

Abstract of “A Study of Curvature Localization in Multilayer Graphene”

by Mrityunjay Kothari, Ph.D., Brown University, May 2019

We discover a new, curvature-localizing, subcritical buckling mode that produces a shallow-kink configuration in multi-layer graphene. Our density functional theory (DFT) analysis reveals the mode configuration - an approximately 2 nm wide boundary layer of localized curvature that connects two regions of uniformly but oppositely sheared stacks of flat atomic sheets. The kink angle between the two regions is limited to a few degrees ensuring elastic deformation. By contrast, a purely mechanical model of sandwich structures shows progressive supercritical curvature localization spread over a 50-100 nm wide boundary layer. We propose an *effective-locality model* of electromechanics, which reveals that the coupling between atomic-layer curvature and electric charge polarization, i.e. quantum flexoelectricity, leads to the emergence of a boundary layer. Within this boundary layer, the curvature is focused primarily within a 0.86 nm fixed band width. Both DFT and the model analyses show focused distribution of the curvature and polarization exhibiting oscillating decay with the boundary layer. The interactions between flexoelectrically generated dipoles lower the potential energy and also switch the stability from supercritical for a mechanical sandwich structure to subcritical for a flexoelectric crinkle. In addition to the structural and stability characterization of crinkles, a general thermodynamic framework of flexoelectric constitutive laws for multilayered graphene (MLG), and apply these laws to explain the role of crinkles in peculiar molecular adsorption characteristics of HOPG surfaces. Our analysis reveals that the nonlocal model can be reduced to a simplified uc-local or e-local model only when the curvature distribution is uniform or highly localized. For the nonlocal model, we calibrated and formulated the layer-number dependent dielectric and intrinsic flexoelectric coefficients of MLGs. In addition, we also obtained layer-number dependent flexoelectric coefficients for uc-local and e-local models.

A peak polarization of 0.12 e/nm is predicted for a 3° end angle and is concentrated in the boundary layer. The charge distribution in agreement with DFT and is significant enough to adsorb charged and polarizable molecules on the surface. This charge segregation is controllable by macroscopic deformation and is expected to be useful in studies of selective graphene-surface functionalization for various applications. Bifurcation analysis of a bilayer graphene on softer substrates shows the existence of crinkle bifurcation and is capable of generating periodic crinkle patterns.

A Study of Curvature Localization in Multilayer Graphene

by

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DEDICATED TO MY GRANDPARENTS

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Chapter 1

Introduction

Graphene and surface patterns are intimately linked. Before the discovery of graphene ([2], [3]), Mermin-Wagner theorem ([4], [5]) conjectured that thermodynamic fluctuations in 2-D materials destroy any long range crystalline order, thus making them unstable. However, as was found later [6], graphene has a unique way of getting around the Mermin-Wagner theorem. Graphene achieves stability by formation of ripples, resulting from the coupling of bending and stretching modes. These ripples - responsible for existence of graphene - are class of surface patterns and in fact, one of the many patterns that graphene has been found to show.

In my dissertation, I focus on exploring and classifying surface patterns in graphene. In doing so, we investigate a new kink-shaped pattern, called *crinkle*, in detail. We find that *quantum flexoelectricity* in graphene [7] plays a crucial rule in the formation of these crinkles. As a general underlying theme in this dissertation, the three areas of focus are surface patterns in graphene, their stability and the role of electro-mechanical coupling in both. Below, I go over these, briefly, to develop the background for the study.

1.1 Surface patterns in graphene

We begin by reviewing historical observations and current understanding of graphene corrugation. We first look at the naturally existing ripples in graphene. It has been reported that single-layer graphene (SLG) and few-layer graphene (FLG) exhibit characteristic *dynamic* ripples as well as *static* corrugations when suspended ([6], [8]). Meyer *et al.* [8] studied dynamic morphologies of suspended SLG sheets, analyzing broadening of transmission electron microscope (TEM) electron beam diffraction, and concluded that suspended SLG sheets are not perfectly flat. Instead, the sheets ripple with a prevailing wavelength (≤ 25 nm) at a frequency of tens of GHz ([6], [8]). They explained that the characteristic rippling is caused by two competing mechanisms. One is thermally excited diverging amplitude of long-wavelength ripples that would lead to crumpling ([5], [9], [10]), and the other is a coupling between bending and stretching in 2D rippling that stabilizes the layer against crumpling [11]. In addition to dynamic rippling, the time-average configuration of fluctuating ripples, i.e. the static configuration, of a suspended FLG is not flat either. Meyer *et al.* [8] also presented a real-space TEM static image of FLG hexagonal lattices, the visibility of which strongly depended on their tilt angle. The FLG image showed static corrugation with characteristic size somewhat smaller than the characteristic SLG ripple size.

A popular method to grow graphene is chemical vapor deposition (CVD). The thermal changes involved in the CVD process may generate residual thermal stresses which are known to induce wrinkling in graphene [12]. Thermal strain engineering can potentially be used to obtain desired surface patterns. Controllable surface patterning of graphene was reported by Bao *et al.* [13] employing the thermal strain differential between graphene and the trenched substrates of Si/SiO₂. The strain incompatibility thus generated is energetically favorable to accommodate by buckling out of

plane, forming controllable ripples. In addition to rippling and wrinkling, SLG and FLG are also known to show racket-type self-folded configurations [14].

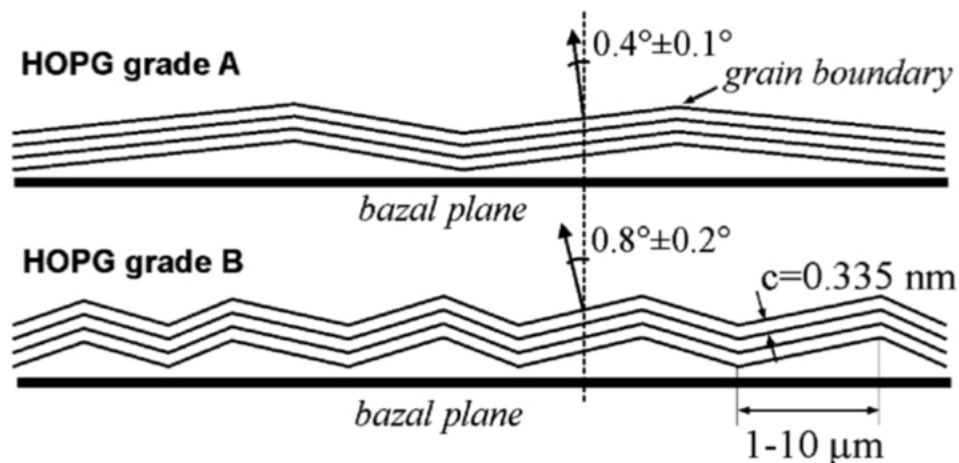


Figure 1.1: *Mosaics* in HOPG. The span varies with the grade of HOPG. *Picture courtesy* [1].

Regarding corrugation of general multi-layer graphene (MLG) or graphite, Ohler et al. [15] reported an X-ray diffraction topographic study of highly oriented pyrolytic graphite (HOPG). This showed crystallographic X-ray peak spreading of the Cu- $K\alpha$ rocking curve, which represents 'mosaic spread' -a non-uniformity measure of atomic-layer parallelism. The mosaic spread of MLG corresponds to discrete tilt-angle variation, up to $\pm 3.5^\circ$, among zones of flat atomic layers that range from tens of nanometers to a few microns, in contrast to smooth wrinkles of SLG [16]

Our benchmark experiments on buckling of suspended MLG in a plane strain setup springs a surprise. In contrast to a typical sinusoidal buckling mode, we observed a kink-shaped buckling mode that we call a *crinkle*. Figure 1.2 shows a schematic of the experimental setup and the resulting crinkle mode (substrate shown is silicon but the results remain same for PMMA gratings too.)

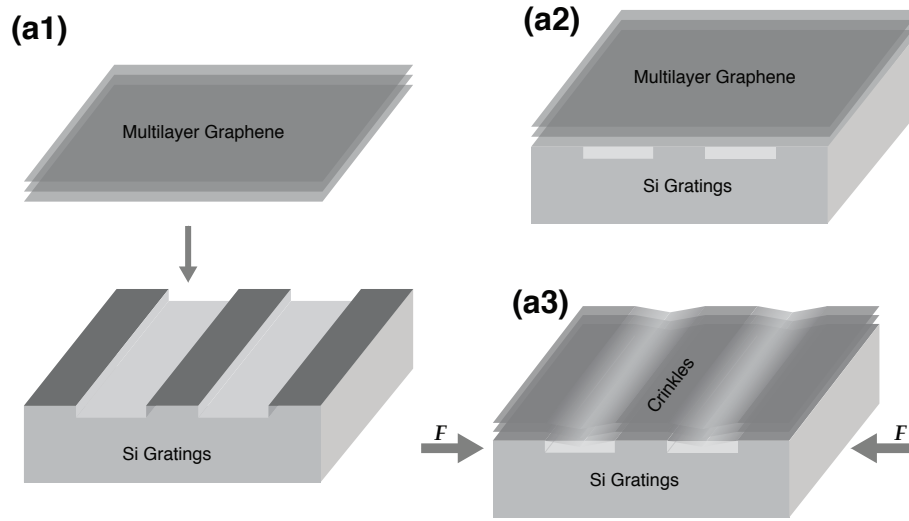


Figure 1.2: Schematic of the crinkle buckling mode in MLG. The MLG is first attached to Si gratings and then subjected to compressive strain.

From these observational results, two major questions arise; what are the conditions of elastostatic graphene deformation to yield smooth ripples versus corrugated flat-zone segments? And, are there lower-energy modes than the harmonic modes? We attempt to answer these questions in chapter 2 by analyzing the benchmark experiments and exhaustive theoretical analysis.

In addition to this, we explore the stability landscape of multi-layer graphene - a) how does the thickness of MLG and its span affect the buckling mode and b) what is the nature of these bifurcations and their post-buckling paths. We find that the aspect ratio indeed has a strong bearing on the final outcome. The critical role, however, is found to be played by flexoelectricity.

1.2 Flexoelectricity

Electromechanical coupling is ubiquitous in nature. Simple physical systems like a lighter, more complex ones like electronic actuators and sensors and even more complex biological systems like

human body all depend on electromechanical couplings in one form or the other. A familiar and widely studied class of coupling is piezoelectricity where the material develops electric polarization in response to mechanical strain. Flexoelectricity is another such class of electromechanical coupling wherein the material develops polarization in response to strain gradient. While similar in effect, piezoelectricity and flexoelectricity are two fundamentally different phenomena. The range of materials exhibiting piezoelectricity is restricted by crystallographic symmetry. The symmetry in the charge distribution precludes centro-symmetric materials from developing any polarization. Flexoelectricity, in contrast, is not restricted by symmetry and a larger class of materials can exhibit it.

The constitutive relation for a non-piezoelectric flexoelectric material can be given as,

$$P_i = \chi_{ij}E_j + \beta_{ijkl}(\nabla\epsilon)_{kl} \quad (1.2.1)$$

where P is the polarization density, χ is the electric susceptibility, E is the electric field, β is the flexoelectric tensor and ϵ is the strain.

Some of the early theoretical work on flexoelectricity was done by Mashkevich, Tolpygo and Kogan ([17], [18]). Soon after, flexoelectricity was experimentally observed by Scott [19] and Bursian [20]. Interestingly, the term flexoelectricity itself was not used until 1981 when it was used in the context of solids for the first time by Indenbom [21]. In more recent experiments, Cross and coworkers found ceramics with high flexoelectric constants ([22], [23]). The new experimental work in flexoelectricity reignited interest in flexoelectricity and its applications have grown at a rapid pace. In recent theoretical advancements, Sharma et. al., Liu ([24], [25], [26]), Purohit et. al. [27] have proposed continuum based field theory for flexoelectricity. In addition to that, other

hybrid methods like continuum-atomistic modeling have also been developed [28].

Flexoelectricity is a length scale dependent phenomenon. At the nano-scale, owing to the small length scale involved, high strain gradients are achievable which can make the flexoelectric effect prominent and provide a fertile ground for interesting multi-physics phenomena. In this dissertation we will focus on flexoelectricity in graphene which does indeed lead to a peculiar crinkle buckling mode in MLG.

1.2.1 Flexoelectricity in graphene

In the *ab initio* study of Kalinin and Meunier [7], single layer graphene was shown to develop polarization when it was bent. This demonstrated a new origin of flexoelectric polarization and is referred to as quantum flexoelectricity or electronic flexoelectricity. Graphene is an electrostatically centrosymmetric crystal, and MLG cannot be polarized by affine deformation, i.e. not piezoelectric. However, symmetry-breaking deformation, i.e. strain gradients, can polarize graphene by shifting the spatial distribution of the quantum states of electrons, making the graphene flexoelectric ([7], [29], [30]). Since graphene is an in-plane conductor at a finite temperature and sustains static polarization only in the direction normal to the lattice layer, graphene is statically both dielectric and flexoelectric, in the normal direction. The static polarization is proportional to the normal component of the point-exclusive external electric field [31] and the local curvature of the layer. In terms of normal components, (1.2.1) can be re-stated as,

$$\check{P} = \alpha \check{E} + \beta \kappa \quad (1.2.2)$$

where $\check{P}$ and $\check{E}$ are, respectively, the polarization density and the electric field in the normal direction, while α and β are the atomic dielectric polarizability and the intrinsic flexoelectric constant for

N layer graphene, respectively. Here the flexoelectric polarization arises due to distortion of electron cloud in graphene. In its pristine flat state, carbon atoms in graphene are sp^2 hybridized with the π -bonds out of plane. Upon bending, the π -electron cloud becomes asymmetric and consequently the layer develops a normal polarization. Figure 1.3 shows the schematic of this process.

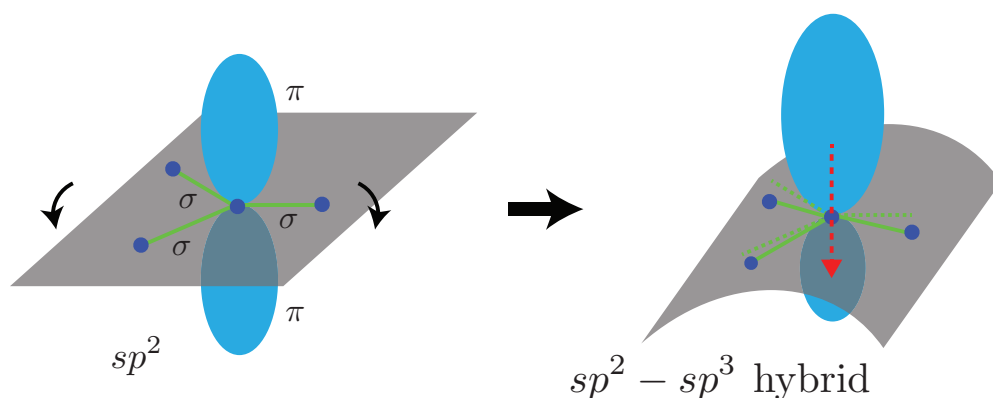


Figure 1.3: Schematic of electron cloud distortion in bent graphene leading to polarization i.e. *quantum flexoelectricity*

Since the flexoelectricity is intrinsically coupled with bending, the buckling and stability analysis of multi-layer graphene must account for the flexoelectric energy. From the point of view of energetics, the potential energy of the deformed graphene at the nano-scale can be significantly varied through long-range non-local electrostatic interactions among flexoelectric dipoles, besides local strain energy variations. Since dipole-dipole interaction energy is sensitive to both the interaction directions and the orientations of the dipoles, we are interested in determining which flexoelectric mechanisms create the experimentally observed subcritical hinge mode of crinkle in MLG buckling. In chapter 2 we carry out the analysis to answer this question.

In chapter 3, we focus on a self-consistent description of flexoelectricity in mutli-layered structures in the context of coupling between flexoelectricity and dielectricity for general 2D layered materials, and extraction of associated material properties from DFT calculations. To this end, we derive an appropriate free energy potential for flexoelectric modeling consistent with thermodynamic framework, and apply such a framework for modeling electro-mechanical deformation of 2D layered materials at the nanometer scale.

Lastly, after having developed the understanding of crinkles on suspended MLG, we consider the buckling of MLG on a softer substrate. We focus on probing the parameter space for existence of crinkle solutions. For the case of graphene, softer substrates do not suppress the crinkle mode. However, if the flexoelectricity is not strong enough, we do not get the crinkle bifurcation.

1.3 Outline of the dissertation

The analysis and characterization of MLG buckling is spread over the next few chapters as follows. In chapter 2, we explore the details of the mechanics of crinkle formation. Benchmark experiments and DFT calculations provide evidence for the kink-shaped crinkle mode. We propose an electro-mechanically coupled model to capture the physics of crinkle formation and find that inclusion of quantum flexoelectricity in the model is able to predict crinkles accurately. The criticality of crinkle mode is then examined in detail and reveals that flexoelectricity switches the stability of buckling from supercritical to subcritical. The fixed width narrow boundary layer in the crinkle is a characteristic of the subcritical bifurcation. Postbuckling analysis of crinkle mode is studied. We find a parameter range for existence of crinkle bifurcation that is applicable to the wider class of layered 2-D materials.

