].
\end{align*}
\] (3.31)
### 3.3.3 Hexagonal mode

The out-of-plane displacement of generalized hexagonal mode is given by [62]

\[
\begin{align*}
        w = \xi t \left[ \cos(kx_1) + 2 \cos\left(\frac{1}{2}kx_1\right) \cos\left(\frac{\sqrt{3}}{2}kx_2\right) \right], \\
    \end{align*}
\]

(3.32)

where the wave number is \(\frac{1}{2}k\) along \(x_1\) direction and \(\frac{\sqrt{3}}{2}k\) along \(x_2\) direction. Solving the governing equations of in-plane displacements \(u_i(x_1, x_2)\) and \(u_j(x_1, x_2)\) gives

\[
\begin{align*}
    u_1 &= \frac{1}{16} \xi^2 t^2 k \left(3 - \nu_f\right) \sin \left(\frac{3}{2} kx_1 + \frac{\sqrt{3}}{2} kx_2\right) + \frac{1}{16} \xi^2 t^2 k \left(3 - \nu_f\right) \sin \left(\frac{3}{2} kx_1 - \frac{\sqrt{3}}{2} kx_2\right) \\
        &+ \frac{1}{16} \xi^2 t^2 k \sin \left(kx_1 + \sqrt{3} kx_2\right) + \frac{1}{16} \xi^2 t^2 k \sin \left(kx_1 - \sqrt{3} kx_2\right) \\
        &+ \frac{1}{16} \xi^2 t^2 k \left(1 - 3\nu_f\right) \sin \left(\frac{1}{2} kx_1 + \frac{\sqrt{3}}{2} kx_2\right) + \frac{1}{16} \xi^2 t^2 k \left(1 - 3\nu_f\right) \sin \left(\frac{1}{2} kx_1 - \frac{\sqrt{3}}{2} kx_2\right) \\
        &+ \frac{1}{8} \xi^2 t^2 k \sin \left(2kx_1\right) + \frac{1}{8} \xi^2 t^2 k \left(1 - 3\nu_f\right) \sin \left(kx_1\right), \\
    u_2 &= \frac{\sqrt{3}}{48} \xi^2 t^2 k \left(3 - \nu_f\right) \sin \left(\frac{3}{2} kx_1 + \frac{\sqrt{3}}{2} kx_2\right) - \frac{\sqrt{3}}{48} \xi^2 t^2 k \left(3 - \nu_f\right) \sin \left(\frac{3}{2} kx_1 - \frac{\sqrt{3}}{2} kx_2\right) \\
        &+ \frac{\sqrt{3}}{16} \xi^2 t^2 k \sin \left(kx_1 + \sqrt{3} kx_2\right) - \frac{\sqrt{3}}{16} \xi^2 t^2 k \sin \left(kx_1 - \sqrt{3} kx_2\right) \\
        &+ \frac{\sqrt{3}}{16} \xi^2 t^2 k \left(1 - 3\nu_f\right) \sin \left(\frac{1}{2} kx_1 + \frac{\sqrt{3}}{2} kx_2\right) - \frac{\sqrt{3}}{16} \xi^2 t^2 k \left(1 - 3\nu_f\right) \sin \left(\frac{1}{2} kx_1 - \frac{\sqrt{3}}{2} kx_2\right) \\
        &+ \frac{\sqrt{3}}{24} \xi^2 t^2 k \left(3 - \nu_f\right) \sin \left(\sqrt{3} kx_2\right). \\
\end{align*}
\]

(3.33)

(3.34)

The membrane energy, bending energy and cohesive energy per unit area in hexagonal mode are obtained as
\[
U_m = \frac{1}{16\pi^2/\sqrt{3k^2}} \int_{x_1=0}^{4\pi/k} \int_{x_2=0}^{4\pi/k} \Phi_n dx_1 dx_2
= \bar{E}t \left[ (1 + \nu)\varphi_0^2 + \frac{3}{4} (1 + \nu) \varepsilon_0^2 \varepsilon^2 t^2 k^2 \varphi_0^2 + \frac{3}{128} (1 + \nu)(11 - 5\nu) \varepsilon_0^4 t^4 k^4 \right], \tag{3.35}
\]
\[
U_b = \frac{1}{16\pi^2/\sqrt{3k^2}} \int_{x_1=0}^{4\pi/k} \int_{x_2=0}^{4\pi/k} \Phi_n dx_1 dx_2 = \frac{\bar{E}^2 \varepsilon_0^2 t^2 k^4}{16}, \tag{3.36}
\]
\[
U_c = \frac{1}{16\pi^2/\sqrt{3k^2}} \int_{x_1=0}^{4\pi/k} \int_{x_2=0}^{4\pi/k} \Phi_n dx_1 dx_2
= \left( C_{c-N}^1 + C_{c-B}^1 \right) \left( \frac{2}{15} \right) \left[ 1 + \frac{135}{2} \left( \frac{\xi t}{h_\varepsilon} \right)^2 - \frac{495}{2} \left( \frac{\xi t}{h_\varepsilon} \right)^3 + \frac{22275}{8} \left( \frac{\xi t}{h_\varepsilon} \right)^4 \right]
- \left( C_{c-N}^2 + C_{c-B}^2 \right) \left[ 1 + 9 \left( \frac{\xi t}{h_\varepsilon} \right)^2 - 15 \left( \frac{\xi t}{h_\varepsilon} \right)^3 + \frac{675}{8} \left( \frac{\xi t}{h_\varepsilon} \right)^4 \right]. \tag{3.37}
\]

### 3.3.4 Equilateral triangular mode

The out-of-plane displacement of generalized equilateral triangular mode is given by [62]
\[
w = \xi t \left[ -\sin \left( kx_1 \right) + 2 \sin \left( \frac{1}{2} kx_1 \right) \cos \left( \frac{\sqrt{3}}{2} kx_2 \right) \right], \tag{3.38}
\]
where the wave number is $\frac{1}{2} k$ along $x_1$ direction and $\frac{\sqrt{3}}{2} k$ along $x_2$ direction, as same as those in hexagonal mode. The in-plane displacements are solved as
\[
\begin{align*}
  u_t &= \frac{1}{16} \xi^2 t^2 k (3 - \nu) \sin \left(\frac{3}{2} kx_1 + \frac{\sqrt{3}}{2} kx_2 \right) + \frac{1}{16} \xi^2 t^2 k (3 - \nu) \sin \left(\frac{3}{2} kx_1 - \frac{\sqrt{3}}{2} kx_2 \right) \\
  &\quad - \frac{1}{16} \xi^2 t^2 k \sin \left(kx_1 + \sqrt{3}kx_2 \right) - \frac{1}{16} \xi^2 t^2 k \sin \left(kx_1 - \sqrt{3}kx_2 \right) \\
  &\quad - \frac{1}{16} \xi^2 t^2 k (1 - 3\nu) \sin \left(\frac{1}{2} kx_1 + \frac{\sqrt{3}}{2} kx_2 \right) - \frac{1}{16} \xi^2 t^2 k (1 - 3\nu) \sin \left(\frac{1}{2} kx_1 - \frac{\sqrt{3}}{2} kx_2 \right) \\
  &\quad - \frac{1}{8} \xi^2 t^2 k \sin \left(2kx_1 \right) - \frac{1}{8} \xi^2 t^2 k (1 - 3\nu) \sin \left(kx_1 \right), \quad (3.39) \\
  u_z &= \frac{\sqrt{3}}{48} \xi^2 t^2 k (3 - \nu) \sin \left(\frac{3}{2} kx_1 + \frac{\sqrt{3}}{2} kx_2 \right) - \frac{\sqrt{3}}{48} \xi^2 t^2 k (3 - \nu) \sin \left(\frac{3}{2} kx_1 - \frac{\sqrt{3}}{2} kx_2 \right) \\
  &\quad - \frac{\sqrt{3}}{16} \xi^2 t^2 k \sin \left(kx_1 + \sqrt{3}kx_2 \right) + \frac{\sqrt{3}}{16} \xi^2 t^2 k \sin \left(kx_1 - \sqrt{3}kx_2 \right) \\
  &\quad - \frac{\sqrt{3}}{16} \xi^2 t^2 k (1 - 3\nu) \sin \left(\frac{1}{2} kx_1 + \frac{\sqrt{3}}{2} kx_2 \right) + \frac{\sqrt{3}}{16} \xi^2 t^2 k (1 - 3\nu) \sin \left(\frac{1}{2} kx_1 - \frac{\sqrt{3}}{2} kx_2 \right) \\
  &\quad + \frac{\sqrt{3}}{24} \xi^2 t^2 k (3 - \nu) \sin \left(\sqrt{3}kx_2 \right) . \quad (3.40)
\end{align*}
\]