In chapter 3, we move on from the structural focused analysis to first, developing formalism for

multi-layered materials and subsequently exploring the nonlocality of flexoelectricity-dielectricity coupling followed by the discussion of flexoelectricity generated surface charges on graphene. We touch upon the layer dependence of properties in graphene. Lastly, in chapter 4, we consider the onset bifurcation analysis of flexoelectric layer on a softer elastic substrate. We conclude with the major outcomes of the dissertation and also outline the scope for future work.

Chapter 2

Subcriticality of flexoelectric crinkles

Note : A version of this chapter is published in Proceedings of the Royal Society A. Data and figures have been used with all co-authors' consent.

Kothari M, Cha M.-H. and Kim K.-S. Subcritical curvature localization in graphene. I. Quantum Flexoelectricity. Proceedings of the Royal Society A (2018).

2.1 Introduction

In this chapter, I talk about the discovery of peculiar curvature localization in graphene at the nanoscale, that produces an unprecedented class of surface corrugation - *the quantum flexoelectric crinkle*. To answer the questions posed at the end of section 1.1, we turn to our benchmark experiment with MLG attached PMMA gratings. Figure 2.1.(a) and (b) show schematics of the suspended-MLG buckling in the experiment. At first, we consider a bilayer graphene to understand major mechanisms of the MLG buckling. We model the bilayer with weak van der Waals interlayer coupling as a sandwich structure to determine the purely mechanical behaviour without electromechanical coupling. Elastic buckling of sandwich structures has been well studied ([32], [33]), and

Hunt et al. [33] reported analysis of interactive buckling in sandwich structures among three different eigen modes of bilayer buckling - snake, hour-glass and overall-bending modes. In this paper, we will call the shear-snake mode as interlayer-shear mode, ignoring the tilt-snake mode [33], because MLG has an extreme stiffness ratio (approx. 250) of the intralayer tension to the interlayer shear. In addition, we find in this paper that the interlayer-shear mode of deformation prevails over the overall-bending mode in buckling at the nanoscale, unless the structure is extremely slender. If the sandwich-structure model is employed, the interlayer-shear-mode buckling is expected to progressively develop a kink configuration as the amplitude grows. The interlayer-shear-mode evolves from a sinusoidal profile to a symmetric kink-like shape with the ends nearly straight as shown in figure 2.1.(b). However, in our experiment, an MLG directly, i.e. not progressively, buckles out of plane into a hinge mode, i.e. the shallow symmetric kink shape, as shown in figure 2.1.(c). In the experiment, the assembly of MLG (approx. 200 layers) attached to PMMA grating of $1\text{-}\mu\text{m}$ grooves is compressed up to approximately 0.1% strain to observe the buckling mode of the suspended MLG with an atomic force microscope (AFM). This remains below the critical symmetric kink angle of $6^\circ - 7^\circ$ required for the MLG to emit interlayer-sliding van der Waals dislocations from the kink ridge [34], and deform inelastically.

The overall-bending mode, also known as Euler bending mode [35], grows in amplitude from an infinitesimal sinusoidal profile of pitchfork bifurcation, progressively to a smooth post-buckling wrinkle configuration in a supercritical state ([36], [37], [38]). When a soft-core sandwich structure attached to a soft substrate or periodically suspended on an elastic substrate is compressed, the structure buckles periodically in an interlayer-shear mode. The interlayer-shear mode of purely mechanical buckling also supercritically develops its post-buckling configuration from an infinitesimal sinusoidal bifurcation profile ([32], [33]). The post-buckling configuration progressively evolves into a series of periodic kinks which we term 'crinkle ruga' or simply 'crinkles' [39]. Here, we

collectively denote all corrugation geometries such as wrinkles, creases, ridges, folds, crumples, and crinkles as 'rugae' ([40], [41], [42], [43]). Figure 2.1.(d) shows a map of wrinkle versus crinkle formation depending on the slenderness of the MLG (see appendix A for the analysis). If the film is extremely slender, i.e. the length is beyond a critical value for a given number of atomic layers, the MLG develops wrinkles in the overall-bending mode under axial compression. Otherwise, MLG develops crinkles. The crinkle, if mechanically modeled as an interlayer-shear mode, supercritical and progressively focuses its curvature within an evolving band width (EBW). By contrast, we find in this paper that if the effects of interlayer as well as interlayer long-range flexoelectric interactions are taken into account, the MLG subcritically buckles into a hinge mode at the onset of buckling, focusing the curvature within a fixed band width (FBW). Then, the mode shape remains invariant while the amplitude grows. The FBW is depicted as a horizontal line near the bottom in figure 2.1.(d). The FBW thickness is obtained by *ab initio* calculations based on quantum density functional theory (DFT) in the following section, and the criticality of the flexoelectric crinkle formation is analyzed in subsequent sections.

Among the critical bifurcations in buckling of sandwich structures, hour-glass mode of buckling, if excited, would undergo subcritical bifurcation [33]. However, the post-buckling equilibrium configuration of the hour-glass mode is a relatively high energy state requiring substantial axial loading [33]. From the energetics point of view, the potential energy of the deformed graphene at the nanoscale can be significantly varied through long-range nonlocal electrostatic interactions among flexoelectric dipoles, besides local strain energy variations. Graphene is an electrostatically centrosymmetric crystal, and MLG cannot be polarized by affine deformation, i.e. not piezoelectric. However, symmetry-breaking deformation, i.e. strain gradients, can polarize graphene by shifting the spatial distribution of the quantum states of electrons, making the graphene flexoelectric ([29], [7], [30]). Since graphene is an in-plane conductor at a finite temperature and sustains

static polarization only in the direction normal to the lattice layer, graphene is statically both dielectric and flexoelectric, in the normal direction. The static polarization is proportional to the normal component of the point-exclusive external electric field [31] and the local curvature of the layer. The dielectric constant was evaluated by DFT for SLG in [44] and FLG in [45], and the overall polarization induced by uniform curvature was provided for SLG in [46], also by DFT. Since dipole-dipole interaction energy is sensitive to both the interaction directions and the orientations of the polarizations, in this paper, we are interested in determining which flexoelectric mechanisms create the experimentally observed subcritical hinge mode of crinkle in MLG buckling.

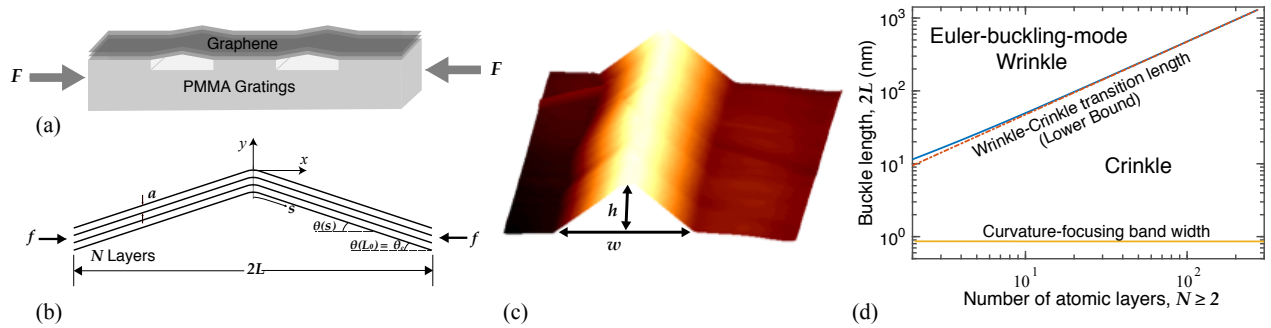


Figure 2.1: (a) A schematic of MLG attached to PMMA gratings, buckling under the compressive lateral load F ; (b) Geometry of buckled N -layered MLG crinkle with end-angle θ_e (The layers are parallel and characterized by angle $\theta(s)$ made with the horizontal, with s being the arclength.); (c) Atomic force microscopy (AFM) image of MLG crinkle with $h = 88\text{nm}$ and $w = 1\mu\text{m}$; (d) Buckling phase map identifying regions of wrinkle mode and crinkle mode for N -layered MLG of length $2L_0$ (curvature-focusing band width for flexoelectric crinkle approximately 0.86nm is marked by the yellow line.)

2.2 Multiphysics buckling models of multilayer graphene

In this section, we first analyze details of the energetics and stable mode shapes of graphene buckling with DFT for a relatively short, 13.2619 nm , span. Then, the results are compared with purely mechanical and electro-mechanical coupling models of MLG crinkles.

2.2.1 DFT analysis of graphene crinkles

We investigate formation and stability of crinkle structures of 1-3 layers of graphene and bulk graphite using DFT calculations, employing the Vienna ab initio simulation package (VASP) [47] with the projector augmented wave (PAW) pseudo-potential [48]. Exchange correlation interactions are treated within the local density approximation. The energy cutoff for the plane-wave basis set is set to 375 eV throughout the whole calculation, and a k-point grid of $1 \times 12 \times 1$ is used for the layered graphene supercell of $13.2619 \text{ nm} \times 0.426 \text{ nm} \times 3 \text{ nm}$. A grid of $1 \times 12 \times 12$ k-points is used for the bulk graphite totaling a volume of $13.2619 \text{ nm} \times 0.426 \text{ nm} \times 0.68 \text{ nm}$. Periodic boundary conditions are used and we set more than 1.5 nm vacuum in z-direction to avoid artificial interaction between layers in different supercell repeated in z-direction. Using the plane-wave-based total energy minimization [49], the structures were relaxed until the force on each atom was less than $0.01 \text{ eV}/\text{\AA}$.

Figure 2.2.(a) shows the top view of the simulation supercell. The end displacements of the multi-layer graphene were constrained but kept free to rotate by setting the lateral (x-direction) length of the supercell close to the value corresponding to the crinkle angle of interest. Then, the structure was fully relaxed to the minimum energy configuration through iterative DFT calculations. Figure 2.2.(b) shows the post-buckling morphology which compares favorably to the experimentally observed crinkle configuration (Fig. 2.1.(c)). This configuration exhibits a distinct crinkle mode which is slightly sensitive to the bending direction, depending on whether it is along armchair or zigzag orientations as seen in the Fig. 2.2.(c). For the bulk simulation, the translational symmetry is enforced along the thickness direction to make all the layers deform identically. The curvature as a function of position is given in Fig. 2.2.(d). The curvature is localized within a boundary layer of $\sim 2 \text{ nm}$ width around the center and vanishes everywhere else. In the boundary layer, the curvature is

highly concentrated or focused within a band width defined by the two symmetric inflection points of the curvature distribution closest to the center. The band width of curvature focusing, ~ 0.86 nm, is nearly invariant with respect to variations of the crinkle end angle. The curvature is focused within the FBW even at a very small kink angle, e.g. 0.1° . The curvature distribution scaled only by the end angle in the FBW implies that the post buckling mode of the MLG crinkle is invariant for different end angles. This is in stark contrast to the Euler buckling mode or the mechanical interlayer-shear mode for which the curvature is broadly distributed over the length of the graphene layers, and the distribution evolves progressively as a function of the end angle. Another important feature of the MLG crinkle configuration is the curvature reversal observed immediately outside of the curvature focusing band, which is not observed in purely mechanical models of sandwich structures.

We also carried out the calculation with various initial configurations to search for possible locally-stable configurations (i.e., local minima of the total energy). The result shows that the sine-wave configuration with the period of the supercell length is also a local energy-minimum configuration. The sinusoidal wrinkle configuration is more stable than the crinkle configuration for SLG. Surprisingly, the crinkle configuration is also locally stable in SLG for the supercell span; the stabilizing mechanism is revealed to be flexoelectric dipole-dipole interactions in following sections. The local energy-minimum characteristics of SLG crinkle is likely an important aspect of understanding possible dynamic hopping in SLG ripples. For two or more layers of graphene, including graphite, however, the crinkle configuration is more stable than the sine-wave. Searching from various trial initial configurations, we couldn't find any other configuration that is more stable than crinkle under the given boundary condition, which implies that the crinkle is potentially in static ground state of MLG for the given boundary condition.

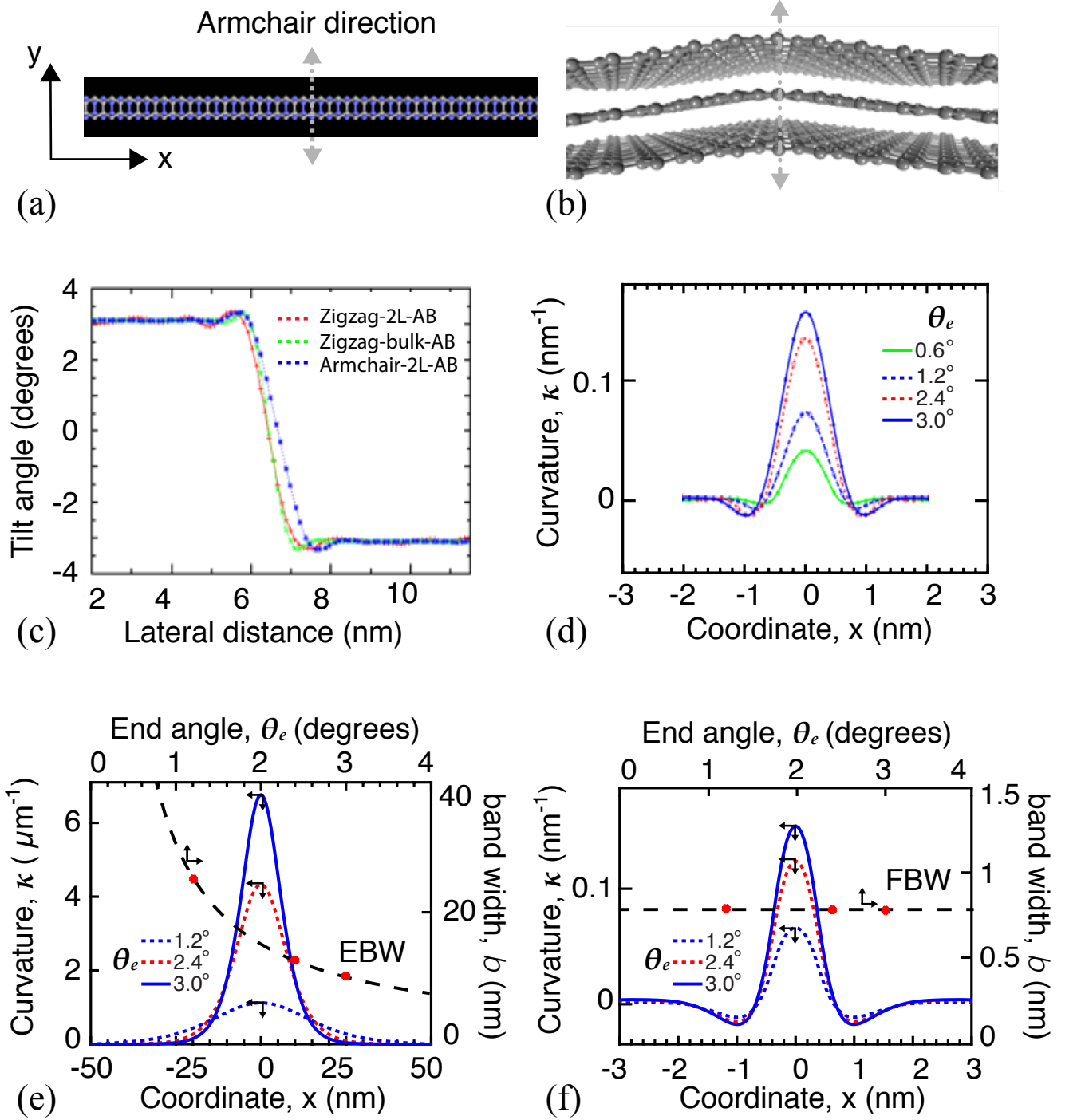


Figure 2.2: DFT analysis (a-b): (a) Top view of simulation supercell for MLG; (b) side view of buckled MLG - the crinkle mode; (c) Crinkle slope profile, $\theta(x)$, for different configurations, showing the zones of flat atomic layers; (d) curvature distribution for different end angles, showing the localization in an approximately 2 nm width around the centre. Nanostructure modeling (e, f): (e) curvature distribution versus position (left and bottom axes), and EBW versus end angle (right and top axes) from the purely mechanical model for 21-layered, 100 nm long MLG; (f) curvature distribution versus position (left and bottom axes), and FBW versus end angle (right and top axes) from the e-local flexoelectric model for 21-layered, 15 nm long MLG.