The membrane energy, bending energy and cohesive energy per unit area in the triangular
mode are obtained as

\[
\begin{align*}
  U_m &= \frac{1}{16\pi^2 / \sqrt{3}k^2} \int_{x_1=0}^{4\pi} \int_{x_2=0}^{4\pi} \Phi_m dx_1 dx_2 \\
  &= \frac{\bar{E}t}{(1 + \nu)e_0^2} + \frac{3}{4} (1 + \nu) \xi^2 t^2 k^2 e_0 + \frac{3}{128} (1 + \nu)(11 - 5\nu) \xi^4 t^4 k^4 , \quad (3.41) \\
  U_b &= \frac{1}{16\pi^2 / \sqrt{3}k^2} \int_{x_1=0}^{4\pi} \int_{x_2=0}^{4\pi} \Phi_b dx_1 dx_2 = \frac{\bar{E} \xi^2 t^4 k^4}{16} , \quad (3.42) \\
  U_c &= \frac{1}{16\pi^2 / \sqrt{3}k^2} \int_{x_1=0}^{4\pi} \int_{x_2=0}^{4\pi} \Phi_c dx_1 dx_2 \\
  &= \left( C_{C-N} + C_{C-B} \right) \left( \frac{15}{2} \right) \left[ 1 + \frac{135}{8} \left( \frac{\xi t}{h_c} \right)^2 + \frac{22275}{8} \left( \frac{\xi t}{h_c} \right)^4 \right] \\
  &\quad - \left( C_{C-N} + C_{C-B} \right) \left[ 1 + \frac{9}{8} \left( \frac{\xi t}{h_c} \right)^2 + \frac{675}{8} \left( \frac{\xi t}{h_c} \right)^4 \right] . \quad (3.43)
\end{align*}
\]
3.3.5 Herringbone mode

The out-of-plane displacement of the herringbone mode $w$ is well approximated by [62]

$$w = \xi_i t \left[ \cos (k_i x_i) - k_i \xi_j t \sin (k_i x_i) \cos (k_j x_j) \right], \quad (3.44)$$

The in-plane displacements can be obtained as

$$u_1 = -\frac{1}{32} t^4 \xi_i^2 \xi_j^2 k_1^3 \sin (2k_i x_i + 2k_j x_j) - \frac{1}{32} t^4 \xi_i^2 \xi_j^2 k_1^3 \sin (2k_i x_i - 2k_j x_j) + \frac{t^3 \xi_i^2 \xi_j^2 k_2^2}{4 (4k_i^2 + k_j^2)^2} \cos (2k_i x_i + k_j x_j)$$

$$+ \frac{t^3 \xi_i^2 \xi_j^2 k_2^2}{4 (4k_i^2 + k_j^2)^2} \cos (2k_i x_i - k_j x_j)$$

$$+ \left[ \frac{t^2 \xi_i^2 k_1}{8} - \frac{1}{16} t^4 \xi_i^2 \xi_j^2 k_1 \left( k_i^2 - \nu k_j^2 \right) \right] \sin (2k_i x_i) - \frac{1}{2} t^3 \xi_i^2 \xi_j^2 k_1^2 \cos (k_j x_j), \quad (3.45)$$

$$u_2 = -\frac{1}{32} t^4 \xi_i^2 \xi_j^2 k_1^2 k_2 \sin (2k_i x_i + 2k_j x_j) + \frac{1}{32} t^4 \xi_i^2 \xi_j^2 k_1^2 k_2 \sin (2k_i x_i - 2k_j x_j)$$

$$+ \frac{t^3 \xi_i^2 \xi_j^2 k_2^2}{4 (4k_i^2 + k_j^2)^2} \cos (2k_i x_i + k_j x_j)$$

$$- \frac{t^3 \xi_i^2 \xi_j^2 k_2^2}{4 (4k_i^2 + k_j^2)^2} \cos (2k_i x_i - k_j x_j)$$

$$- \frac{1}{16} t^4 \xi_i^2 \xi_j^2 k_1^2 \left( \nu k_i^2 - k_j^2 \right) \sin (2k_j x_j). \quad (3.46)$$

The membrane energy, bending energy and cohesive energy per unit area in the herringbone mode are obtained as
The total energy for each mode is the summation of the corresponding membrane energy, bending energy and cohesive energy and it is a function of buckling geometry such as wave number and amplitude. Minimization of the total energy in Matlab with respect to the buckling geometry yields the solution.
3.4 Results and discussion

The graphene buckles once the equi-biaxial compressive strain $\varepsilon_0$ exceeds a critical value, $\varepsilon_c$. It should be noted that the critical strain, $\varepsilon_c$, and the corresponding wave number $k_c$, can be solved analytically by minimizing the total energy for the one-dimensional mode, square checkerboard mode, hexagonal mode and equilateral triangular mode but not for the herringbone mode due to the involvement of too many parameters (i.e., $k_1$, $k_2$, $\xi_1$, $\xi_2$). For example, for one-dimensional mode, by minimizing the total energy $U_{total}$ we can obtain

$$\frac{\partial U_{total}}{\partial k} = 0 = \bar{E}t \left[ \frac{1}{2} \xi^2 t^2 k (1 + \nu) \varepsilon_0 + \frac{1}{8} \xi^4 t^4 k^3 \right] + \frac{\bar{E} \xi^2 t^5 k^3}{12}, \quad (3.50)$$

$$\frac{\partial U_{total}}{\partial \xi} = 0 = \bar{E}t \left[ \frac{1}{2} \xi t^2 k^2 (1 + \nu) \varepsilon_0 + \frac{1}{8} \xi^3 t^4 k^4 \right] + \frac{\bar{E} \xi t^5 k^4}{24}$$

$$+ \left( C_{C-N}^1 + C_{C-B}^1 \right) \left[ 6\xi \left( \frac{t}{h_c} \right)^2 + 99\xi^3 \left( \frac{t}{h_c} \right)^4 \right]$$

$$- \left( C_{C-N}^2 + C_{C-B}^2 \right) \left[ 6\xi \left( \frac{t}{h_c} \right)^2 + \frac{45}{2} \xi^3 \left( \frac{t}{h_c} \right)^4 \right]. \quad (3.51)$$

Let $b_1 = \frac{1}{2} \bar{E}t (1 + \nu)$, $b_2 = \frac{1}{24} \bar{E}t^5$, $b_3 = 6 \left( C_{C-N}^1 + C_{C-B}^1 - C_{C-N}^2 - C_{C-B}^2 \right) \left( \frac{t}{h_c} \right)^2$ and

$$b_4 = \left[ 99 \left( C_{C-N}^1 + C_{C-B}^1 \right) - \frac{45}{2} \left( C_{C-N}^2 + C_{C-B}^2 \right) \right] \left( \frac{t}{h_c} \right)^4$$

so that we can rewrite Eq. (3.51) as

$$\xi^2 = - \frac{b_1 k^2 \varepsilon_0 + b_2 k^4 + b_3}{3b_2 k^4 + b_4}. \quad (3.52)$$
For $\xi = 0$ (pre-buckling state), we have $b_1 k^2 \varepsilon_0 + b_2 k^4 + b_3 = 0$, in which

$$\varepsilon_0 = -\frac{b_1 k^2 + b_3}{b_1 k^2},$$

(3.53)

which reaches a minimum value of $-\frac{2b_2}{b_1}$ when $k^2 = \sqrt{\frac{b_2}{b_1}}$ corresponding to the critical compressive strain and critical wave number as

$$\varepsilon_c = \frac{2\sqrt{Et^3 \left(C_{C-N}^l + C_{C-B}^l - C_{C-N}^2 - C_{C-B}^2\right)}}{(1+\nu)Et h_e},$$

(3.54)

$$k_c = \left[\frac{144 \left(C_{C-N}^l + C_{C-B}^l - C_{C-N}^2 - C_{C-B}^2\right)}{Et^3 h_e^2}\right]^{\frac{1}{4}}.$$

(3.55)

For the solutions beyond the critical strain, no analytical solutions could be found and Matlab is used to find the solutions numerically. We take the representative values $t = 0.34$ nm, $Et = 2203.25$ eV/nm$^2$, $Et^3 = 1.5$ eV, and $\nu = 0.21$ [109], and $\varepsilon_c = 0.0055$ and $k_c = 7.64$ nm$^{-1}$ from Eq. (3.54) and (3.55). They agree well with the numerical simulation by Matlab as shown in Fig. 3.4. It is found that only when the compressive strain is larger than the critical strain, $\varepsilon_c$, there exist a non-zero solution for the magnitude even on a perfectly flat substrate surface. As the compressive strain increases, the predicted amplitude increases while the wave length ($\lambda = 2\pi/k$) decreases. Similar conclusions can also be obtained for other buckling patterns and we will focus on their energies in the following.
Figure 3.4 (a) Amplitude coefficient $\xi$ and (b) wave length $\lambda = 2\pi/k$ of the graphene monolayer versus the magnitude of compressive strain for one-dimensional mode.

Figure 3.5 shows the cohesive energy, bending energy, membrane energy and total energy for each buckling pattern. It is noted that the bending energy becomes non-zero only if the compressive strain is larger than the critical strain, which is quite same for all the buckling modes. When the compressive strain is slightly larger than the critical strain, the graphene may buckle to any buckling pattern since the difference of total energy for the buckling patterns is negligible. In this case, the geometric imperfection plays a key role in selecting the buckling mode. As the compressive strain increases to be much larger than the critical strain, the triangular modes has the highest total energy and the herringbone mode has the lowest total energy due to the significantly reduction in membrane energy, and is therefore the energetically favorable mode. These results are very similar to the system of a thin film perfected bonded to a compliant substrate [59-62] and could be very useful for the strain engineering of graphene.
Figure 3.5 (a) Cohesive energy $U_c$, (b) bending energy $U_b$, (c) membrane energy $U_m$ and (d) total energy $U_{total}$ versus the compressive strain $\varepsilon_0$ applied on graphene monolayer for each buckling mode.

3.5 Summary

We have established an energy method to investigate the one-dimensional, square checkerboard, hexagonal, equilateral triangular and herringbone buckling patterns in a graphene/h-BN heterostructure under equi-biaxial compression. Total energy consisting of cohesive energy, graphene membrane energy and graphene bending energy is obtained analytically for each buckling pattern. It is found that the total energies are quite same for all buckling modes at a compression slightly larger than the critical strain while the
herringbone mode has the lowest total energy at a compression much larger than the critical compression. As compared to other buckling patterns, the herringbone mode significantly reduces the membrane energy of graphene at the expense of slight increase of the graphene bending energy and cohesive energy.
Chapter 4

Modeling of thermocapillary flow to purify single-walled carbon nanotubes

4.1 Background information

Owning to their exceptional electrical properties such as high carrier mobility and current switching ratios [110-112], single-walled carbon nanotubes (SWNTs) are very attractive in the electronic materials research community for wide applications in logic transistors/circuits [113-119], radiofrequency transistors [70, 120-124], optoelectronic devices [125-127] and sensors [128-130]. The ideal configuration of SWNTs is horizontally aligned arrays of purely semiconducting SWNTs (s-SWNTs), which could provide transport pathways from source to drain with effective performance that greatly exceeds that of randomly oriented SWNTs due to absence of tube-to-tube junctions [111, 131]. However, SWNTs are grown as a mixture of both metallic and semiconducting tubes by any production process currently available, which largely hamper their practical application to electronics.

Existing techniques of creating horizontally aligned arrays of purely semiconducting SWNTs fall into two categories. The first is to purify the SWNTs and then assemble them into arrays, and includes ultracentrifugation [75, 76], chromatography [77-79] and others. These approaches have been shown to provide capabilities in yielding s-SWNTs in arrays, but the resulting s-SWNTs are typically short,

\[ \text{Significant portions of this chapter have been submitted as “Modeling of Thermocapillary Flow to Purify Single-Walled Carbon Nanotubes,” J. Song, C. Lu, C. Zhang, S. H. Jin, Y. Li, S. N. Dunham, X. Xie, F. Du, Y. Huang and J. A. Rogers, Soft Matter before this dissertation is submitted. Some portions of this chapter were published as “Fundamental Effects in Nanoscale Thermocapillary Flow,” S. H. Jin, J. Song, H. U. Chung, C. Zhang, S. N. Dunham, X. Xie, F. Du, T. Kim, J. Lee, Y. Huang and J. A. Rogers, Journal of Applied Physics 115, 054315 (2014). Reproduced with permission from the journal. This work was highly collaborative. I was not involved in the experiments. That content is included because it provides critical context to the theoretical analysis.} \]
chemically coated and in low degrees of alignment [80-84]. The second is to produce the SWNT into arrays with nearly perfect alignment (> 99.9% of SWNTs within 0.01° of the preferred growth direction) through chemical vapor deposition (CVD) based growth on quartz substrate [131, 132] and then purify them. The removal of metallic SWNTs (m-SWNTs) is the main challenge to use such arrays in demanding semiconducting applications. Various techniques based on electrical [89], chemical [90, 133, 134] or optical [88] effects of SWNTs attempt to overcome this challenge, but none could approach the purity requirement in semiconducting applications (> 99.9999% s-SWNTs) [135].