2.2.2 Purely mechanical model of MLG crinkles

From the DFT analysis presented in 2.2.1, we confirm the existence of a curvature-localizing mode, crinkle, as the lower-energy mode of graphene buckling, pronounced in MLG. The mechanism for formation of crinkle, however, is difficult to completely trace with DFT, as it is computationally very expensive or not possible to simulate larger test cases. To mitigate these limitations and better understand the crinkling process, we formulate a mechanics-based model of a crinkle. To identify the dominant mechanism of crinkle formation, in this section, we first analyze the buckling of elastic layers with weak interlayer-shear coupling without electromechanical considerations. For the mechanics-based modeling, we follow the notation introduced in Fig. 2.1.(b), where we consider N -layer MLG, with interlayer spacing $a = 0.34nm$ and total length $2L_0$. The bending stiffness per unit depth of each layer is denoted as Q_b and the interlayer shear modulus is μ . For the nano-structural model, we make use of DFT-evaluated material properties, $Q_b = 1.0eV$ [16], and $\mu = 4GPa$ [50]. The continuum plate theories for SLG predict vanishing bending modulus for vanishing thickness. However, the bending energy of SLG originates from relative twisting and rotation of bond angles as well as π -orbital electron cloud shifting, and does not vanish. This energy density is treated as $1/2Q_b\kappa^2$ with κ being the curvature. In addition, we utilize the interatomic distance of the graphene atomic lattice, $c = 0.142nm$, the in-plane atomic-layer elastic modulus, $Y^{(2D)} = 2000eV/nm^2$ [51] for dimensional analyses.

The symmetric shape of the crinkle is characterized by the angle $\theta(s)$ that it makes with the horizontal and is parametrized by the arc length s . The entire assembly is under constraint force f to maintain the applied lateral strain. The DFT results indicate that layers deform nearly identically. Since the layers are held together by weak van der Waals forces, we assume translational symmetry in the thickness direction. Owing to the high in-plane stiffness of graphene, the layers are assumed

to be inextensible. Under these kinematic assumptions, the strain energy of the system has two contributions, namely the individual-layer bending of the layers and the interlayer shear between them. The energy per unit depth contribution from these sources is given as,

$$U_m = \int_{-L_0}^{L_0} \left(\frac{Q_b N}{2} \left(\frac{d\theta}{ds} \right)^2 + \frac{\mu(N-1)a}{2} \tan^2 \theta \right) ds \quad (2.2.1)$$

where the first term represents the bending energy of the layers with the curvature, $\kappa = \frac{d\theta}{ds}$, and the second term the interlayer shear energy. The layers shear by an angle θ with respect to each other and the resulting shear strain is $\tan \theta$ leading to stored interlayer shear energy between consecutive layers. The total potential energy per unit depth of the system is then given as,

$$\Pi = U_m - \int_{-L_0}^{L_0} f \left(1 - \cos \theta \right) ds \quad (2.2.2)$$

with the last term being the external potential energy of the compressive loading. From the potential energy functional $\Pi(\theta)$ of (2.2.2) with (2.2.1), the Euler-Lagrange equation can be readily obtained for the energy minimizing shape $\theta(s)$,

$$Q_b \theta''(s) - \mu(N-1)a \tan \theta \sec^2 \theta + f \sin \theta = 0 \quad (2.2.3)$$

for $-L_0 \leq s \leq L_0$, where $(A)'$ denotes $\frac{dA}{ds}$. The critical buckling load for pinned-pinned boundary conditions i.e. $d\theta/ds(\pm L_0) = 0$ is given as,

$$f_{cr} = \mu(N-1)a + \frac{\pi^2 Q_b N}{4L_0^2} \quad (2.2.4)$$

To give some perspective, we evaluate the critical load for a 100 nm long MLG specimen with 21 layers, and find that bending makes up less than 0.005% of the buckling load. The buckling load is predominantly due to interlayer-shear resistance, and as the length of the layers increases, the bending contribution vanishes.

To carry out the post-buckling analysis, we numerically minimize the potential energy. We vary the constraint force f to obtain different end angles, θ_e . We express our results in terms of θ_e in

order to present a more natural comparison with the DFT results. Figure 2.2.(e) shows the results for one such case with $2L_0 = 100nm$ and 21 layers. For small end angles, the curvature is smoothly distributed over the entire length. As the end angle increases, a progressive symmetric curvature localization occurs. The observed peak curvatures are $\sim 0.0067nm^{-1}$ for a 3° end angle, which is much smaller than the DFT predictions in section 2.2.1 for the same end angles. This discrepancy is attributable to buckling of quantum-flexoelectric dipole-dipole interactions at the nanoscale, which is not accounted for in the purely mechanical model. The quantum flexoelectric effect is treated in depth in section 2.3. In the meantime, to understand the localization behavior in greater detail, we investigate the band width of curvature focusing given by the two symmetric inflection points of the curvature distribution. For the three cases in Fig. 2.2.(e), the band widths of curvature focusing are about $25.1nm$, $12.64nm$ and $10.22nm$ in ascending order of the end angles. These band widths are much larger, and change with the increasing end angle in contrast to DFT results where the band width of curvature focusing is nearly fixed at $0.86nm$. In the limit of very large L_0 , two length scales remain in the problem - the interlayer spacing a and another from bending stiffness and interlayer shear, $\sqrt{Q_b/\mu a}$. For the purely mechanical model, a always appears together with μ through the product μa thus making $\sqrt{Q_b/\mu a}$ the only relevant length scale. The EBW of curvature focusing for small θ_e and large L_0 evolves with θ_e as is evident in Fig. 2.2.(e). From our numerical study this dependence of EBW is found to be $\sim \frac{\pi}{2\theta_e} \sqrt{\frac{Q_b}{\mu a}}$, where the constant $\pi/2$ is introduced to match the best fit curve. Consequently, the curvature focusing observed here is achieved progressively and this mode is not an intrinsic hinge mode of MLG buckling. The curvature localization arises from an energetic competition between bending and interlayer shear energies, where the dominant buckling mechanism is interlayer shear, and bending serves to regularize the localization. Although this purely mechanical model does not completely capture the physics of crinkle formation, it does highlight one of the mechanisms of curvature localization in MLG.

2.2.3 Electro-mechanical coupling models of MLG crinkle

In section 2.2.2 we employed a purely mechanical model to study the post-buckling evolution of MLG crinkles and showed that the interplay of interlayer shear and bending energies provides one mechanism of supercritical crinkle formation. Still there are discrepancies between the mechanical model results and DFT predictions. Buckling of MLG creates a strain gradient, i.e. bending curvature of the layers, which breaks the symmetry in the electron cloud distribution in graphene. This separation of positive and negative charge centers in graphene produces a net polarization distribution across the layer. This phenomenon, also known as *quantum flexoelectricity*, is particularly strong in MLG, and a purely mechanical formulation is not able to capture this effect. For a non-piezoelectric flexoelectric material such as graphene, the combined effect of dielectricity and flexoelectricity on polarization, P_i , is given by the following relation,

$$P_i = \alpha_{ij}E_j + \beta_{ijkl}(\nabla\epsilon)_{jkl} \quad (2.2.5)$$

where α_{ij} is the atomic polarizability tensor, E_j is the local electric field component, β_{ijkl} is the flexoelectric tensor and ϵ is the strain [52]. As discussed in the Introduction section, graphene is statically dielectric and flexoelectric in the direction normal to the lattice layer, and (2.2.5) for graphene is reduced to,

$$\check{P} = \alpha\check{E} + \beta_{(N)}\kappa \quad (2.2.6)$$

where $\check{P}$ and $\check{E}$ are, respectively, the polarization density and the electric field in the normal direction, while α and $\beta_{(N)}$ are the atomic dielectric polarizability and the intrinsic flexoelectric constant for N layer graphene, respectively. The atomic dielectric polarizability α is given by, $\alpha = \chi/(\chi + 1)\epsilon_0 h$, with the electric susceptibility χ , the electric permittivity in vacuum $\epsilon_0 (= 8.854 \times 10^{-12} F.m^{-1})$, and the effective dielectric thickness of graphene h , based on the atomic polarization model of [31]. The values of $\chi = 5.9$ and $h = 0.22nm$ were obtained by DFT in [44].

Regarding flexoelectricity, we employ, in this paper, a further simplified model of local coupling between $\check{E}$ and κ , in which the electric field $\check{E}$ induced by layer-bending is effectively proportional to the curvature κ such that

$$\check{P} = \beta_{(N)}^* \kappa \quad (2.2.7)$$

where $\beta_{(N)}^*$ is the *effective flexoelectric constant* of N-layer MLG. The highly localized curvature distribution in MLG crinkles allows us to reduce (2.2.6) to an *effective-locality (e-locality) constitutive relationship* of flexoelectricity. The function $\beta_{(N)}^*/\beta_{(1)}^{(uc)} \cong B_1 - B_2 e^{-B_3 N}$ is obtained by best-fitting a single case ($\theta_e = 3^\circ$ of our e-locality model results to the corresponding DFT results for various N-layers MLGs. The coefficients (B_1, B_2, B_3) are found to be (7.235, 6,841, 0.1377), and the effective flexoelectric constant for a uniform curvature distribution of SLG is given as $\beta_{(1)}^{(uc)} = 0.11e$ by DFT calculation performed in [46].

Electrostatic interactions among the polarized dipoles in the graphene layers provide an energetic contribution to the potential energy. The kinematic assumptions of MLG deformation remain the same as in the purely mechanical model of the previous section. Then, the electrostatic interaction energy is expressed as

$$U_{elec} = -\frac{\beta_{(N)}^{*2}}{2\pi\epsilon_{(N)}} \sum_{n=1}^N \sum_{m=1}^n \int_{-L_0}^{L_0} \int_{-L_0}^{L_0} \kappa(s_n) \kappa(s'_m) \frac{\{1 - \delta_{mn} q(s_n, s'_m)\} \{A(s_n, s'_m) + B(s_n, s'_m)\}}{[\{x(s_n) - x(s'_m)\}^2 + \{y(s_n) - y(s'_m)\}^2]^2} ds_n ds'_m \quad (2.2.8)$$

$$A(s_n, s'_m) = \cos\{\theta(s_n) + \theta(s'_m)\} [-\{x(s_n) - x(s'_m)\}^2 + \{y(s_n) - y(s'_m)\}^2]$$

$$B(s_n, s'_m) = 2 \sin\{\theta(s_n) + \theta(s'_m)\} \cdot \{x(s_n) - x(s'_m)\} \{y(s_n) - y(s'_m)\}$$

$$q(s_n, s'_m) = \begin{cases} 1/2, & \text{for } |s_n - s'_m| > r_0 \\ 1, & \text{for } |s_n - s'_m| \leq r_0 \end{cases}$$

where r_0 is the cut-off radius of the interaction integration and m,n are indices for the layers for

which interactions are considered. Here, $\epsilon_{(N)}$ is the average electric permittivity of N-layered MLG in the normal direction to the layers. Local electric permittivity is layer-position dependent in general [45]; however, we employ the average value for every layer as an approximation for our kinematic assumptions of MLG deformation. $A(s_n, s'_m)$ and $B(s_n, s'_m)$ arise out of interaction between two parallel lines of dipoles which are oriented at angles $\theta(s_n)$ and $\theta(s'_m)$ with respect to the normal.

As commonly treated in long-range interactions among singular-field sources, we account for the intralayer dipole-dipole interaction with a cut-off radius. While performing the integration in (2.2.8), we omit a small symmetric region around the dipole. The way of using cut-off radius to circumvent singularity issues has a physical reasoning behind it. In atomically thin layered materials, the dipoles are not distributed continuously but separated approximately by the lattice parameter distance (nearest neighbors), and thus avoid singularities. Our choice of cut-off radius $\sim 0.15\text{nm}$ is approximately the same as lattice parameter. Within the cut-off radius, the energy required to uniformly bend graphene is already accounted for in the bending energy, $1/2Q_b\kappa^2$. The bending stiffness value used in the calculations has been obtained from DFT analysis to delineate the bending stiffness from the effect of dipole-dipole interactions.

Augmenting the purely mechanical model with the flexoelectric interaction energy, the total potential energy is formulated as

$$\Pi = \int_{-L_0}^{L_0} \left(\frac{Q_b N}{2} \left(\frac{d\theta}{ds} \right)^2 + \frac{\mu(N-1)a}{2} \tan^2 \theta - f(1 - \cos \theta) \right) ds + U_{elec} \quad (2.2.9)$$

Again, we numerically minimize $\Pi(\theta)$ to get the lowest energy configuration of MLG. Similar to the purely mechanical model, we vary the constraint force f to control the shape but choose to express our results in terms of θ_e . This is indeed possible, as there is a one-to-one relationship between f and θ_e as will become clear later in this chapter. Figure 2.2.(f) shows the curvature distributions (refer to the left and bottom axes) for different end angles for a 15 nm long, 21-layered

MLG. The curvature distribution is highly localized in a $\sim 2nm$ band and the peak is much larger compared to the purely mechanical model predictions. The curvature distribution also shows a reversal region, which was absent in the purely mechanical model but predicted by the DFT. Another point of difference between the two models is the boundary layer characterized by the band width of curvature focusing. The e-locality model predicts the 0.86 nm FBW of curvature focusing as shown in Fig. 2.2.(f) (refer to the right and top axes) in contrast to the EBW exhibited by the purely mechanical sandwich structure model. The much smaller boundary layer is a result of a new length scale in the problem arising from the introduction of flexoelectricity. Once we nondimensionalize 2.2.9, we have another nondimensionalized quantum-flexoelectric crinkle parameter, $\pi a Q_b \epsilon_{(N)} / \beta_{(N)}^{*2}$, in addition to the purely mechanical crinkle parameter, $(\pi / 2a\theta_e) \sqrt{Q_b / \mu a}$, introduced in section 2.1.2. Dependence of (2.2.9) on the quantum-flexoelectric crinkle parameter implies that the energetic competition between flexoelectricity and layer bending yields a band width scaling as $\pi a^2 Q_b \epsilon_{(N)} / \beta_{(N)}^{*2}$, such that higher bending stiffness implies wider band width and higher flexoelectric constant implies narrower width.

2.3 Analysis of crinkle curvature localization and amplification in graphene

The electromechanical model employing our e-locality constitutive relationship of flexoelectricity, assuming local coupling between $\hat{E}$ and κ , shows all the qualitative features of flexoelectric crinkle as predicted by DFT. In this section, we take a deeper look at the quantitative features of the different models.

2.3.1 Post-buckling characteristics of flexoelectric graphene crinkle

Figure 2.3.(a) shows a comparison of the peak curvature variation versus the kink angle (defined as $\theta(L_0) - \theta(0)$) among the DFT, the e-local flexoelectric and the mechanical sandwich structure models. The length of our 21-layer MLG is chosen to be $2L_0 = 15nm$ for both purely-mechanical and flexoelectric models. All three models predict a linear variation of the peak curvature with respect to the kink angle in the post-buckling configuration. Defining the slope of the linear variation as the *curvature focusing factor*, the DFT and the flexoelectric models both predict a curvature focusing factor of $\sim 0.052nm^{-1}/degree$. This is more than 20 times that of the purely mechanical sandwich structure model, $\sim 0.0023nm^{-1}/degree$ show in Fig. 2.2.(e). Thus, the long range dipole-dipole interactions in the flexoelectric layers enhance the curvature focusing more than 20 times. In comparison, the curvature focusing factor for 15 nm long MLG shown in Fig. 2.3.(a) is $\sim 0.004nm^{-1}/degree$, since the length of the MLG is shorter than the mechanical boundary layer width. Figure 2.3.(b) exhibits the constraint force normalized by the critical load of pure-shear buckling, $20\mu a$ for our 21-layer MLG model, to keep the end (or kink) angle in the post-buckling configuration, for two different models. One is for the purely mechanical sandwich structure model, the black curve, and the other for the e-local flexoelectric model, the blue curve. These two models match up those of Fig. 2.3.(a) for $2L_0 = 15nm$. The result of the purely mechanical sandwich structure model corresponds to the constraint force for the interlayer-shear-mode buckling. The interlayer-shear mode of buckling is well known to be supercritical and progressive, and the constraint force versus end angle plot shows a quadratic dependence at the small-angle range. The critical load of the purely mechanical interlayer-shear-mode bifurcation is about 0.53% higher than $20\mu a$ due to finite-length effect of using $2L_0 = 15nm$ specimen. On the other hand, the critical load for flexoelectric crinkle formation (the blue curve in Fig. 2.3.(b)) is about 0.48% higher than $20\mu a$, which is lower than the critical load of purely mechanical buckling. The e-local model predicts

that with respect to perturbations of complex harmonic modes, the bifurcation is subcritical and the constraint-force should jump to the stable branch of the crinkle post-buckling evolution, shown in blue, in Fig. 2.3.(b).

2.3.2 Complex harmonic bifurcation analysis of critical multi-layer graphene buckling

In this sub-section, we perform a linear bifurcation analysis with the e-locality model formulated in section 2.2.3. From the full energy expression (2.2.8), we invoke the linearized small-angle approximation and obtain the following Euler-Lagrange equation for the system,

$$Q_b N \theta''(x) + \{f - \mu(N-1)a\} \theta(x) + \frac{\beta_{(N)}^{*2}}{\pi \epsilon_{(N)}} \int_{-L_0}^{L_0} \theta'(\xi) g'_{(N)}(\xi - x) d\xi = 0 \quad (2.3.1)$$

For $-L_0 \leq x, \xi \leq L_0$, where $g_{(N)}(x - \xi)$ is the dipole-dipole interaction kernel that depends on the number of layers N and the geometry. It excludes $|\xi - x| < r_0$ for interlayer interactions with r_0 the cut-off radius. Now, we look for nontrivial solutions for the above equation for the bifurcation analysis. To this end, we apply the Fourier transformation,

$$\hat{\phi}(k) = \int_{-\infty}^{\infty} e^{-ikx} \phi(x) dx \quad (2.3.2)$$

to (2.2.1) with i the unit imaginary number, and obtain,

$$\left\{ f - \mu(N-1)a - k^2 \left(Q_b N - \frac{\beta_{(N)}^{*2}}{\pi \epsilon_{(N)}} \hat{g}_{(N)} \right) \right\} \hat{\theta} = G_{(N)}(\tilde{k}; \tilde{f}) \hat{\theta} = 0 \quad (2.3.3)$$

where $\hat{\theta}$ is the Fourier transformation of the function $\{\theta(x) \text{ for } |x| \leq L_0, \text{ and } \theta(x) = \theta(L_0) \text{ for } |x| > L_0, \text{ and } \tilde{k} = ak \text{ and } \tilde{f} = f/\mu(N-1)a\}$ denote non-dimensionalized wavenumber and non-dimensionalized constrained force respectively. For nontrivial solutions of $\hat{\theta}$, we must satisfy $G_{(N)}(\tilde{k}; \tilde{f}) = 0$. Here, we evaluate the critical complex-harmonic buckling load of a bilayer ($N=2$) graphene to get physical insight of curvature localization at the onset of bifurcation without loss of generality.

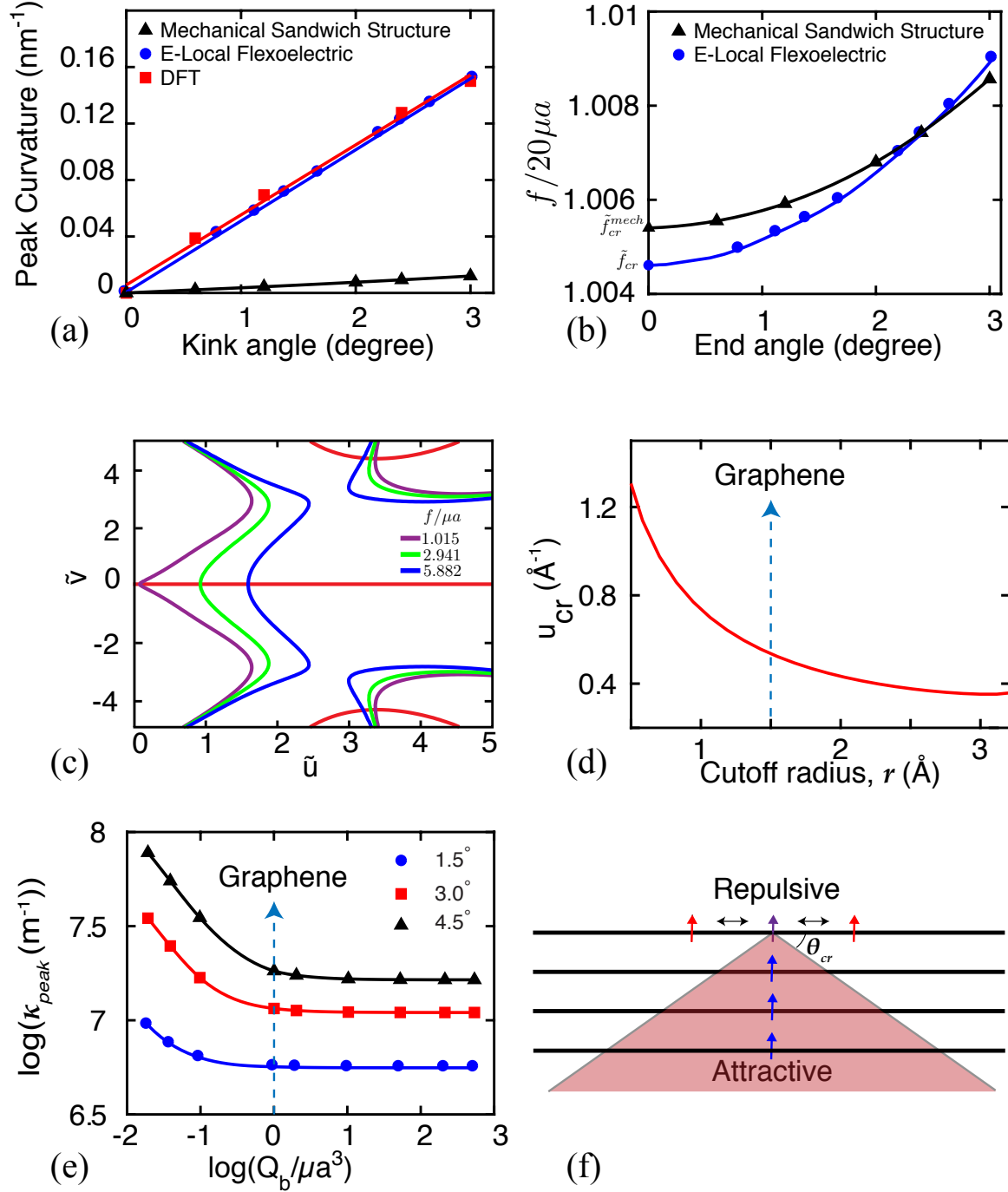


Figure 2.3: (a) Comparison of peak curvature predictions by the purely mechanical model, the e-local flexoelectric model and the DFT as a function of kink angles for 21-layered and 15 nm long MLG; (b) Evolution of the constraint force f with end angle for the purely mechanical and the e-local models; (c) bifurcation diagram for complex harmonic perturbations from the flat state for a bilayer graphene (red line indicates the solutions for imaginary part, $I_{(2)}(\tilde{u}, \tilde{v}) = 0$, while other colours indicate solutions for real part, $R_{(2)}(\tilde{u}, \tilde{v}) = 0$, for different constraint forces.); (d) Effect of the cut-off radius r_0 on the critical wavenumber u_{cr} (marker indicates the value used in the analysis for MLG.); (e) peak curvature dependence on material properties (this highlights the mechanism of curvature focusing in the purely mechanical model); (f) schematic of interlayer and intralayer dipole interactions in MLG.

For the bilayer model, the kernel $g_{(2)}(\xi - x)$ is given as

$$g_{(2)}(\xi - x) = \frac{-(\xi - x)^2 + a^2}{\{(\xi - x)^2 + a^2\}^2} - \frac{2\{1 - q(\xi, x)\}}{(\xi - x)^2} \quad (2.3.4)$$

where the first term comes from interlayer interactions while the second term arises from intralayer interactions. The Fourier transform of $g_{(2)}$, using the definition (2.2.2), is calculated to be

$$\hat{g}_{(2)}(k) = \pi|k|e^{-a|k|} + \pi|k| - 2kSi(kr_0) - 2\cos(kr_0)/r_0 \quad (2.3.5)$$

where Si denotes the sine-integral function. Complex solutions of $G_{(2)}(\tilde{k}; \tilde{f}) = 0$, given by splitting the equations into real and imaginary parts for $\tilde{k} = \tilde{u} + i\tilde{v}$, yield

$$G_{(2)}(\tilde{k}; \tilde{f}) = R_{(2)}(\tilde{u}, \tilde{v}; \tilde{f}) + i I_{(2)}(\tilde{u}, \tilde{v}) = 0 \quad (2.3.6)$$

Equation (2.3.6) shows that the imaginary-part solution, $I_{(2)}(\tilde{u}, \tilde{v}) = 0$, does not depend on the constraint force, $\tilde{f}$, and is plotted as red curves on the $(\tilde{u}, \tilde{v})$ plane in Fig. 2.3.(c), for a bilayer graphene. On the other hand, the real-part solution, $R_{(2)}(\tilde{u}, \tilde{v}; \tilde{f}) = 0$, depends on $\tilde{f}$, and is plotted for different values of $\tilde{f}$ with various colored curves. Intersection points between the red curve and other colored curves represent the admissible complex wavenumbers corresponding to different values of $\tilde{f}$. The intersection points in Fig. 2.3.(c) reveal one real ($\tilde{v} = 0$) and two complex conjugate ($\tilde{v} \neq 0$ with same $\tilde{u}$) roots of (2.3.6). Since the solution of (2.3.6) should trace the red curves in Fig. 2.3.(c), the red curves represent the fundamental solution branch of bilayer graphene buckling obtained by the complex harmonic analysis. The red line of the real root ($\tilde{v} = 0$) shows the fundamental solution branch for sinusoidal buckling modes. Along this line, admissible buckling modes and corresponding loads are determined by the boundary conditions, similar to the pitchfork bifurcation in Euler column buckling. On the other hand, the complex conjugate roots represent the critical quantum flexoelectric buckling mode, $\theta \sim (A_1 e^{\nu x} + A_2 e^{-\nu x}) \sin ux$, at the nanoscale. For a long span ($L_0 \gg a$) of the bilayer graphene, A_1/A_2 vanishes to satisfy the

end condition, $\theta \rightarrow 0$ at $x = L_0$ for this mode. In Fig. 2.3.(c), three complex-conjugate root sets, $(\tilde{u}, \tilde{v}) = (3.385, 4.410), (3.317, 4.426), (3.214, 4.441)$, are displayed for three buckling loads, $\tilde{f} = 1.015, 2.941, 5.882$. The results show that the critical wavenumber and the decay length of the critical quantum flexoelectric buckling mode hardly change with variation of the critical buckling load $\tilde{f}$. However, the critical wave length, ~ 0.63 nm, and the critical decay length, ~ 0.48 nm, for $\tilde{f} \sim 1.015$ are somewhat shorter than those of the post-buckling mode observed in the crinkle ridge boundary layer. It is believed that at the onset of buckling the long wavelength harmonic mode and the quantum flexoelectric crinkle mode are concurrently activated at the critical load. Then, the critical onset mode jus to the subcritical post-buckling mode of two straight crinkle wings linked by the curvature focusing boundary layer, adjusting the wavelength and the decay length of curvature distribution. Our parameter study shows that the complex conjugate roots only exist for the quantum flexoelectric crinkle parameter in the range of $1.01 < \frac{\pi a Q_b \epsilon_{(2)}}{\beta^{*2}} < 31.6$. When the value approaches 1.01, the mode becomes harmonic with its wavenumber close to that of the graphene lattice, indicating the trend of spontaneous phase transition from sp_2 to sp_3 . On the other hand, when the parameter value exceeds 31.6, the flexoelectric constant is too small to excite the quantum flexoelectric buckling; it can only support the long wavelength buckling. The bilayer graphene has the value 3.48, indicating that graphene is an ideal material to form quantum flexoelectric crinkles.

2.3.3 Mechanisms of curvature localization in graphene

So far, our energy minimization and bifurcation analyses of the e-local model for flexoelectricity predict the formation of flexoelectric crinkles and the results are in good agreement with the DFT findings. We now take a close look at the energetic interplay that leads to curvature localization in both purely mechanical and electromechanical buckling.

In the purely mechanical model, in the absence of any bending rigidity, a perfectly sharp mathematical kink is the energy minimizing solution that satisfies the boundary conditions. However, with a non-zero bending rigidity, there is an energy competition between interlayer-shear and layer-bending modes. A larger boundary layer allows reduction in the shear energy, which primarily comes from the straight sections of the shape. Thus, we see a smoothly distributed curvature over the length of the sample. However, we would like to point out here that even the purely mechanical model shows non-negligible amount of curvature amplification for small values of $Q_b/\mu a^3$ as shown in figure 2.3.(e), but for the material properties of graphene, this effect is not significant.

As discussed in the Introduction, long range nonlocal flexoelectric interactions in the model allow for significant energy variations, especially reduction of energy through *attractive* dipole-dipole interactions. The curvature reversal exhibited by the flexoelectric crinkle plays the key role in the energy reduction in the e-local model. Since we employ local coupling in the constitutive relationship, reversal of curvature also implies reversal of polarization. Figure 2.3.(f) shows the schematic of dipole-dipole interactions. There are two types of dipole-dipole interactions – interlayer and intralayer. Interlayer interactions among the dipoles present in the red region are attractive and lower the potential energy. The presence of multiple layers increases the energetic favorability of crinkle formation. Since the crinkle curvature and hence polarization are highly localized, all the interaction is within the shaded (red) region in figure 2.3.(f). Intralayer interactions are repulsive for parallel and attractive for anti-parallel dipoles, which is the primary reason why crinkles display the characteristic curvature reversal. The curvature reversal leads to reversal of polarization, and thus the strong attractive intralayer interactions reduce the total energy. This explains the origin of the FBW of curvature focusing. The electrical interaction keeps reducing the potential energy as the boundary layer becomes smaller and smaller. Thus, at the onset of bifurcation there is a spontaneous reduction of boundary layer width which is impeded only by the non-vanishing bending rigidity of

graphene. This competition between bending energy and flexoelectric energy gives rise to a boundary layer, substantially smaller than the purely mechanical boundary layer (~ 2 nm compared to ~ 50 nm). The two mechanisms of curvature focusing work together for flexoelectric crinkles. The energetic competition between layer-bending energy and interlayer-shear energy provides a macroscopic broad-band focusing, while the competition between layer-bending and flexoelectric energy gives a much narrower FBW of curvature focusing and much larger curvature amplification.

2.4 Discussion

2.4.1 Reduced couplings of flexoelectricity and dielectricity

It is a pleasant surprise that a simple e-local flexoelectric polarization model, (2.2.7), can capture the major characteristics of critical curvature localization in graphene predicted by DFT analysis. Since $\hat{E}$ in (2.2.6) is a point-exclusive external electric field, the electric field is generated by all other dipoles distributed in the entire MLG except for the dipole within the cut-off radius, and thus the polarization is inherently nonlocal. However, we lumped the contribution of the nonlocal dielectric interaction term in (2.2.6) into a single e-local flexoelectric constant $\beta_{(N)}^*$ in (2.2.7). This lumping for 'uniform curvature distribution' in SLG provides the uc-local polarization constant, $\beta_{(1)}^{(uc)} = 0.11e$, reported in [46]. Similar to electric permittivity, $\epsilon_{(N)}$, the uc-local polarization constant, $\beta_{(N)}^{(uc)}$, is layer-number, N , dependent, and $\beta_{(21)}^{(uc)} \sim 0.718e$, for example. In contrast, a crinkle has a non-uniform curvature distribution, and we obtain a slightly larger value of the e-local flexoelectric constant, $\beta_{(21)}^* = 0.745e$, by best-fitting the 3° -crinkle curvature distribution predicted by the e-local model to that of the DFT analysis. The value, $\beta_{(21)}^* = 0.745e$, is MLG crinkle specific. In general, the reduced flexoelectric model, from $(\alpha_{(N)}, \beta_{(N)})$ to $(\beta_{(N)}^*)$, is not applicable to

solve non-uniform curvature problems. However, the peculiar characteristics of the localized curvature distribution, $\kappa(x, \theta_e) = \theta_e \psi(x)$, in the nanoscale MLG crinkle boundary layer allows us to use the reduced effective flexoelectric constant, where $\psi(x)$ is the universal shape function of the crinkle. In the crinkle boundary layer, the antiparallel flexoelectric dipoles in mutually opposite curvature distributions enhance the additional point-exclusive dielectric polarizations. Furthermore, FBW of the boundary layer makes the dielectric polarizations also proportional to the curvature. These two effects make the effective flexoelectric constant $\beta_{(21)}^*$ larger than the intrinsic flexoelectric constant, $\beta_{(21)} = 0.726e$. In contrast, flexoelectric dipoles of uniform curvature distribution are parallel to each other and hence the dielectric polarizations are induced in the opposite direction to the flexoelectric dipoles. Therefore, $\beta_{(N)}^{(uc)}$ is smaller than $\beta_{(N)}$. In other words, the net polarization is amplified by dielectricity from the intrinsic flexoelectric polarization in MLG crinkles, and is reduced in uniformly curved MLGs. Although a 3D-continuum electromechanical constitutive relation in the entire space can be made in a unified manner with thermodynamic representation ([24], [26]), 3D-continuum kinematics cannot effectively follow the deformation of layered structures of inextensible 2D materials. The e-local modeling is found effective in accounting energetics for MLG crinkle deformations. A comparison of the results using $\beta_{(1)}^{(uc)}$ with those using $\beta_{(21)}^*$ is provided in appendix B.