![Figure 4.1 Schematic illustration of main stages in the process of thermocapillary enhanced purification of SWNTs.](image)

Recently, Jin et al. [74] introduced a superb purification technique referred as thermocapillary enabled purification (TcEP) to enable complete, large-scale elimination of m-SWNTs and exceed the purity requirement. Figure 4.1 shows the schematic illustration of the purification process. A partial top-gate transistor structure is fabricated on the SWNT arrays grown on a quartz substrate. Uniform thermal evaporation forms an ultrathin (~25 nm) amorphous film of a small-molecule organic species α,α',α″-Tris(4-
hydroxyphenyl)-1-ethyl-4-isopropylbenzene (i.e. MG2OH) on the top of SWNT arrays. The transistor structure then induce current flow and associated Joule heating only in m-SWNTs, which drive mass transport in the thin film and form local trenches above the m-SWNTs. Reactive ion etching physically eliminates the m-SWNTs, which are all exposed in this manner, while leaves the s-SWNTs unaltered. Removing the thin film and electrode structures completes the process to yield arrays of only s-SWNTs in configurations well suited for planar integration into diverse classes of devices and sensors that demand, or benefit from, exclusively semiconducting operation. Figure 4.2(a) shows an AFM image of a m-SWNT coated with thin film (~ 25 nm) after Joule heating (~ 1.77 W/m) with substrate temperature 348 K for 70 minutes. A typical cross-sectional trench profile extracted from experimental measurement is shown in Fig. 4.2(b). The key parameters associated with the trench profile, trench width $W_{tc}$ and trench depth $H_{tc}$, are also defined.
Figure 4.2 (a) An AFM image of a SWNT coated with thin film (~ 25 nm) after Joule heating (~ 1.77 W/m) with substrate temperature 348 K for 70 minutes; (b) A typical cross-sectional trench profile extracted from experimental measurement.

A full understanding of the physics associated with this process is critical for further optimization and use of this physics, not only in purification of SWNTs, but also in nanolithography, device fabrication and other areas as well. Our objective is to develop an analytical model as well as a fully coupled thermo-mechanical-fluid numerical model to study this process. Although some major physics of the thermocapillary flow have been explored in Jin et al.'s work [74], the focus of this paper, in addition to provide details of models, aims at establishing a scaling law for the trenches in terms of geometrical parameters (e.g., film thickness), material properties (e.g., surface tension coefficient and viscosity) and loading parameters (e.g., power density) to provide guidelines to optimize the trench geometry, which is important for the formation of a s-SWNT array with large densities required in semiconducting applications.
This chapter is outlined as follows. The thermal modeling for temperature distribution is developed in Sec. 4.2, while the modeling of thermocapillary flow to form trenches is presented in Sec. 4.3. A scaling law for the thickness profile is established in Sec. 4.4. The results and discussion are given in Sec. 4.5.

4.2 Thermal modeling for temperature distribution

In this section, we describe procedures to determine the temperature distribution resulting from a SWNT embedded in a thin film of MG2OH with thickness \( h_f \) on a quartz substrate with power dissipation per unit length \( Q_0 \) as shown in Fig. 4.3(a). Because the thickness of quartz substrate, \( \sim 10 \) mm, is much larger than that of film (\( \sim 25 \) nm), it is modeled as a semi-infinite substrate. The origin of the coordinate system \((x, y, z)\) is located at the center of the SWNT with \( x \) along the direction normal to the SWNT axis, \( y \) along the SWNT axis, and \( z \) pointing from quartz substrate to the MG2OH film. Due to the large aspect ratio of SWNT (i.e., the length \( \sim 10 \) µm and the diameter \( \sim 1 \) nm), the SWNT can be modeled as an \( L \)-long line heat source. The resulting temperature rise can then be obtained by integrating the one due to a point heat source, which is to be obtained below from the solution due to a circular disk heat source as shown in Fig. 4.3(b). The temperature rise from the ambient temperature \( \Delta T_d = T_d - T_\infty \) due to a circular disk heat source with radius \( r_0 \) satisfies the steady-state heat conduction equation

\[
\frac{\partial^2 \Delta T_d}{\partial r^2} + \frac{1}{r} \frac{\partial \Delta T_d}{\partial r} + \frac{\partial^2 \Delta T_d}{\partial z^2} = 0, \tag{4.1}
\]

where \((r, z)\) are the cylindrical coordinates with the origin at the center of the heat source [Fig. 4.3(b)].
The finite element analysis shows that the heat losses from radiation and
convection are negligible. The top surface of film \((z = h_f)\) can be assumed to be thermal
insulation which gives

\[-k_f \frac{\partial \Delta T_d}{\partial z} \bigg|_{z=h_f} = 0, \tag{4.2}\]

where \(k_f\) is the thermal conductivity of thin film. Across the film/substrate interface
\((z = 0)\), the temperature is continuous

\[\Delta T_d \big|_{z=0^-} = \Delta T_d \big|_{z=0^+}, \tag{4.3}\]

and the heat flux is also continuous except the region of heat source \((z = 0, r \leq r_0)\)

\[-k_f \frac{\partial \Delta T_d}{\partial z} \bigg|_{z=0^-} + k_s \frac{\partial \Delta T_d}{\partial z} \bigg|_{z=0^-} = \begin{cases} 0 & r > r_0 \\ \frac{P}{\pi r_0^2} & 0 \leq r \leq r_0 \end{cases}, \tag{4.4}\]

with \(k_s\) as the thermal conductivity of substrate and \(P\) as the total power of the disk heat
source. The ambient temperature at the bottom surface of substrate \((z = -\infty)\) gives

\[\Delta T_d \big|_{z=-\infty} = 0. \tag{4.5}\]
The Hankel transform \( \Delta T_d(\xi, z) = \int_0^\infty \Delta T_d(r, z) J_0(\xi r) r \, dr \) of the steady-state heat conduction Eq. (4.1) gives the following ordinary differential equation,

\[
\frac{d^2 \Delta T_d}{dz^2} - \xi^2 \Delta T_d = 0.
\]  

(4.6)

where \( J_0 \) is the 0\(^{th} \) order Bessel function of the first kind. The equation above has the solution

\[
\Delta T_d(\xi, z) = A(\xi) e^{-\xi z} + B(\xi) e^{\xi z}.
\]

(4.7)

where \( A(\xi) \) and \( B(\xi) \) are to be determined and are denoted by \( A_f \) and \( B_f \) for film, and \( A_s \) and \( B_s \) for the substrate, respectively. The Hankel transform of the boundary and continuity conditions in Eq. (4.2)-(4.5) yields

\[ A_f e^{-\xi z} - B_f e^{\xi z} = 0, \]  

(4.8)

\[ A_f + B_f = A_s + B_s, \]  

(4.9)

\[ k_f \xi (A_f - B_f) - k_s \xi (A_s - B_s) = \frac{PJ_1(\xi r_0)}{\pi r_0 \xi}, \]  

(4.10)

\[ A_s = 0, \]  

(4.11)

where \( J_1 \) is the 1\(^{st} \) order Bessel function of the first kind. Solving Eq. (4.8)-(4.11) yields

\[
\begin{bmatrix}
  A_f \\
  B_f \\
  A_s \\
  B_s
\end{bmatrix} = \begin{bmatrix}
  P J_1(\xi r_0) \\
  2\pi k_f r_0^2 \left[ \cosh(\xi h_f) + \frac{k_f}{k_s} \sinh(\xi h_f) \right] \\
  e^{\xi h_f} \\
  e^{-\xi h_f} \\
  0 \\
  2\cosh(\xi h_f)
\end{bmatrix},
\]

(4.12)