2.4.2 Critical constraint force and the post-buckling mode of MLG

For a quantitative assessment of post-buckling behavior of MLG, we consider the lowest admissible critical load $f_{(2)}$ of sinusoidal interlayer-shear-mode buckling, from equation (2.3.3), for a bilayer ($N = 2$) graphene of length $2L_0 = 15$ nm,

$$\tilde{f}_{(2)} = 1 + \frac{k^2}{\mu a} \left(2Q_b - \frac{\beta_{(2)}^{*2}}{\pi \epsilon_{(2)}} \hat{g}_{(2)} \right) \quad (2.4.1)$$

which evaluates to $\tilde{f}_{(2)} = 1.0164$ for $k = \pi/15 \text{ nm}^{-1}$, $\mu a = 1.36 \text{ N/m}$, $Q_b = 1 \text{ eV}$, and $\beta_{(2)}^{*2} \hat{g}_{(2)}(k)/\pi \epsilon_{(2)} = -1.175 \text{ eV}$. A negative $\beta_{(2)}^{*2} \hat{g}_{(2)}(k)/\pi \epsilon_{(2)}$ implies that the intralayer flexoelectric dipole-dipole interaction of parallel dipoles effectively increase the bending rigidity.

The critical load for the purely mechanical model evaluates to $\tilde{f}_{(2)} = 1.0103$, which is higher than the lowest post-buckling load of crinkle as seen in Fig. 2.3.(b). This result indicates that the fundamental state bifurcates at $\tilde{f}_{(2)} = 1.0164$ with a sinusoidal mode which together with the quantum-flexoelectric buckling mode triggers cascading bifurcations of higher orders. These bifurcation events reduce the load to the lowest post-buckling load of crinkle, becoming a subcritical harmonic bifurcation. Once the flexoelectric crinkle is formed at an infinitesimal end angle, subsequent post-buckling load increases with growing end angle, and all the crinkle modes remain identical. The post-buckling mode of the flexoelectric crinkle, $\theta' \sim \frac{\sin k_{(\text{FBW})} x}{x}$ within the boundary layer, ensures the characteristics of FBW curvature focusing. If β^* is set to zero, i.e. no flexoelectricity, we recover the purely mechanical supercritical bifurcation and the boundary layer exhibits characteristics of EBW curvature focusing.

A similar phenomenon of subcritical harmonic bifurcation with the invariance of post-bifurcation mode starting at a lower load was previously discovered for the case of creasing in a neo-Hookean solid surface under lateral plane-strain compression ([53], [54], [55], [56]). For creasing, this mode is singular. The singular crease field was introduced by the cascading subcritical higher order harmonic bifurcations [41] at the critical compressive strain for harmonic bifurcation [54], called the Biot strain, 0.46 [57]. Alternatively, it could be also introduced by singular perturbation [55] such that the crease initiated at a compressive strain of 0.35, which is smaller than the Biot strain. For both flexoelectric crinkle and crease cases, the mode grows self-similarly, unlike the progressive growth observed in the supercritical buckling of purely mechanical models.

2.4.3 Crinkle flexoelectric polarization and potential applications

The critical curvature localization in MLG amplifies the peak curvature by two orders of magnitude from that of an equivalent sinusoidal wrinkle to within 0.86 nm FBW for a typical span of the MLG

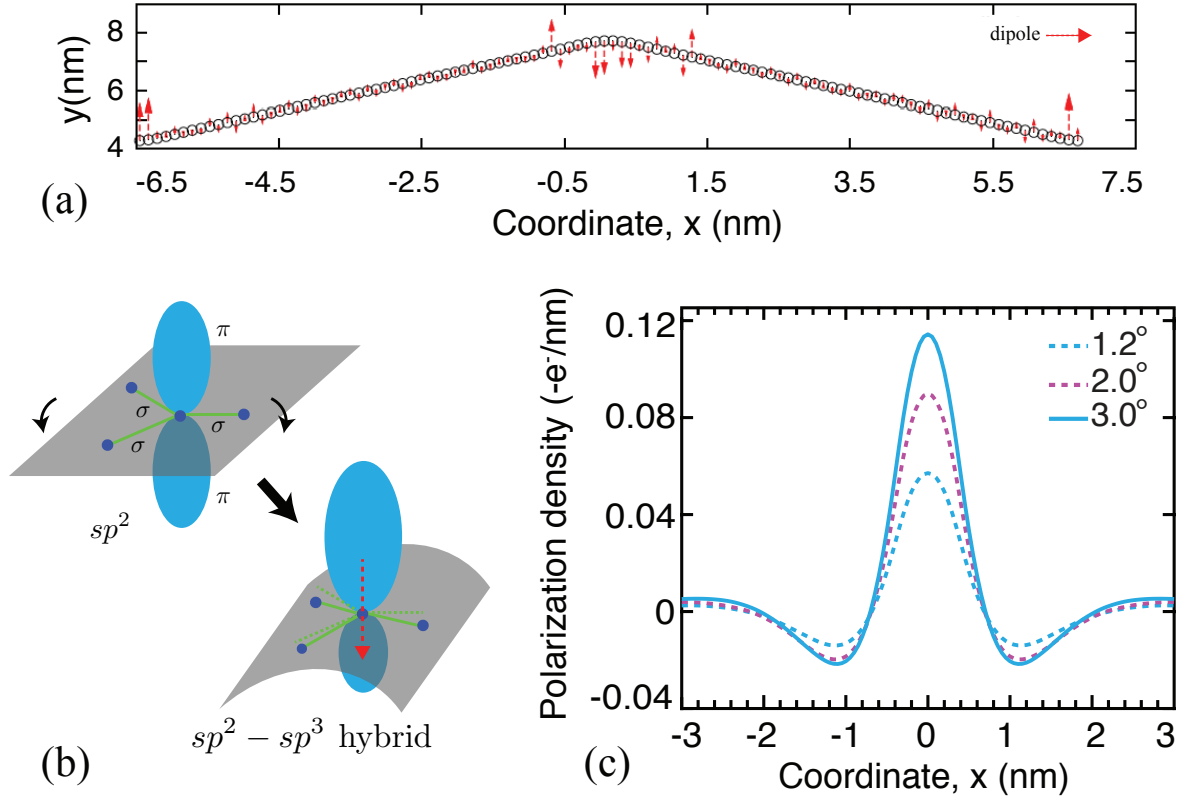


Figure 2.4: Figure 4.(a) Qualitative plot of atomic polarization for a cross section of flexoelectric crinkle from DFT analysis; (b) a schematic of electron cloud distortion in bent graphene leading to polarization i.e. quantum flexoelectricity; (c) polarization density for 21-layered, 15 nm MLG predicted by e-local model.

layers, for instance, $2L_0 = 100$ nm in Fig. 2.2.(e). For example, the case of a wrinkle with 3° end angle for $2L_0 = 100$ nm has its peak curvature of 0.0016 nm^{-1} , while the equivalent purely-mechanical crinkle amplifies this to 0.0068 nm^{-1} , and the flexoelectric crinkle to 0.16 nm^{-1} . The amplification factor is proportional to L_0 . An important feature of the MLG crinkle is the development of highly concentrated flexoelectric polarization along the crinkle ridges and valleys. Figure 2.4.(a) shows the

DFT-evaluated flexoelectrically polarized dipoles of specific atoms on a cross-section of the crinkle. Note the localization and reversal of polarization. As the curvature decays, the polarization also vanishes away from the crinkle ridge. Figure 2.4.(b) highlights the mechanism of intrinsic flexoelectric polarization, where bending leads to π electron cloud shift (in blue) that produces the polarization. The intrinsic flexoelectric polarization further induces additional dielectric polarization. As we obtained in 3.1, the curvature focusing factor for flexoelectric crinkle was $0.052 \text{ nm}^{-1}/\text{degree}$, and this large curvature amplification indeed produces a significant net polarization density with peak values reaching 0.12e/nm for a 3° kink angle as shown in Fig. 2.4.(c).

Curvature localization and amplification lead to development of surface electric charge concentration in the FBW along the crinkle ridges and valleys on the top and bottom free surfaces of MLG. The surface electric charges are negative on the tops of ridges and positive on the bottoms of valleys. This yields a nanoscale line charge, focused in a 0.86 nm band, and the intensity of the charge concentration can be regulated by controlling the end angle or the level of compression. We posit that the effects of the crinkle-induced surface line charges have been indirectly observed in literature ([58], [59]). For instance, DNA molecules are adsorbed along well-ordered lines [58], and C_{60} Buckyballs line up in a regular pattern [59] on HOPG surfaces. We believe that these previously unexplained observations are caused by the presence of flexoelectric line charges resulting from crinkles. HOPG contains naturally existing flexoelectric crinkles along the domain boundaries of the mosaics [15] as discussed in the introduction. The HOPG crinkle networks are likely generated by inhomogeneous stress fields due to defects introduced during the manufacturing process. DNA molecules are negatively charged, and the DNA molecules are likely adsorbed along the troughs of the crinkle valleys [58]. A straightforward energy minimization calculation accounting for the interactions among the crinkle line charge and the dielectric charges of the Buckyballs shows that

the optimal distance between the Buckyballs should be about 2nm, which is close to the experimentally observed spacing [59]. Typical interaction potential depth between the crinkle line charge and charged molecules or large neutral molecules (or nanoparticles) are much deeper than the Boltzmann activation energy, $k_B T = 25.7$ meV, at room temperature, $T = 298K$. Therefore, we expect that flexoelectric crinkles will be useful in studying self-organizing molecular adsorption for various applications. Besides the potential applications of flexoelectric crinkle charges in adsorption problems, the kinematics and energetics of flexoelectric crinkles can provide new insight on dynamic ripple characteristics in graphene [8]. As DFT analysis reveals that SLG crinkle is a metastable configuration for $2L_0 = 13.26$, the crinkle mode can develop a characteristic phonon mode of ripples in graphene other than the sinusoidal mode, for wavelengths of $4L_0 < 26.5$ nm, and dynamic mode hopping in different modes can play a significant role in thermodynamic energy partitioning and phonon transfer.

Chapter 3

Constitutive non-locality of flexoelectricity and dielectricity

Note : A version of this chapter has been submitted for publication in Proceedings of the Royal Society A. Data and figures have been used with all co-authors' consent.

Kothari M, Cha M.-H. and Kim K.-S. Subcritical curvature localization in graphene. II. Nonlocal flexoelectricity-dielectricity coupling. Proceedings of the Royal Society A (2018).

3.1 Introduction

In chapter 2, we used a specific constitutive relation, e-local model, for flexoelectricity of graphene to understand a peculiar localization mode, crinkle, in graphene. In chapter 3, our interest is in self-consistent description of flexoelectricity in multi-layered structures in the context of coupling

between flexoelectricity and dielectricity for general 2D layered materials, and extraction of associated material properties from DFT calculations. We begin by first deriving an appropriate free-energy potential for flexoelectric modeling consistent with thermodynamic framework, and apply such framework for modeling electromechanical deformation of 2D layered materials with a field-of-view resolution in nanometer scale.

Among the early body of theoretical work on flexoelectricity of crystals ([17], [18]), a phenomenological constitutive law was postulated by Kogan [18] for bulk polarization density, P_i , in non-piezoelectric materials,

$$P_i = \chi_{ij}E_j + \beta_{ijkl}(\nabla\epsilon)_{jkl} \quad (3.1.1)$$

where χ_{ij} represents electric susceptibility tensor, E_j electric field, β_{ijkl} flexoelectricity tensor, and $(\nabla\epsilon)_{jkl}$ strain gradient. In more recent works on continuum modeling of flexoelectricity and general electro-mechanical formulation ([24], [25], [26], [60]), the constitutive relation is derived in a context of internal-free-energy ($\mathcal{F}$) formulation. In their work, the total internal free energy is described as a functional of displacement, $\mathbf{u}$, the bulk polarization density, $\mathbf{P}$, and the scalar electric potential, ξ , as

$$\mathcal{F}[\mathbf{u}, \mathbf{P}] = \int_{\Omega} W[\mathbf{u}, \mathbf{P}]d\Omega + \int_{\mathbb{R}^3} \frac{\epsilon_0}{2} |\nabla\xi|^2 dV \quad (3.1.2)$$

where W represents a free energy density defined only in the volume of the material Ω , while $\mathbb{R}^3$ denotes the entire space.

When the description is further reduced to that of a *local differential-type material behavior*, the internal energy per unit volume, U , can be expressed in terms of fundamental work-conjugate displacement variables – strain, strain gradient and electric displacement, $\{\epsilon, \nabla\epsilon, \mathbf{D}\}$ – of stress, couple stress and the electric field, $\{\boldsymbol{\sigma}, \mathbf{m}, \mathbf{E}\}$. The internal energy is explicitly expressed as

$$\int_{\mathbb{R}^3} U(\boldsymbol{\varepsilon}, \boldsymbol{\nabla} \boldsymbol{\varepsilon}, \mathbf{D}) dV = \int_{\Omega} \int_0^{\boldsymbol{\varepsilon}} \boldsymbol{\sigma} d\boldsymbol{\varepsilon} d\Omega + \int_{\Omega} \int_0^{\boldsymbol{\nabla} \boldsymbol{\varepsilon}} \mathbf{m} d\boldsymbol{\nabla} \boldsymbol{\varepsilon} d\Omega + \int_{\mathbb{R}^3} \int_0^{\mathbf{D}} \mathbf{E} d\mathbf{D} dV \quad (3.1.3)$$

where all the products on the right hand side are scalar products. Then, this expression leads to constitutive relations,

$$\boldsymbol{\tau}(\boldsymbol{\varepsilon}, \boldsymbol{\nabla} \boldsymbol{\varepsilon}, \mathbf{D}) = \frac{\partial U}{\partial \boldsymbol{\eta}} \quad (3.1.4)$$

where $\boldsymbol{\tau}$ represents the set of variables $\{\boldsymbol{\sigma}, \mathbf{m}, \mathbf{E}\}$ and $\boldsymbol{\eta}$ the set $\{\boldsymbol{\varepsilon}, \boldsymbol{\nabla} \boldsymbol{\varepsilon}, \mathbf{D}\}$. In the *linear-response range of the constitutive relation*, $\boldsymbol{\tau}(\boldsymbol{\varepsilon}, \boldsymbol{\nabla} \boldsymbol{\varepsilon}, \mathbf{D})$, the internal energy has a quadratic form,

$$U = \frac{1}{2} \boldsymbol{\eta} \bullet \mathbf{Q} \bullet \boldsymbol{\eta} \quad (3.1.5)$$

where $\mathbf{Q}$ represents symmetric electromechanical-property coefficients. $\mathbf{Q}$ comprises of six sets of material properties in the most general case. For a non-piezoelectric material, ignoring the strain gradient effect on mechanical stress, the coefficient set $\mathbf{Q}$ reduces to four sets that correspond to stress/strain stiffness, couple-stress/strain-gradient stiffness, inverse electric permittivity and flexoelectric coefficients respectively. However, the total number of coefficients in $\mathbf{Q}$ is too large to be practical for measurement in highly anisotropic materials and/or 2D-layered materials. On the other hand, when we consider deformation of 2D layered structure like multilayer graphene, the electromechanical deformation is primarily composed of distinct modes, such as interlayer shear and individual layer bending, and often localizes at a narrow band of nanometer-scale width. Therefore, it is more practical to treat the internal energy as those of individual layers described with the framework of (3.1.5) and those of interlayer deformation.

For modeling deformation of 2D layered structures, we write the internal energy per unit area of individual layer, $U_{(L)}$, for a 1D layer deformation mode. This reduces $\mathbf{Q}$ to its 2-dimensional analog

$\mathbf{Q}_{(2D)}$ and leads to four coefficients:

$$U_{(L)}[\varepsilon, \kappa, D] = \frac{1}{2}Y^{(D)}\varepsilon^2 + \frac{1}{2}Q_b^{(D)}\kappa^2 + \beta^{(D)}\kappa D + \frac{1}{2\varepsilon^{(D)}}D^2 \quad (3.1.6)$$

where, ε denotes the stretching strain and κ the curvature of the layer, while $Y^{(D)}$, $Q_b^{(D)}$, $\beta^{(D)}$ and $1/\varepsilon^{(D)}$ are the components of $\mathbf{Q}_{(2D)}$. Employing *Legendre transform* [61] for variable change from D to P , and noting that $D = \varepsilon_0 E + P$, we define a new free-energy potential $\phi_{(L)} \equiv \phi_{(L)}[\varepsilon, \kappa, P]$. The transformation enables us to exclude the domain integral over $\mathbb{R}^3 \setminus \Omega$ in evaluating the total free energy of the system, which makes computational analysis simpler. The transformed free-energy potential is expressed as,

$$\phi_{(L)}[\varepsilon, \kappa, P] = U_{(L)}[\varepsilon, \kappa, P] - \frac{\varepsilon_0}{2}E^2 = \frac{1}{2}Y^{(P)}\varepsilon^2 + \frac{1}{2}Q_b^{(P)}\kappa^2 + \beta^{(P)}\kappa P + \frac{1}{2\chi^{(P)}}P^2 \quad (3.1.7)$$

and the corresponding constitutive relations are given by (3.1.4) to have,

$$\left\{ \sigma = Y^{(P)}\varepsilon, \quad m = \left(Q_b^{(P)}\kappa + \beta^{(P)}P \right), \quad E = \beta^{(P)}\kappa + \frac{1}{\chi^{(P)}}P \right\}$$

where $Y^{(P)}$, $Q_b^{(P)}$, $\beta^{(P)}$ and $1/\chi^{(P)}$ are the coefficients for $\{\varepsilon, \kappa, P\}$ -based description.

Specializing for the case of graphene, we employ inextensibility of the layer as a limiting approximation which drops ε -dependence of $\phi_{(L)}$ and σ in 3.1.7, and rearrange (3.1.7 ()) to get,

$$\check{P} = \alpha \check{E} + \beta \kappa \quad (3.1.8)$$

Here $\check{()}$ denotes the component normal to graphene layer, $\check{P}$ the polarization density per unit area, the 2-D atomic-layer polarizability of graphene, $\check{E}$ the point exclusive electric field that includes the field generated by polarization elsewhere, and $\beta = -\beta^{(P)}\chi^{(P)}$ the 2D flexoelectric coefficient. The point exclusive description of $\check{E}$ in (3.1.8) represents nonlocal flexoelectricity-dielectricity coupling in graphene. For the rest of the paper, we make use of (3.1.8) as the constitutive law of nonlocal flexoelectric polarization coupled with dielectric polarization. However, this formulation makes the polarization-induced electric field singular, and the singularity is typically regulated

by the cut-off radius technique discussed in the previous chapter ([62], [63]). Note that while Claussius-Mossoti relationship expresses the electric susceptibility, χ , of a material in terms of the atomic polarizability, α^* , of the constituent atoms for a bulk formulation, for modeling 2-D layered materials like graphene we employ (3.1.8) in terms of atomic-layer polarizability per unit area, α .

The organization of the paper is as follows: In section 2 we discuss the reduced models of flexoelectricity and the importance of flexoelectricity-dielectricity coupling. The analysis of the nonlocal model is presented in section 3.3 followed by DFT studies on adsorption of molecules on crinkles in section 3.4. We discuss the implications of the nonlocality in section 3.5.

3.2 Flexoelectricity Models

As aforementioned, in this chapter, we focus on flexoelectricity in multilayer graphene (MLG). In chapter 2, we discussed the discovery of a new subcritical buckling mode of MLG which shows high curvature localization. DFT studies indicated that the curvature of the crinkle mode remains focused in a very narrow band of width 0.86 nm which remains fixed even as the amplitude of the mode increases. There, presented was a reduced model of flexoelectricity that lumps together the flexoelectric and dielectric effects. The model predicted crinkle formation with peak curvatures 0.15 nm^{-1} and peak polarization density $0.11 e \text{ nm}^{-1}$ for a 3° end angle, leading to concentration of static electric charges at the crinkle ridges and valleys on the free surface. However, the peak polarization density was found to be significantly higher than that predicted by the single-layer flexoelectric constant of uniform curvature [7]. In order to address the apparent multitude of flexoelectric constants, we develop a model including flexoelectricity-dielectricity coupling consistent with thermodynamic framework. This model is inherently nonlocal since the flexoelectric and dielectric polarization interact and influence each other. In this section we discuss two reduced models

of quantum flexoelectricity in graphene and lay the background for a general model.

3.2.1 Reduced constitutive models of flexoelectricity

Figure 3.1.(a1) depicts the configuration (gray curve), curvature distribution (solid line), and polarization distribution (dash-dot line) in a uniformly bent graphene layer. The polarization is proportional to curvature, and the proportionality constant is called the 2D *uniform-curvature flexoelectric constant* $\beta^{(uc)}_{(1)}$. Kalinin et al. [7] evaluated $\beta^{(uc)}_{(1)} = 0.11e$ with first-principle calculations, naming it as quantum flexoelectric coefficient, for

$$\check{P} = \beta^{(uc)}_{(1)} \kappa \quad (3.2.1)$$

where the subscript of $\beta^{(uc)}_{(1)}$ indicates a single layer. Here we call (3.2.1) uc-local model.

On the other hand, for a much more complex non-uniform bending, the above model falls short. Figure 3.1.(a2) illustrates non-uniform distributions of configuration, curvature and polarization near a crinkle ridge, indicating that polarization is under-predicted by the uc-local model. Calibration with the DFT analysis of crinkles [63] yields an effective flexoelectric constant of a multilayer graphene crinkle ridge as $\beta^*_{(21)} = 0.759e$, which is 6.9 times $\beta^{(uc)}_{(1)}$, for

$$\check{P} = \beta^* \kappa \quad (3.2.2)$$

Here, $\beta^*_{(21)}$ stands for average flexoelectric constant of individual layer in 21-layer graphene for modeling with inextensible-layer limit. In part I [63], we employed the reduced model (3.2.2) without explicit involvement of dielectric constant α like in (3.1.8). The lumping of the inherent nonlocality in the flexoelectricity-dielectricity coupling into a local constitutive relationship is exact for uniform curvature distribution while it is an approximation for the crinkle problem. However, in general, the reduced models *do not* work for an arbitrary non-uniform curvature distribution and

therefore, a more detailed explicit treatment of dielectricity is undertaken in following sections.

3.2.2 Flexoelectricity-dielectricity coupling

Multilayer graphene is anisotropic in its response to electric field. It acts as an in-plane conductor at finite temperature and as a dielectric in the direction normal to the lattice layer. A full treatment of flexoelectricity for general curvature distribution involves long range dipole-dipole interactions through electric fields generated by the polarization distribution, leading to flexoelectricity-dielectricity coupling in the normal direction (3.1.8).

Figure 3.1.(b1)-(b4) illustrate flexoelectricity-dielectricity coupling mechanisms in dipole-dipole interactions near a crinkle ridge of MLG, based on the curvature distribution obtained by DFT in [63]. Figure 3.1.(b1) shows the net polarization (blue arrows) developed in a crinkle boundary layer. Due to curvature reversal, we get regions of positive and negative net polarization. This picture does not take into account any dielectric interactions explicitly. To uncouple flexoelectricity and dielectricity effects, we show the intrinsic flexoelectric polarization and the associated electric fields in Fig. 3.1.(b2). Bending of graphene creates a curvature which breaks the symmetry in the electron cloud distribution in graphene. This separation of positive and negative charge centers in graphene produces a polarization, which we refer to as the intrinsic flexoelectric polarization (black arrows). The intrinsic polarization thus developed, produce electric fields which influence the polarization in their neighborhood - either amplifying it (Fig. 3.1.(b2)) or weakening it (Fig. 3.1.(b3)). The combined effect leads to the net polarization. As illustrated for the intralayer case, the interlayer interactions follow a similar interaction mechanism (Fig. 3.1.(b4)). Note that the size of blue arrow is larger than black arrow in Fig. 3.1.(b2) and smaller in Fig. 3.1.(b3), indicating the amplifying and weakening effects respectively. Within the layer, anti-parallel dipoles reinforce each other since the additional dielectric polarization points in the same direction as the intrinsic

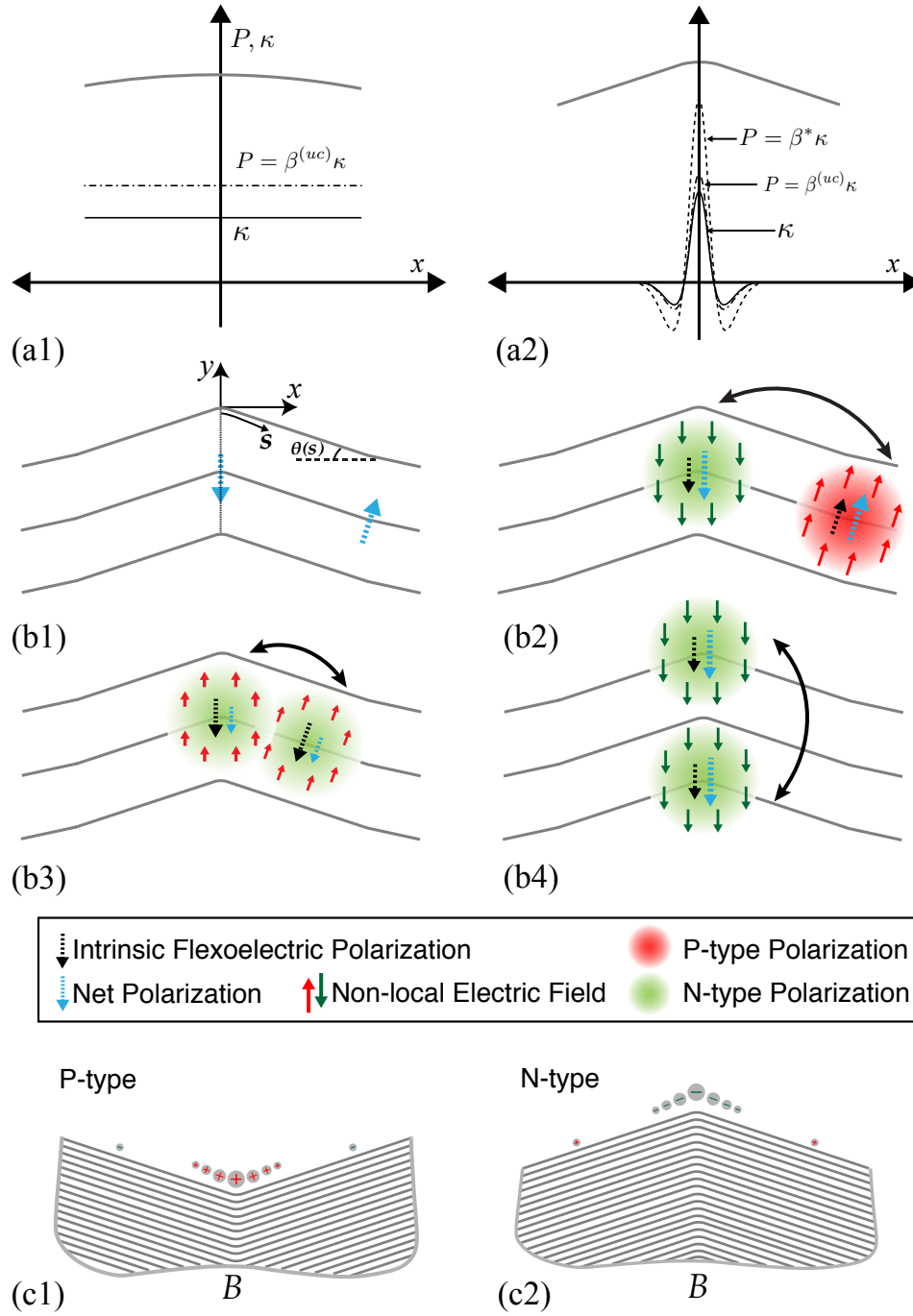


Figure 3.1: (a1) Polarization distribution for a uniform curvature case; (a2) Polarization distribution for a crinkle curvature distribution; (b1) Overall picture of the polarization on the layer, curvature reversal causes polarization reversal; (b2) In the intralayer case, electric fields amplify the anti-parallel polarization and (b3) diminish the parallel polarization; (b4) Interlayer interactions amplify the parallel polarization

flexoelectric polarization. In contrast, the parallel dipoles weaken each other because the dielectric polarization points opposite to the intrinsic flexoelectric polarization. Similarly, in Fig. 3.1.(b4) the blue arrows are larger since parallel dipoles reinforce each other in the interlayer setting. This is why crinkles, because of the signature curvature reversal, show a much larger $\beta_{(21)}^*$ in comparison to $\beta_{(1)}^{(uc)}$. Depending on the parity of bending, the flexoelectric charges developed on the surface can be positive or negative, as illustrated in Fig. 3.1.(c1) and (c2). Following the nomenclature introduced in [64], the positive charged crinkle is called P-type and the negative charged, N-type crinkle.

3.3 Analysis of the nonlocal flexoelectric model

3.3.1 Formulation

In this section we employ the nonlocal flexoelectricity-dielectricity coupling in the buckling and post-buckling analysis of suspended MLG in a plane-strain setting. We consider the setup in [63], with N-layer MLG, interlayer spacing $a = 0.34 \text{ nm}$ and total length $2L_0$. The bending stiffness of each layer in the $\{\kappa, P\}$ -based description is denoted as $Q_b^{(P)}$ and the interlayer shear modulus is μ . For the nano-structural model, we make use of DFT-evaluated material properties, $Q_b^{(P)} = 1.0 \text{ eV}$ [16], and $\mu = 4 \text{ GPa}$ [50]. The atomic polarizability of graphene is reported in the literature to be $\alpha^* \sim 0.85 \text{ \AA}^3$ ([65], [66]). Following the same kinematic assumptions as [63], the layers deform identically and are inextensible. Under these assumptions, the total free-energy potential Φ as defined in 3.1.7, can be given as the sum of mechanical and electrostatic parts. The mechanical part, Φ_{mech} , has two contributions, namely the bending of individual layers and interlayer shear.

$$\Phi_{mech} = \int_{-L_0}^{L_0} \left(\frac{Q_b N}{2} \left(\frac{d\theta}{ds} \right)^2 + \frac{\mu (N-1) a}{2} \tan^2 \theta \right) ds \quad (3.3.1)$$

where $\theta(s)$ is the slope angle and $\kappa = d\theta/ds$ is the curvature of the layer.

The electrostatic part, Φ_{elec} , is given as,

$$\Phi_{elec} = -\frac{1}{2\pi\epsilon_{(N)}} \sum_{n=1}^N \sum_{m=1}^n \int \int_{-L_0}^{L_0} \check{P}(s_n) \check{P}(s'_m) \frac{\{1 - \delta_{mn} q_1(s_n, s'_m)\} \{A(s_n, s'_m) + B(s_n, s'_m)\}}{[\{x(s_n) - x(s'_m)\}^2 + \{y(s_n) - y(s'_m)\}^2]^2} ds_n ds'_m \quad (3.3.2)$$

$$A(s_n, s'_m) = \cos\{\theta(s_n) + \theta(s'_m)\} [-\{x(s_n) - x(s'_m)\}^2 + \{y(s_n) - y(s'_m)\}^2]$$

$$B(s_n, s'_m) = 2 \sin\{\theta(s_n) + \theta(s'_m)\} \cdot \{x(s_n) - x(s'_m)\} \{y(s_n) - y(s'_m)\}$$

$$q_1(s_n, s'_n) = \begin{cases} 1/2, & \text{for } |s_n - s'_n| > r_0 \\ 1, & \text{for } |s_n - s'_n| \leq r_0 \end{cases}$$

where r_0 is the cut-off radius of the interaction integration and m, n are indices for the layers whose interaction is being counted. Note that in the nonlocal model, 3.3.2 employs $\check{P}$, as compared to κ employed in the e-local model in 2.2.8.

The electric field, $\check{E}$, resulting from any arbitrary polarization distribution, $\check{P}$, over N layers of graphene can be expressed as a linear operation on polarization,

$$\check{E}^{(i)}(s'_m) = \frac{1}{2\pi\epsilon_{(N)}} \sum_{n=1}^N \int_{-L_0}^{L_0} \check{P}(s_n) \frac{\{1 - \delta_{mn} q_2(s_n, s'_m)\} \{A(s_n, s'_m) + B(s_n, s'_m)\}}{[\{x(s_n) - x(s'_m)\}^2 + \{y(s_n) - y(s'_m)\}^2]^2} ds_n \quad (3.3.3)$$

$$A(s_n, s'_m) = \cos\{\theta(s_n) + \theta(s'_m)\} [-\{x(s_n) - x(s'_m)\}^2 + \{y(s_n) - y(s'_m)\}^2]$$

$$B(s_n, s'_m) = 2 \sin\{\theta(s_n) + \theta(s'_m)\} \cdot \{x(s_n) - x(s'_m)\} \{y(s_n) - y(s'_m)\}$$

$$q_2(s_n, s'_n) = \begin{cases} 0, & \text{for } |s_n - s'_n| > r_0 \\ 1, & \text{for } |s_n - s'_n| \leq r_0 \end{cases}$$

where s is the arclength parameter, $\theta(s)$ the slope angle of the layers, m the index of layer where the electric field is being calculated, r_0 the cut-off radius, and index n sums over all the layers.