The inverse Hankel transform \( \Delta T_d(r, z) = \int_0^\infty \Delta T_d(\xi, z) J_0(\xi r) \xi d\xi \) then gives the temperature distributions in the film \( \Delta T_d^f(r, z) \) and substrate \( \Delta T_d^s(r, z) \) due to the disk
heat source as

\[ \Delta T_d^\text{film} (r, z) = \frac{P}{\pi k, r_0} \int_0^\infty J_1(\xi r_0) J_0(\xi r) \cosh \left[ \frac{\xi (h_f - z)}{k_f} \right] \frac{\cosh (\xi h_f) + \frac{k_f}{k_s} \sinh (\xi h_f)}{\xi} \, d\xi, \quad (4.13) \]

\[ \Delta T_d^\text{substrate} (r, z) = \frac{P}{\pi k, r_0} \int_0^\infty J_1(\xi r_0) J_0(\xi r) \cosh \left[ \frac{\xi (h_f - z)}{k_f} \right] e^{\xi z} \frac{\cosh (\xi h_f) + \frac{k_f}{k_s} \sinh (\xi h_f)}{\xi} \, d\xi. \quad (4.14) \]

Approaching the disk radius \( r_0 \) to zero (i.e., \( J_1(\xi r_0) / r_0 \) goes to \( \xi / 2 \)) yields the temperature rise in the film \( \Delta T_p^f (r, z) \) and in the substrate \( \Delta T_p^s (r, z) \) due to a point heat source as

\[ \Delta T_p^\text{film} (r, z) = \frac{P}{2\pi k_s} \int_0^\infty J_0(\xi r) \cosh \left[ \frac{\xi (h_f - z)}{k_f} \right] \frac{\cosh (\xi h_f) + \frac{k_f}{k_s} \sinh (\xi h_f)}{\xi} \, d\xi, \quad (4.15) \]

\[ \Delta T_p^\text{substrate} (r, z) = \frac{P}{2\pi k_s} \int_0^\infty J_0(\xi r) \cosh \left[ \frac{\xi (h_f - z)}{k_f} \right] e^{\xi z} \frac{\cosh (\xi h_f) + \frac{k_f}{k_s} \sinh (\xi h_f)}{\xi} \, d\xi. \quad (4.16) \]

For a point heat source at \((0, \eta, 0)\) with heat generation \( P = Q_0 d\eta \), the integration of Eq. (4.15) and (4.16) with \( r = \sqrt{x^2 + (\eta - y)^2} \) gives the temperature rise at point \((x, y, z)\) due to a line heat source as

\[ \Delta T_p (x, y, z) = \frac{Q_0}{2\pi k_s} \int_{-L/2}^{L/2} d\eta \int_0^\infty J_0 \left( \frac{\xi \sqrt{x^2 + (\eta - y)^2}}{k_f} \right) \cosh \left[ \frac{\xi (h_f - z)}{k_f} \right] \frac{\cosh (\xi h_f) + \frac{k_f}{k_s} \sinh (\xi h_f)}{\xi} \, d\xi, \quad (4.17) \]
\[\Delta T_{\text{substrate}} (x, y, z) = \frac{Q_0}{2\pi k_s} \int_{-L/2}^{L/2} d\eta \int_0^{\infty} J_0 \left( \xi \sqrt{x^2 + (\eta - y)^2} \right) \frac{\cosh (\xi h_f) e^{\xi z}}{\cosh (\xi h_f) + \frac{k_f}{k_s} \sinh (\xi h_f)} \, d\xi. \] (4.18)

It should be noted that the temperature rise is proportional to the power density applied in the SWNT. The temperature rise on the surface \((z = h_s)\) of thin film is then given by

\[\Delta T_{\text{surface}} (x, y) = \frac{Q_0}{2\pi k_s} \int_{-L/2}^{L/2} d\eta \int_0^{\infty} J_0 \left( \xi \sqrt{x^2 + (\eta - y)^2} \right) \frac{\cosh (\xi h_f) e^{\xi z}}{\cosh (\xi h_f) + \frac{k_f}{k_s} \sinh (\xi h_f)} \, d\xi. \] (4.19)

A three-dimensional finite element model is also established to study the temperature distribution in the system and validate the analytical model. Eight-node, hexahedral brick elements in the finite element software ABAQUS are used to discretize the geometry (including film, substrate and SWNT). Due to the symmetries of the system, only a quarter model is considered. A volume heat source is applied on the SWNT. The zero heat flux boundary is applied at the top surface of the film, and a constant temperature \(T_\infty\) is applied at the bottom of the quartz substrate. The lateral dimension \((\sim 10 \mu m \times 50 \mu m)\) of the system and the substrate thickness \((\sim 100 \mu m)\) are taken as large enough to ensure the accuracy of the results.

### 4.3 Modeling of thermocapillary flow

The motion of the thermocapillary flow in thin film can be approximated as unidirectional since the SWNT length \((L \sim 30 \mu m)\) is much larger than its diameter \((\sim 1.0 \text{ nm})\). As shown in Fig. 4.4, a two dimensional model is established for the thickness profile \(h(x,t)\) by following the approach of Darhuber et al. [136] to assume
the thin film as a Newtonian liquid with the Navier-Stokes equations reduced to

\[ \frac{\partial p}{\partial x} = \mu \frac{\partial^2 u}{\partial z^2}, \quad \frac{\partial p}{\partial z} = 0 \]  

(4.20)

where \( u(x,z,t) \) is the velocity along \( x \) direction, \( p \) is the pressure and \( \mu \) is the film viscosity. Local heating of a liquid film at a position \( x \) reduces the surface tension \( \gamma(x) \), which usually depends linearly on the surface temperature of film [i.e., \( \gamma = \gamma_0 - \gamma_1 \Delta T_{surface}(x) \) with \( \gamma_0 \) as the surface tension at \( T = T_\infty \) and \( \gamma_1 \) the temperature coefficient of surface tension], to produce a thermocapillary shear stress

\[ \tau = \frac{d\gamma}{dx} = -\gamma_1 \frac{d\Delta T_{surface}(x)}{dx}, \]  

(4.21)

at the air-liquid interface, which pulls liquid toward regions of cooler surface. The surface temperature \( \Delta T_{surface}(x) \) is given from Eq. (4.19) by setting \( y = 0 \), i.e.,

\[ \Delta T_{surface}(x) = \frac{Q_0}{2\pi k_x} \int_{-l/2}^{l/2} \int_0^\infty \frac{J_0 \left( \xi \sqrt{x^2 + \eta^2} \right)}{\cosh \left( \frac{\xi h_f}{k_x} \right) + \frac{k_f}{k_x} \sinh \left( \frac{\xi h_f}{k_x} \right)} d\xi d\eta. \]  

(4.22)

Figure 4.4 The schematic diagram of the two-dimensional system for the thermocapillary flow modeling.
The boundary conditions are given by

\[ u(x,z=0,t) = 0, \quad \mu \frac{\partial u}{\partial z}(x,z=h,t) = \tau \]  \hspace{1cm} (4.23)

which corresponds to non-slip condition at the liquid-solid (i.e., film/substrate) interface and a shear stress at the liquid-air interface. For the thickness profile with small slopes, the pressure can be written as

\[ p(x,t) = -\gamma \frac{\partial^2 h}{\partial x^2} \]  \hspace{1cm} (4.24)

Solving Eq. (4.20), (4.23) and (4.24) yield the velocity

\[ u(x,z,t) = \frac{1}{\mu} \left[ \gamma \frac{\partial^2 h}{\partial x^2} \left( zh(x,t) - \frac{z^2}{2} \right) + \tau z \right] \]  \hspace{1cm} (4.25)

The kinematic condition requires \( \frac{dh}{dt} \) being equal to the surface flow speed normal to the air-liquid interface and leads to the evolution equation for the film thickness,

\[ \frac{\partial h}{\partial t} + \nabla \cdot Q = 0 \]  \hspace{1cm} (4.26)

where \( Q_x = \int_{0}^{h} u(x,z,t) \, dz \) and \( Q_y = 0 \) are the volumetric flow rate per unit length. Therefore, the governing equation for the film thickness is obtained as

\[ \frac{\partial h}{\partial t} + \frac{\partial}{\partial x} \left[ \frac{\gamma h^2}{2\mu} + \frac{h^3}{3\mu} \frac{\partial}{\partial x} \left( \gamma \frac{\partial h^2}{\partial x^2} \right) \right] = 0 \]  \hspace{1cm} (4.27)

with boundary conditions \( h(\pm\infty,t) = h_f \) and \( \frac{\partial^2 h}{\partial x^2}(\pm\infty,t) = 0 \) (zero pressure), and initial condition \( h(x,t=0) = h_f \).

A two-dimensional fully coupled thermo-mechanical-fluid analysis is performed using COMSOL to validate the above analytical model. The thin film is modeled as a Newtonian liquid while the substrate and SWNT are solid. A volume heat source is
applied on the SWNT. The boundary conditions for heat transfer include a constant temperature $T_\infty$ at the bottom of substrate and heat insulations at other boundaries.

Surface tension with the form of $\gamma = \gamma_0 - \gamma_1 \Delta T_{\text{surface}}(x)$ is applied on the top surface of thin film and a non-slip boundary is applied at the interface of film and substrate. The lateral dimension is taken as a few tens micrometers ($\sim 20 \mu m$) and the substrate thickness ($\sim 30 \mu m$) to ensure the accurate calculation. The diameter of SWNT is set as 2 nm. It should be noted that this two-dimensional model for thermocapillary flow yields a temperature change as the thickness profile changes while the temperature [Eq. (4.22)] used in the analytical model is assumed to be independent of the thickness profile. This assumption is well validated by the good agreement between the analytical prediction of the thickness profile, the finite element simulations and experiments, which are shown in Sec. 4.5.

4.4 A scaling law for the thickness profile

The thickness profile in Eq. (4.27) are very complex since it depends on multiple material parameters (e.g., viscosity $\mu$, surface tension $\gamma$, thermal conductivities $k_f$ and $k_s$), geometric parameter (e.g., film thickness $h_f$) and loading parameter (e.g., power per unit length $Q_0$). In this section, we will establish a simple scaling law to clearly show the influences of various parameters on the thickness profile.

By introducing the non-dimensional terms $\overline{\Delta T_{\text{surface}}} = k_s \Delta T_{\text{surface}} / Q_0$, $\overline{x} = x / h_f$, $\overline{\xi} = \xi h_f$, and $\overline{\eta} = \eta / h_f$, the surface temperature rise in Eq. (4.22) can be written in the non-dimensional form as
\[ \Delta T_{\text{surface}}(x) = \frac{1}{2\pi} \int_{-L/(2h_f)}^{L/(2h_f)} d\eta J_0\left( \tilde{x} \sqrt{\tilde{x}^2 + \eta^2} \right) \frac{1}{\cosh(\tilde{\xi}) + \frac{k_f}{k_s} \sinh(\tilde{\xi})} d\tilde{\xi}. \]  

(4.28)

Since the SWNT length (~ 30 µm) is much larger than the film thickness (~ 25 nm), \( L/h_f \) can be approximated as infinity, which yields a simple scaling law for the surface temperature rise such that the normalized surface temperature rise \( k_f \Delta T_{\text{surface}} / Q_0 \) depends on only one non-dimensional parameter: the normalized thermal conductivity \( k_f / k_s \), i.e.,

\[ \frac{\Delta T_{\text{surface}}}{Q_0} = \frac{k_f}{k_s} \Delta T_{\text{surface}} = \frac{\Delta T_{\text{surface}}}{Q_0} \left( \frac{k_f}{k_s} \right). \]  

(4.29)

Let \( \tilde{h} = h / h_f \), \( \tilde{\tau} = \gamma_0 \tau / (\mu_0 k_f h_f) \), \( \tilde{\mu} = \mu / \mu_0 \), \( \tilde{\tau} = -d\Delta T_{\text{surface}} / d\tilde{\xi} \) and \( \tilde{\gamma} = k_f \gamma_0 / (Q_0 \gamma_1) = \Delta T_{\text{surface}} \) with \( \mu_0 \) as the viscosity at \( T = T_\infty \) and \( \mu \) the viscosity at \( T \). Eq. (4.27) can then be written in the non-dimensional form as

\[ \frac{\partial \tilde{h}}{\partial \tilde{\tau}} + \frac{\partial}{\partial \tilde{\xi}} \left\{ -\tilde{h}^2 \frac{d\Delta T_{\text{surface}}}{d\tilde{\xi}} + \frac{\tilde{h}^3}{3\tilde{\mu}} \frac{\partial}{\partial \tilde{\xi}} \left[ \left( k_f \gamma_0 / (Q_0 \gamma_1) - \Delta T_{\text{surface}} \right) \frac{\partial^2 \tilde{h}}{\partial \tilde{\xi}^2} \right] \right\} = 0, \]  

(4.30)

which yields a simple scaling law for the thickness profile such that the normalized thickness profile depends on three non-dimensional parameters: the normalized viscosity \( \tilde{\mu} \), the normalized thermal conductivity \( k_f / k_s \) and \( k_f \gamma_0 / (Q_0 \gamma_1) \), i.e.,

\[ \frac{\bar{h}}{h_f} = \bar{h}(\tilde{x}, \tilde{T}; \tilde{\mu}, \frac{k_f}{k_s}, \frac{k_f \gamma_0}{Q_0 \gamma_1}), \]  

(4.31)
4.5 Results and discussion for the scaling law

Figure 4.5 shows the dependence of the normalized surface temperature distribution $k_s \Delta T_{surface}/Q_0$ in Eq. (4.28) on the normalized thermal conductivity $k_f/k_s$. We take two values of the normalized thermal conductivity ($k_f/k_s = 1/30$ and 1) to show its effect. The result from the three-dimensional finite element model for $k_f/k_s = 1/30$ is also shown for comparison. The good agreement validates the analytical expression for the surface temperature rise in Eq. (4.28). It is shown that the surface temperature rise as well as the temperature gradient due to Joule heating is localized within a range of 5 times film thickness ($x < 5h_f$), which is critical to form a local trench. The maximum normalized temperature rise occurs at the center of SWNT (i.e., $x = 0$) while the maximum normalized temperature gradient occurs at the location of one time thickness (i.e., $x = h_f$). The increase of $k_f/k_s$ decreases both the normalized temperature rise and temperature gradient locally in the range of 5 times thickness ($x < 5h_f$) but has a negligible effect on the results out of that range ($x > 5h_f$). For example, as $k_f/k_s$ increases 1/30 to 1, the maximum temperature rise decreases $\sim 10\%$ at $x = 0$ and $\sim 0.8\%$ at $x = 5h_f$. 
Let's focus on the system of MG2OH on a quartz substrate in Jin et al.'s work to purify the SWNTs [74], the thermal conductivities of MG2OH film and quartz substrate are $k_f = 0.2 \text{ W/m/K}$ [74] and $k_s = 6 \text{ W/m/K}$ [137], respectively, which gives

![Figure 4.5](image1)

Figure 4.5 The normalized (a) temperature rise and (b) temperature gradient at the surface of thin film along the $x$ direction.
The small rise in surface temperature (only in a few degrees) yields a small change in viscosity and therefore, $\bar{\mu} \approx 1$. Equation (4.31) then becomes

$$\bar{h} = \frac{h}{h_f} = \bar{h}\left(\bar{x}, \bar{t}, \bar{\mu} \approx 1, \frac{k_f}{k_s} = \frac{1}{30}, \frac{k_f \gamma_0}{Q_0 \gamma_1}\right),$$

(4.32)

which only depends on one non-dimensional parameter $\frac{k_f \gamma_0}{Q_0 \gamma_1}$. 