Combining 3.3.3 with the nonlocal constitutive relation (3.1.8), we express $\check{P}$ as a function of the shape of the layer as,

$$\check{E} = \mathcal{L}_1 [\check{P}] \quad (3.3.4)$$

$$\check{P} - \alpha \check{E} \equiv \check{P} - \mathcal{L}_1 [\check{P}] \equiv \mathcal{L}_2 [\check{P}] = \beta \kappa$$

where $\mathcal{L}_1$ and $\mathcal{L}_2$ are linear operators.

Thus, (3.3.1), (3.3.2), (3.3.3) and 3.3.4 complete the formulation of the minimization problem in terms of total potential energy $\Pi[\theta]$ where,

$$\Pi[\theta] = \Phi_{mech} + \Phi_{elec} - \int_{-L_0}^{L_0} f(1 - \cos\theta) ds \quad (3.3.5)$$

and f is the constraint force necessary to maintain the configuration.

The functional $\Pi[\theta(s)]$ can then be numerically minimized to obtain the postbuckling configuration of MLG subject to the pinned-pinned (i.e. *no moment*) boundary conditions. Figure 3.2 shows the collection of results for a 21-layer, 15 nm long MLG. Cut-off radius for the calculation, r_0 , was chosen to be 0.14 nm which is approximately the same as the lattice parameter of graphene. The intrinsic flexoelectric constant was obtained by calibration of numerical model with DFT. This calibration was done by best fitting a single case ($\theta_e = 3^\circ$) to the DFT results of [63]. The value of intrinsic flexoelectric constant, $\beta_{(21)}^{(in)}$, was obtained to be 0.733e.

Comparison of peak curvatures predicted by nonlocal model to DFT results in Fig. 3.2.(a1) show a good agreement for different end-angles. In the post-buckling evolution, the crinkle mode shape is found to remain the same while the amplitude increases with the end angle, thus explaining the observed linear trend in the peak curvatures. Figure 3.2.(a1) inset shows the localized curvature distribution with the fast-decaying oscillating tail. The distance between the closest inflection points on either side of origin is treated as a measure of localization - *the curvature focusing band width* - and it is found to be 0.86nm, agreeing well with the DFT findings. Figure 3.2.(a2) shows the peak

polarization density comparison between the uc-local model and the nonlocal flexoelectric model.

As explained in section 2.1 and section 2.2, the uc-local model is found to severely under-predict the peak curvature compared with the nonlocal model which predicts about 6.9 times higher peak polarization values than the uc-local model. This remarkable difference between the two models is due to the inadequacy of the uc-local model in accounting for flexoelectricity-dielectricity coupling. The inset shows the distribution of polarization density for three different end angles. The mode shape of the polarization distribution nearly remains the same and is only scaled by the amplitude that is dependent on the end angle practically in a linear fashion.

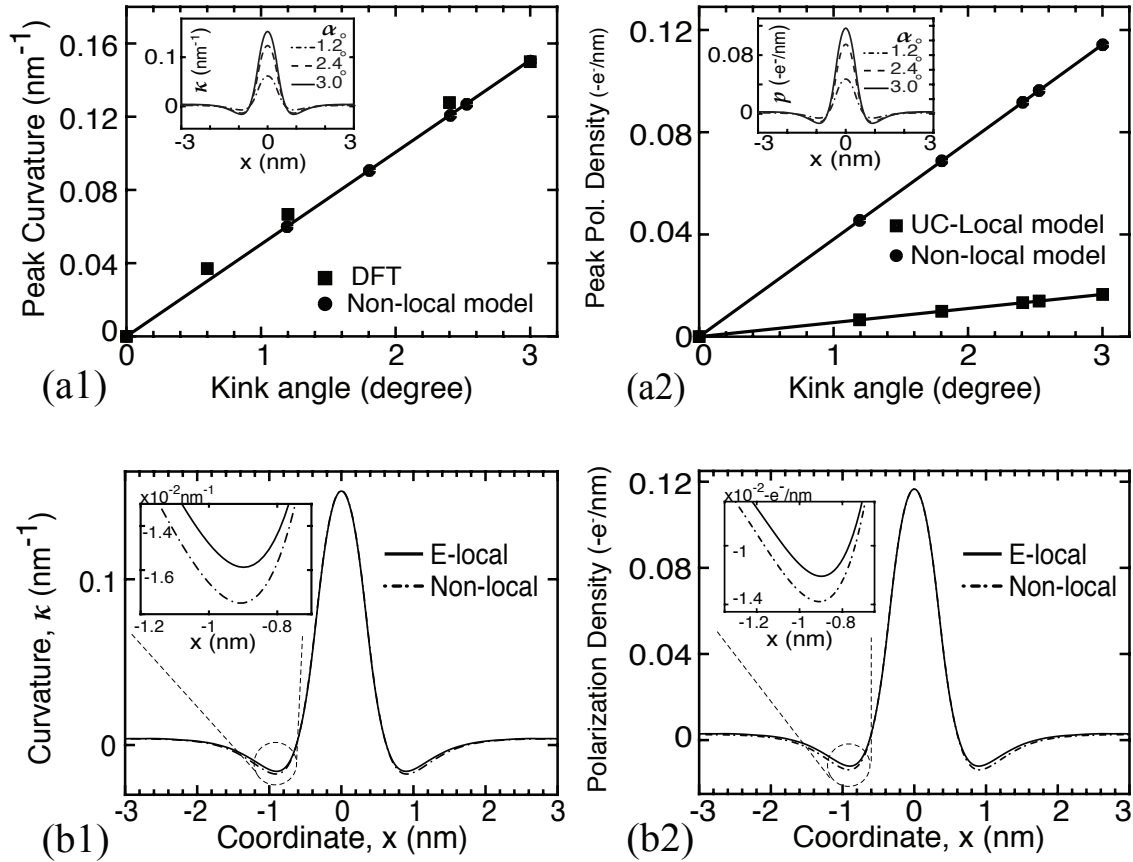


Figure 3.2: (a1) Peak curvature comparison between non-local model and DFT results; (a1 inset) curvature distribution for 21-layer 15 nm sample; (a2) peak polarization density comparison between non-local and uc-local model; (a2 inset) polarization density distribution for 21-layer 15 nm sample; (b1) Comparison between e-local and non-local model curvature distribution and (b2) polarization density distribution highlighting the differences.

3.3.2 Effect of dielectricity

Figures 3.2.(b1) and (b2) highlight the difference between e-local model and nonlocal model results. As discussed in the section 2.2, for a localized and oscillating curvature distribution, the flexoelectric-dielectric coupling reinforces the curvature peaks and valley, amplifying the polarization. Thus, in order to understand the difference between the e-local model and nonlocal model, we look closely at the curvature valley in Fig. 3.2.(b1) (inset shows the blown-up view). The nonlocal model has deeper curvature valley because the oscillating polarization in the neighboring regions contribute to amplify the net polarization which further enhances curvature localization. The peak curvatures of the nonlocal model are calibrated to match the peak curvatures of DFT results, so they do not show this variation at the peak. Similarly, the Fig. 3.2.(b2) shows the deeper valleys in polarization plot. This deeper polarization reversal provides an even lower energetic state due to attractive interactions between the dipoles. The e-local model, due to the lumping of dielectric and flexoelectric effects into a single term, misses out on this detail. The difference between the e-local model and nonlocal model is subtle here, as it should be, since the e-local model has been shown to work well for modeling crinkles. However, for modeling a general non-uniform curvature distribution, the reduced models - uc-local and the e-local model - may not work well and the nonlocal model must be applied.

3.4 Flexoelectric polarization and molecular adsorption

Figure 3.3.(a1) shows comparison between polarization distributions predicted by the nonlocal-model and the DFT analysis. The comparison is made through width-dependent mean polarization

density, $\bar{P}(x)$, near a crinkle ridge up to 4nm width. Here, $\bar{P}(x)$ is defined as,

$$\bar{P}(x) = \frac{1}{x} \int_{-x/2}^{x/2} P(\xi) d\xi \quad (3.4.1)$$

where $P(\xi)$ is the polarization density at ξ measured from the maximum or minimum point of polarization for a crinkle valley or a ridge respectively. For the cases considered for comparison - 1.8° and 3° end angle of the crinkle - we find good agreement between the DFT and the nonlocal-model results for most of the width of averaging, x , except for x close to cut-off radius, as expected. The continuum model interpretation starts to break down for x comparable to the cut-off radius. The peculiar oscillations seen in the DFT mean polarization density can be attributed to the averaging scheme of polarization with the reciprocal space wave function for x in the real space not aligned with periodic atomic locations with the Bader method ([67], [68]).

The flexoelectric polarization leads to development of surface line charges along the crinkle valleys and ridges. The ridges are negatively charged, while the valleys are positively charged, to produce N-type and P-type crinkles respectively. The apparent line charges can cause preferential adsorption of molecules. A very striking manifestation of the line charges can be seen in adsorption of buckyballs along crinkle valleys in HOPG. Buckyballs (C_{60}) are highly polarizable dielectric molecules. In presence of strong enough external field, dielectrically polarized buckyballs are attracted to the field source. Figure 3.3.(b1) shows buckyballs sprinkled over a HOPG surface. Instead of arranging themselves in clusters as the minimum energy state of buckyballs in absence of external electric field, they choose to align themselves in relatively long straight line segments with clear spacing and distinct directional preference to their arrangement [64]. A similar finding was previously reported in [59] (Fig. 3.3.(b1) inset). In the higher resolution inset picture, we see that the inter-buckyball spacing is 2.5 nm. Here, we consider a simple model of a line charge that induces a dielectric dipole in every buckyball, and aligns the electrically polarized buckyballs with a spacing distance l .

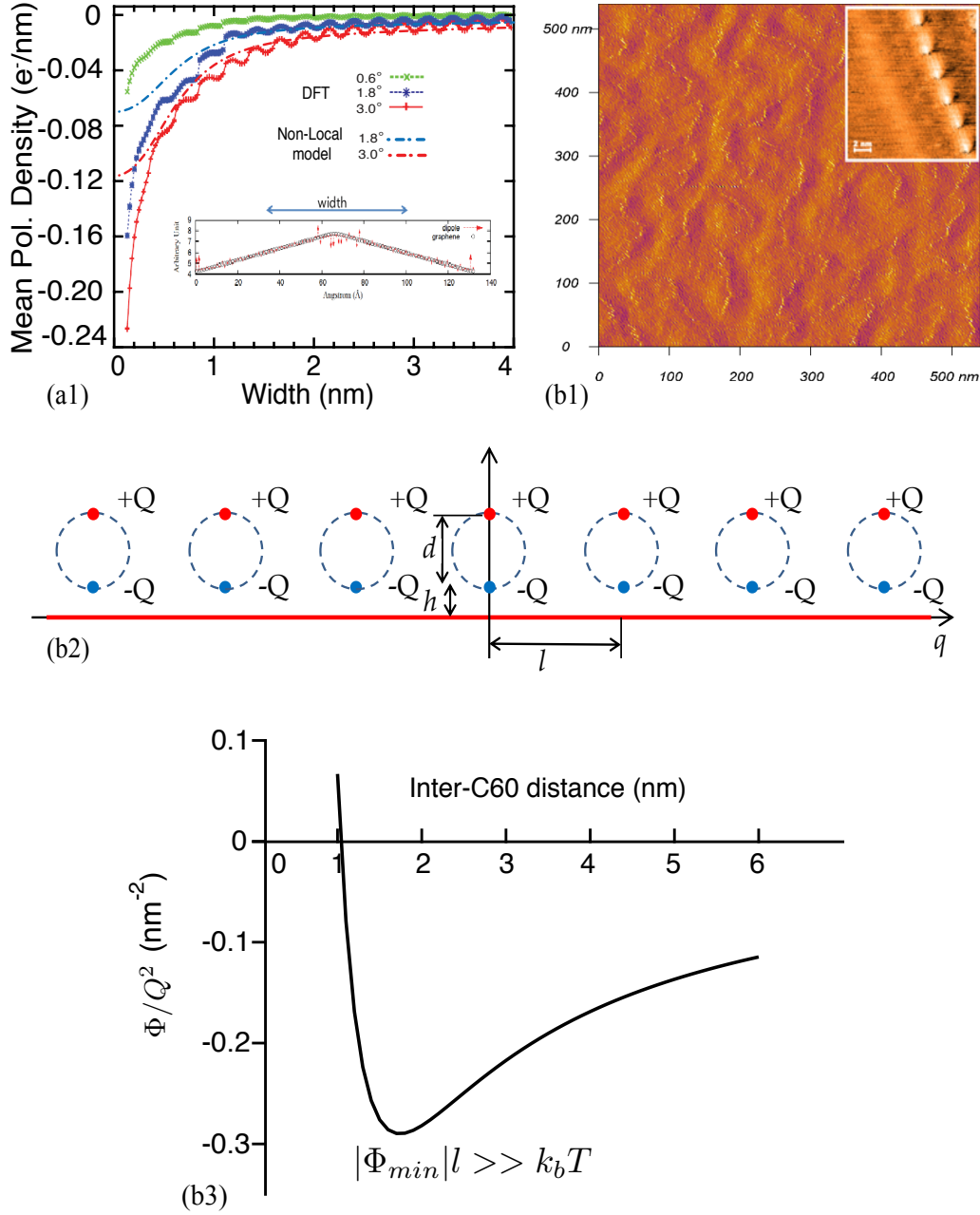


Figure 3.3: (a) Mean polarization density comparison between non-local model and DFT results; (b1) Bucky ball adsorption on HOPG; (b1 inset) higher resolution image showing the periodicity of buckyballs on HOPG; (b2) Schematic of buckyballs on crinkle ridge; (b3) Potential energy of the system as a function of inter-buckball spacing l .

The dipole arm length is denoted d , and the distance between the buckyball and the line charge h as shown in Fig. 3.3.(b2). The dipoles are attracted to the line charge of the crinkle valleys or

ridges by the electric field gradient. The attraction potential per unit length of the line charge is inversely proportional to the inter-spacing distance l . This apparent aggregation attraction is balanced with inter-dipole repulsions. Expression of the net buckyball-interaction potential is derived in the Appendix. Figure 3.3. (b3) shows a plot for the potential energy as a function of the spacing l . The energy minimum is attained 2 nm with rough estimations of h and d , which is in relatively close agreement with the experimental observation. Thus, the alignment of buckyballs on the HOPG surface can be explained by existence of crinkles and the resulting flexoelectric surface charge concentrations along the valleys and ridges. Our simulation shows alignment of the buckyballs along the valleys of the crinkles is more stable than along the ridges. In addition, we analyzed adsorption potentials of H_2 and O_2 molecules with DFT. The adsorption potentials of H_2 and O_2 increase ~ 20 eV and ~ 30 eV at the crinkle ridge respectively, which represents 11 – 12 % increase over the adsorption on a flat HOPG surface.

3.5 Discussion

3.5.1 From nonlocal model to reduced models

Having established the mathematical formalism for the nonlocal model, we employ this development to concretely derive the two reduced models discussed in section 3.2 from this general model.

We first consider a uniformly bent single layer of graphene. The curvature is assumed to be small enough that the layer can be assumed straight for calculation purposes. From the symmetry of the problem and assuming $L_0 \gg r_0$, polarization density of the single layer, $\check{P}_{(1)}$, is constant everywhere.

Under these assumptions, equation (3.3.3) reduces to

$$\check{E}(s) = \int_{-L_0}^{L_0} \check{P}(s') g_{(1)}(s-s') ds' \quad (3.5.1)$$

where $g_{(1)}(s-s') = \frac{-1}{2\pi\epsilon_{(1)}} \frac{q_2(s,s')}{\{(x(s)-x(s'))^2\}}$. Performing the integration, we get that $\check{E}_{(1)} = -\check{P}_{(1)}/(\pi\epsilon_{(1)}r_0)$

where r_0 is the cut-off radius. Plugging back into the constitutive relation and simplifying we get

the linear operator $\mathcal{L}_2[\check{P}_{(1)}] = \{1 + \alpha/(\pi\epsilon_{(1)} r_0)\} \check{P}_{(1)}$. In other words,

$$\check{P}_{(1)} = \beta_{(1)}^{(uc)} \kappa = \frac{\beta_{(1)}^{(in)} \kappa}{1 + \alpha/(\pi\epsilon_{(1)} r_0)} \quad (3.5.2)$$

The coefficient, $\beta_{(1)}^{(in)}/\{1 + \alpha/(\pi\epsilon_{(1)} r_0)\}$, is referred to as the 'flexoelectric constant' in Kalinin et. al. [7]. Note that in the current study the intrinsic flexoelectric constant for single layer graphene is not known. However, the above equation provides a way to evaluate $\beta_{(1)}^{(in)} \cong 0.16e$ for $\beta_{(1)}^{(uc)} \cong 0.11e$. The uniform curvature limit, thus leads to a very simplified dependence of electric field on the polarization and this allows the reduction of the $\mathcal{L}_2$ linear operation to just a pre-factor. The reduction in $\beta_{(1)}^{(uc)}$ value as compared to the intrinsic flexoelectric constant is due to the weakening effect of dielectric polarization on intrinsic polarization as discussed in section 3.2.2.