Figure 4.6 Evolution of the trench profile.
Figure 4.6 compares the predicted thickness profile to the two-dimensional fully coupled thermo-mechanical-fluid analysis for \( \frac{k_{\gamma_0}}{Q_0\gamma_1} = 245 \). The numerical results for \( \overline{\tau} = 40 \) and \( \overline{\tau} = 400 \) are also shown for comparison. The good agreement between analytical modeling and numerical simulations validates the analytical model although several assumptions are introduced in the modeling (e.g., the independence of the temperature on the thermocapillary flow). As the time increases, the trenches gradually widen and deepen as the displacement material forms ridges at the edges. It should be noted that the viscosity doesn't play a role in determining the thickness profile but it could increase or decrease the trench formation time since it appears in the normalized time.

\[ \gamma_1 \frac{Q_0 t}{(\mu_0 k_z H_j)} \]
Figure 4.7 The normalized (a) trench width and (b) trench depth versus the normalized time.

The dependence of the normalized trench width $\frac{W_{tc}}{hf}$ and trench depth $\frac{H_{tc}}{hf}$ on the non-dimensional parameter $\frac{k_r \gamma_0}{Q_0 \gamma_1}$ is shown in Fig. 4.7. A smaller $\frac{k_r \gamma_0}{Q_0 \gamma_1}$ gives a larger normalized trench width and trench depth. To further understand the effect of the unique parameter $\frac{k_r \gamma_0}{Q_0 \gamma_1}$ on the trench profile, we redraw the results in Fig. 4.7 as Fig. 4.8 of the normalized trench width versus the normalized trench depth. The normalized full trench width corresponding to the normalized full trench depth (i.e., $\frac{H_{tc}}{hf} = 1$) is critical to form a s-SWNT array with large densities required in semiconducting applications. The results suggest that a smaller $\frac{k_r \gamma_0}{Q_0 \gamma_1}$ is helpful to generate a narrower normalized full trench width, which can serve as a guideline for optimizing the system. In
addition, a thinner film thickness is also helpful for a narrower full trench width since the full trench width is proportional to the film thickness.

Due to limited data on viscosity and surface tension of MG2OH, we take the surface tension of polystyrene (i.e., $\gamma = 50.40 - 0.0738\Delta T_{\text{surface}}(x)$ mJ/m$^2$) [138], which exhibits behaviors like the MG2OH, as an approximation and fit the viscosity $\mu_0$ to compare with experimental measurement. Figure 4.9 shows the comparison of the trench width versus time between the analytical prediction and experiments for the power density $16.7$ W/m and ambient temperature $T_\infty = 303$ K. The fitted viscosity $\mu_0$ is $4 \times 10^8$ Pas at 303 K. These results indicate a novel measurement technique for quantifying the viscosity of thin film.
4.6 Further validation of the model with experiments on polystyrene/quartz

In Sec. 4.5, we used the surface tension of polystyrene (PS) as an approximation and a fitted viscosity in order to compare the analytical predictions to experiments for MG2OH/quartz due to the missing material properties of MG2OH. In this section, we focus on the system of PS/quartz to further validate the analytical models without any parameter fitting because the material properties of polystyrene can be found in the literatures. Systematic studies on the effects of molecular weight \((M_w)\), substrate (or ambient) temperature \((T_\infty)\) and power density \((Q_0)\) highlight the essential aspects of thermocapillary flow in polystyrene associate with the viscosity.

Studies involve PS with \(M_w\) between 2.5 kg/mol to 30 kg/mol. A typical film thickness is \(h_f = 30\) nm. Thermocapillary flow occurs on a temperature-controlled substrate \((T_\infty = 353\) K). The process involves applying a DC bias for 10 minutes. For PS,
surface tension parameters, $\gamma_0$ and $\gamma_1$ are taken as $47.4 \times 10^{-3}$ N/m and $0.078 \times 10^{-3}$ N/m/K [139], respectively, for all PS materials examined since $\gamma_0$ and $\gamma_1$ depend only slightly on $M_w$ (less than 5% change for $\gamma_0$ and 20% change for $\gamma_1$ with $M_w$ between 2 kg/mol to 30 kg/mol) [139]. Here, $k_f = 0.15$ W/m/K [140] and $k_s = 0.15$ W/m/K [137] in Eq. (4.19). The viscosity, $\mu$, can be connected to $M_w$ via the Vogel equation [141],

$$\mu = A e^{\frac{B}{\alpha_f(T - T_k)}}$$

where $A$ is the structure factor, $B/\alpha_f$ is a constant, and $T_k$ is the Vogel temperature, respectively. Literature [141] suggests that, $B/\alpha_f \sim (1620 \pm 50)$ K, $A = 1.925 \times 10^{-8} M_w^{1.25}$ Pas, and $T_k = 321.4 - 8.3 \times 10^4 M_w^{-1}$ K, both with $M_w$ in g/mol. We use $B/\alpha_f = 1640$ K, chosen within the range defined by the literature, but with a specific value that leads agreement between experiment and theory for the trench width ($\sim 0.62 \mu$m) at $T_w = 353$ K, $Q_0 = 30$ W/m and $M_w = 2.5$ kg/mol after 10 minutes of heating.

Figure 4.10(a) shows a collection of AFM images of trenches that form under $T_x = 353$ K, $Q_0 = 30$ W/m and $M_w = 2.5$ kg/mol after 10 minutes of heating using PS with $M_w$ from 17.5 kg/mol to 2.5 kg/mol. The results show that $W_{T_c}$ increases significantly with decreasing $M_w$, as summarized by the red symbols in Fig. 4.10(b). Calculated viscosities from the Vogel equation appear as blue symbols in Fig. 4.10(b). The dashed line in Fig. 4.10(b) shows the predicted value of $W_{T_c}$ for parameters equivalent to experiment: 10 minutes of heating at $T_x = 353$ K and $Q_0 = 30$ W/m. The results agree remarkably well with experiment. The scaling trends arise mainly from variations in $A$, which yields a power law dependence of $\mu$ on $M_w$ ($\propto M_w^{1.25}$) [141].
Figure 4.10 (a) AFM images of films of PS with molecule weights \( M_w \) ranging from 2.5 kg/mol to 17.5 kg/mol after inducing nanoscale thermocapillary flows by Joule heating in an underlying SWNT (power dissipation \( Q_0 \sim 30 \) W/m) at a substrate temperature, \( T_\infty = 353 \) K and (b) dependence of \( W_{tc} \) on \( M_w \) of PS (red circles). Also plotted is the zero-shear viscosity, \( \mu \) of PS determined by the Vogel equation (blue triangles). The dashed line corresponds to \( W_{tc} \) computed by using an analytical model for nanoscale thermocapillary flow.

The values of \( T_\infty \) and \( Q_0 \) are also important. Figure 4.11 shows results of thermocapillary flow in PS with \( M_w = 2.5 \) kg/mol and \( Q_0 = 30 \) W/m for 10 min, with \( T_\infty \) between 313 K to 353 K. The results show that \( W_{tc} \) increases dramatically with increasing in \( T_\infty \). The Arrhenius type scaling arises from the temperature dependence of \( \mu \), as confirmed from results computed with the analytical model. Figure 4.12 shows effects of changing \( Q_0 \) from 8.4 to 151 W/m for \( T_\infty = 353 \) K and PS with \( M_w = 2.5 \) kg/mol. Clearly, as with \( T_\infty \), \( W_{tc} \) depends strongly on \( Q_0 \). The trench width is nicely replicated with analytical solution without any fitting, thereby providing further indication that \( \mu \) is, to within experimental uncertainties, entirely responsible for the
observed variations. We note that the calculations cease to be valid above a critical value $h(x=0,t)=0$.

Figure 4.11 (a) AFM images after nanoscale thermocapillary flow in a film of PS ($M_w=2.5 \text{ kg/mol}$) induced by Joule heating of an underlying SNWT at a power per unit length of 30 W/m, for substrate temperatures between 313 K to 353 K and (b) Trench width ($W_{Te}$) and zero-shear viscosity ($\mu$) of polystyrene as a function of substrate temperature ($T_\infty$) between 313 K to 393 K, for PS films with different $M_w$ (2.5, 9 and 30 kg/mol). The solid symbols and dashed lines correspond to measured and computed values for $W_{Te}$. The open symbols correspond to values of $\mu$ computed using the Vogel equation.
Figure 4.12 (a) AFM images after nanoscale thermocapillary flow in a film of PS ($M_w = 2.5$ kg/mol) induced by Joule heating of an underlying SNWT at powers per unit length of between $8.4$ W/m to $214$ W/m, at a substrate temperature ($353$ K) and (b) $W_{Te}$ as a function of power per unit length dissipated in the SWNT ($Q_0$) from $8.4$ W/m to $214$ W/m for PS films with different $M_w$ ($2.5$, $9$ and $30$ kg/mol). The solid symbols and dashed lines correspond to measured and computed values for $W_{Te}$. 
4.7 Summary

We have developed an analytical model, validated by the coupled thermo-mechanical-fluid finite element analysis, to study the thermocapillary flow of thin film to purify the SWNTs. A simple scaling law for the normalized thickness profile shows that the normalized thickness during thermocapillary motion depends only on three non-dimensional parameters: the normalized viscosity $\mu/\mu_0$, the normalized thermal conductivity $k_f/k_s$ and $k_s\gamma_0/\eta_0\gamma_1$, where $\mu_0$ is the viscosity at the ambient temperature, $k_f$ and $k_s$ are the thermal conductivities of thin film and substrate, respectively, $Q_0$ is the power density on SWNTs, $\gamma_0$ is the surface tension of thin film at the ambient temperature, and $\gamma_1$ is the temperature coefficient of surface tension. For the system of MG2OH/quartz substrate under a low power density, the normalized thickness profile only depends on one parameter $k_s\gamma_0/\eta_0\gamma_1$ and it is shown that a smaller $k_s\gamma_0/\eta_0\gamma_1$ is helpful to yield a narrower full trench width. In addition, a thinner film thickness is also helpful for a narrower full trench width. The analytical model is further validated with experiments for the system of PS/quartz without any parameter fitting. These may serve as design guidelines for system optimization.
Chapter 5

Conclusions and future works

5.1 Conclusions

In this work, we studied fundamental mechanical properties of graphene/h-BN heterostructure, which has a great potential for high performance graphene electronics. First, a continuum framework is established to develop the cohesive law for the interfaces in the graphene/h-BN heterostructure due to van der Waals forces. The cohesive law is obtained in terms of the area density of carbon atoms on the graphene and those of boron and nitrogen atoms on the h-BN layer, number of h-BN layer and the parameters in van der Waals interaction. It is shown that the cohesive law in the graphene/multi-layer h-BN model is dominated by the first three h-BN layers which are closest to graphene. In another words, for graphene/h-BN heterostructure with more than three layers of h-BN, only the summation for \( i = 1, 2 \) and 3 are needed since the contribution of further layers can be neglected. Second, the buckling of graphene on h-BN substrate under equi-biaxial compression with five buckling patterns suggested by literature [62] is studied. Total energy consisting of cohesive energy, graphene membrane energy and graphene bending energy is obtained analytically for each buckling mode. It shows that the total energies are quite same for all buckling modes at a compression slightly larger than the critical strain while the herringbone mode has the lowest total energy at a compression much larger than the critical compression.

In addition, an analytical model, as well as a coupled thermo-mechanical-fluid finite element model, is developed to study the thermocapillary flow of thin film to purify the SWNTs. The predicted results agree well with experimental measurements such that
the models are reliable for further optimization. It is shown that thermocapillary force due to the high temperature gradient makes the trench instead of the low temperature itself. A simple scaling law for the normalized thickness profile shows that the normalized thickness during thermocapillary motion depends only on three non-dimensional parameters: the normalized viscosity $\mu/\mu_0$, the normalized thermal conductivity $k_f/k_s$ and $k_s\gamma_0/Q_0\gamma_1$ (where $\mu_0$ is the viscosity at the ambient temperature, $k_f$ and $k_s$ are the thermal conductivities of thin film and substrate, respectively, $Q_0$ is the power density on SWNTs, $\gamma_0$ is the surface tension of thin film at the ambient temperature, and $\gamma_1$ is the temperature coefficient of surface tension). For the system of MG2OH/quartz substrate under a low power density, the normalized thickness profile only depends on one parameter $k_s\gamma_0/Q_0\gamma_1$ and it is shown that a smaller $k_s\gamma_0/Q_0\gamma_1$ is helpful to yield a narrower full trench width. In addition, a thinner film thickness is also helpful for a narrower full trench width. The analytical model is further validated with experiments for the system of PS/quartz without any parameter fitting. These may serve as design guidelines for system optimization.

5.2 Future works

Graphene/h-BN heterostructure has showed great potential to improve the performance of graphene device. Although we have developed a continuum framework to investigate its mechanical properties, one key question still remains unknown. That is how the deformation affects the electrical performance of the heterostructure. Therefore, a future work is to develop a framework combining the atomistic continuum theory and
k-space tight binding method to understand the electromechanical properties of graphene/h-BN heterostructure.

For the purification of SWNTs, Joule heating [74] is used to induce the thermocapillary flow in our studies, but it has limitations. Although effective, this method has practical disadvantages related to (1) the need for multiple depositions and etching steps to form the necessary electrodes and gating structures; (2) physical contact with these electrodes to allow selective current injection; and (3) residue and other contamination that often remains, even after removal of these materials following the purification process. To avoid these issues, microwave radiation can be used to selectively heat the m-SWNTs to levels that initiate the thermocapillary flows. Microwave radiation represents a noninvasive heating technique which is simple, scalable and economical. For low cost, desktop sources of microwaves, the intensity is far below the level required for non-negligible direct heating of SWNTs, due to their extremely small absorption cross-sections. More experimental and theoretical studies are in demand.
References