For a highly localized curvature distribution like the crinkle, we expect that the general model also reduces to an e-local model approximately. To this end, we design a calibration test for computational brevity. We choose the following function to represent the crinkle curvature distribution.

$$\kappa_{test}(x; \lambda) = \kappa_0 \cos kx e^{-tkx} \quad (3.5.3)$$

with $k = 2\pi/\lambda$, for a parameter λ , as it resembles the curvature distribution of the crinkle – highly localized and oscillatory. The peak curvature, period and decay length of the test-function can be tuned independently. In this calculation, we calibrate the peak curvature κ_0 , the wavelength and the decay-length parameter t of a test-function to match the peak curvature of the 3° crinkle. From the curvature distribution and employing equation (3.3.3) we calculate the net polarization. In the e-local approximation, the net polarization and curvature are proportional and related by the effective flexoelectric constant. Denoting the ratio of the calculated peak polarization and peak

curvature by β^* , we plot the results in Fig. 3.4.(a1) as a function of the wavelength λ of the test-function. The results are shown for a 21-layered, 15 nm long MLG specimen. Results show, that for test-function with the same wavelength as the crinkle curvature distribution i.e. $\lambda/40.6 \text{ nm}$, the effective flexoelectric constant is $6.89\beta_{(1)}^{(uc)}$. This is in agreement with the e-local model. The results indicate that e-local model, obtained as a limiting case of the general model with flexoelectricity-dielectricity coupling, is a good approximation. We note that the Fig. 3.4.(a1) remains insensitive to the amplitude of the test-function and thus is a universal calibration curve for any crinkle angle.

The oscillatory nature of the curvature distribution enhances the intrinsic flexoelectric polarization by augmenting it with the dielectric polarization. The invariance in the shape of distribution, as discussed in [63] ensures that the polarization and curvature scale linearly with the end angle (Fig. 3.2.(a1) and (a2)), thereby reducing equation (3.1.8) to the e-local model,

$$\check{P} = \beta^* \kappa \quad (3.5.4)$$

3.5.2 Layer dependence of properties

The dielectric properties of graphene are known to be dependent on the number of layers and the location of the layer in MLG. The microscopic picture of electrical interactions in the layers is sensitive to the number of layers and the location, and thus the dielectric and flexoelectric properties over the number of layers are layer-number dependent. Regarding dielectric properties of few layer graphene, Kaxiras et.al. [45] showed with DFT analysis that relative permittivity increases nearly linearly with electric field for small electric fields. Hotta et al. [69] reports that the bulk relative permittivity, ϵ_r , of graphite is 30. Figure 4.(a2) inset shows an exponential interpolation of the relative permittivity, $\epsilon_r(N) = \epsilon_r(1) + (\epsilon_r(\infty) - \epsilon_r(1)) \left\{ 1 - e^{-S(N-1)/(\epsilon_r(\infty) - \epsilon_r(1))} \right\}$, with $S = d\epsilon_r(N)/dN$ at $N = 1$, that depends on the number of layer N , and fits both the few layer and bulk limit. Now,

our

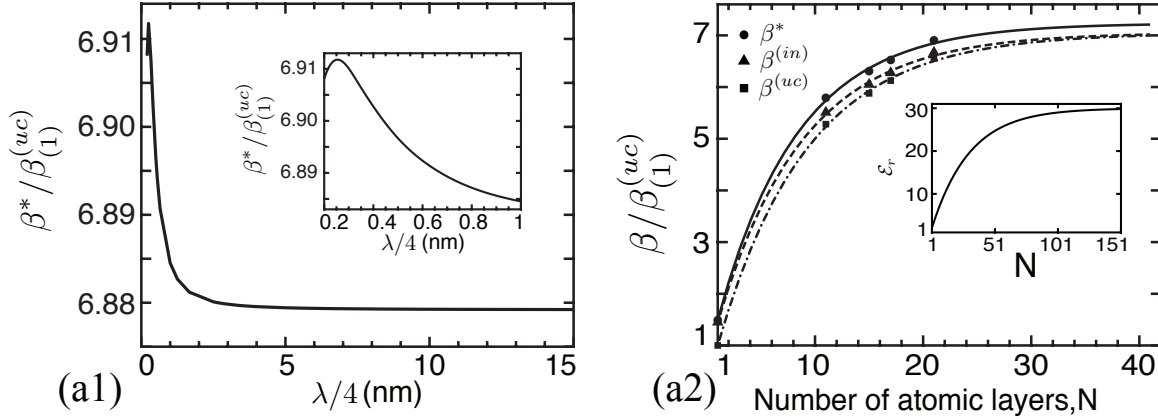


Figure 3.4: (a1) Calibration curve for β^* as function of wavelength λ ; (a2) Evolution of the flexoelectric coefficients and relative permittivity with the number of layers N .

interest is in flexoelectric coefficients that depend on the number of layers. Qualitatively, increasing the number of layers raises attractive interlayer interactions that lower the potential energy in the crinkle morphology. Thus, the effective flexoelectric coefficient should increase. Similarly, the interlayer attractive interaction intensifies with increasing number of layers for uniformly curved MLG as well, and the uniform-curvature flexoelectric coefficient is also expected to increase. To calculate the layer-number dependent behavior of flexoelectric coefficients, we first evaluate the intrinsic flexoelectric coefficient, $\beta_{(N)}^{(in)}$, for various number of layers by iterating the coefficient value until the peak curvature of the nonlocal model matches that obtained by the DFT analysis for a 3° end-angle case. The coefficient $\beta_{(N)}^{(in)}$ is shown in Fig. 3.4.(a2). Once we have the intrinsic flexoelectric constant, we evaluate $\mathcal{L}_2$ in (3.3.4) for uniform curvature distribution to obtain the uc-local flexoelectric coefficient $\beta_{(N)}^{(uc)}$. Fig. 3.4.(a2) shows that the coefficient $\beta_{(N)}^{(uc)}$ also increases with the number of layers and saturates to a bulk value. Lastly, the e-local flexoelectric coefficient, $\beta_{(N)}^*$, can be simply obtained by the ratio of the peak polarization to the peak curvature. The coefficient $\beta_{(N)}^*$ increases with the number of layers and saturates to a bulk value. As discussed in

section 3.2.2, we find that $\beta^* > \beta^{(in)} > \beta^{(uc)}$. In summary, our fitting yields the following expressions for flexoelectric coefficients : $\beta_{(N)}^* = 7.235 - 6.841e^{-0.1377N}$; $\beta_{(N)}^{(in)} = 7.052 - 6.357e^{-0.1266N}$; $\beta_{(N)}^{(uc)} = 7.046 - 6.817e^{-0.1205N}$; $\epsilon_{r(N)} = 30 - 28.8594e^{-0.0333N}$.

Chapter 4

Substrate effect on crinkles

In the preceding chapters, we developed the theory of flexoelectricity in MLG and found that for certain geometries of MLG, flexoelectric interactions can dominate the buckling process and lead to the formation of kink-shaped crinkle mode. In the process, the bifurcation becomes subcritical and surface curvature of buckled MLG is localized to a narrow boundary layer of $\sim 2nm$ width. Till now, we have focused our attention on the buckling of free-standing graphene. Here, we extend the work to MLG bonded to a softer elastic substrate. Elastic substrates can be used as a tool to guide and control the morphology of the MLG and produce periodic patterns. From numerous computational studies of MLG attached to softer substrates, we expect wrinkling as a natural candidate for the post-buckling surface morphology. However, the effect of flexoelectric interactions in MLG and potential dielectric interactions between MLG and the substrate have not been studied yet in the literature, to the best of our knowledge. In this chapter, we study the bifurcation landscape for a bilayer graphene (BLG) with the change in substrate properties.

4.1 Theoretical formulation

To explore the buckling of BLG in a plane-strain setting, we consider the setup as shown in figure 4.1. BLG is assumed to be perfectly bonded to the substrate and the assembly is subjected to lateral compression. The difference in the mechanical properties of BLG and substrate, give rise to a mismatch in their response to the compression and causes BLG to buckle to accommodate the compressive strain. For the purposes of analysis, we continue with the same kinematic assumptions as before - a) graphene is inextensible and b) layers deform in an identical fashion and maintain translational symmetry in the thickness direction.

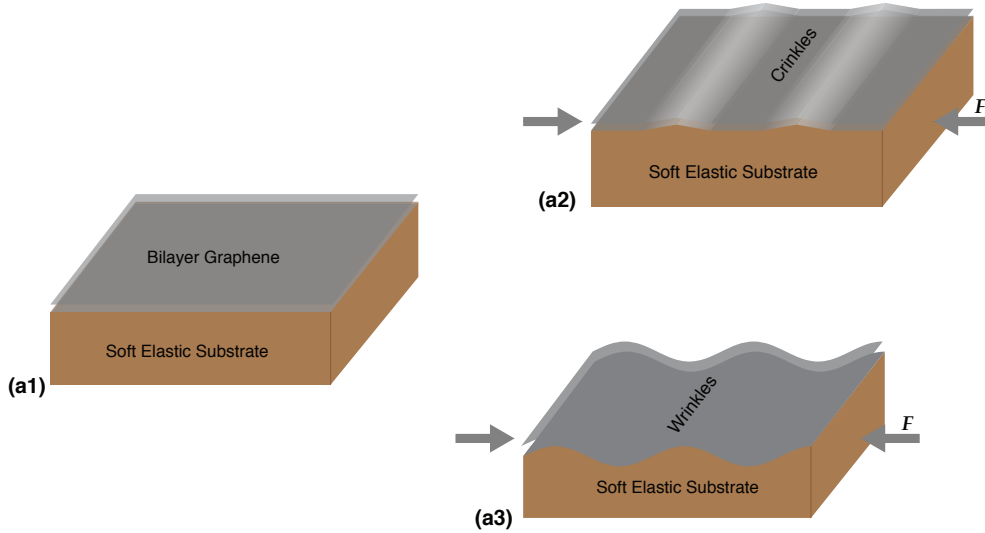


Figure 4.1: (a1) Graphene attached to softer elastic substrate and; (a2)-(a3) some possible post-buckling states.

We focus the analysis on classifying the bucking mode(s) and how they evolve, if they do, with changing substrate stiffness. The substrate is assumed to be incompressible with stiffness denoted

by μ_s . We employ here the bifurcation analysis technique that was used in chapter 2. By analyzing the Fourier Transform of the Euler Lagrange equation for real and complex roots, we probe the BLG graphene for existence of wrinkle or crinkle bifurcations. The total energy function, Π , is obtained by modifying 2.2.9 to add the substrate contribution, U_{sub} ,

$$\Pi = \int_{-L}^L \left(\frac{Q_b N}{2} \left(\frac{d^2 w}{dx^2} \right)^2 + \frac{\mu(N-1)a}{2} \left(\frac{dw}{dx} \right)^2 - f(\sqrt{1+w'^2} - 1) \right) dx + U_{elec} + U_{sub} \quad (4.1.1)$$

where the energy of the substrate is given by,

$$U_{sub} = \frac{1}{2} \int_{-L}^L T(x)w(x)dx \quad (4.1.2)$$

with Q_b being the bending stiffness of individual graphene layer, μ the interlayer shear stiffness, a the interlayer spacing, f the constraint force, $w(x)$ the displacement and $T(x)$ being the normal traction on the top surface. Electrical interaction energy, U_{elec} , is given by 2.2.8, now written in terms of x instead of the arclength s .

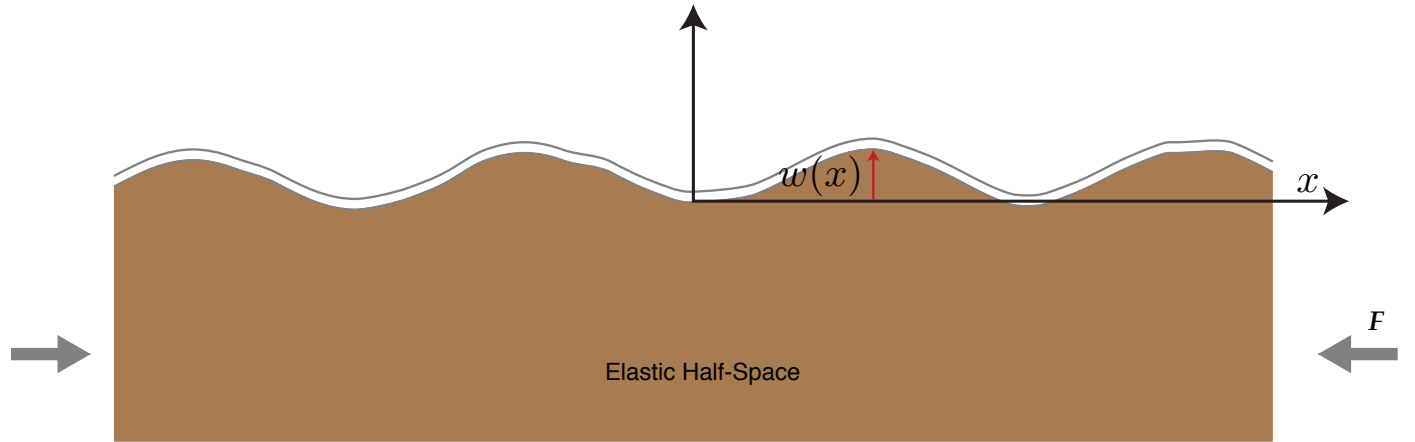


Figure 4.2: Schematic of the plane-strain setup.

From 4.1.1 and 4.1.2, under the assumption of small displacements, the Euler-Lagrange equation is obtained and its Fourier transformed form becomes,

$$2Q_b k^4 - k^2(f - \mu a) - \frac{\beta_{(2)}^{*2}}{\pi \epsilon_{(2)}} k^4 \hat{g}_{(2)}(k) + \bar{E}k = 0 \quad (4.1.3)$$

where $\hat{T}(k) = \bar{E}k\hat{w}(k)$, $\bar{E} = E/2(1 - \nu^2)$, E is the Young's modulus of the substrate and ν is the Poisson's ratio. Recalling from 2.3.5 that,

$$\hat{g}_{(2)}(k) = \pi|k|e^{-a|k|} + \pi|k| - 2kSi(kr_0) - 2\cos(kr_0)/r_0 \quad (4.1.4)$$

The critical bifurcation load, f_{cr} , is found by recasting 4.1.3 as,

$$f = \mu a + \left(2Q_b - \frac{\beta_{(2)}^{*2}}{\epsilon_{(2)}} \hat{g}_{(2)}(k) \right) k^2 + \frac{\bar{E}}{k} \quad (4.1.5)$$

and subsequently minimizing f with respect to k . Following the methodology in chapter 2, we look for complex solutions of 4.1.3 with $f = f_{cr}$. As seen in chapter 2, existence of any complex conjugate roots in the range of interest would indicate the presence of crinkle solutions. In the purely mechanical case, the critical load is denoted by f_0 and is given as, $f_0 = \mu a + 6Q_b \left(\frac{\bar{E}}{4Q_b} \right)^{2/3}$. The corresponding wavenumber is given as, $k_0 = \left(\frac{\bar{E}}{4Q_b} \right)^{1/3}$. Henceforth, a $\tilde{()}$ will indicate non-dimensionalization of wavenumber with a .

A word on the length scales

Prior to the analysis and interpretation of the results, it is instructive to examine the various length scales that appear in this problem. Recall the two length scale from chapter 2 - *evolving band width* for *mechanical* crinkle and *fixed band width* for flexoelectric crinkle respectively. Interlayer spacing a is a material length scale for graphene. Since, we employ a cut-off radius formulation for counting intralayer energy interactions, we introduce a length scale r_0 which is taken to be same as the lattice parameter for graphene. Consideration of the substrate, adds a new length scale to the problem that typically decides the periodicity of the surface pattern as is well known from the study of layer-on-substrate elastic systems [32]. In analyzing the results from bifurcation analysis, it is important to note that the range of wavelength of interest is decided by two length scales - lower

limit is the cut-off radius and the upper limit is the maximum wavelength predicted for layer-on-substrate system [32]. Thus for physically meaningful results, we restrict our range of interest to $\tilde{u} \in (0, 4.3), \tilde{v} \in (-5, 5)$.

4.2 Results and Discussion

In this section, we will focus on the onset of bifurcation and how the characteristic wavenumber changes with the inclusion of flexoelectricity and substrate. We start by taking a look at the variation of f_{cr} as the effective flexoelectric coefficient changes. Figure 4.3(a) shows that with increasing β^* , f_{cr} increases monotonically for different substrate stiffnesses. The indicator line marks β^* for graphene. We noticed that if the flexoelectric constant is increased beyond a certain limit, the f_{cr} becomes negative indicating that layer can spontaneously buckle and is unstable in its flat state but that region is beyond the scope of our current treatment.

The incipient wavenumber for the purely mechanical case, ignoring any flexoelectric interactions, is given as $k_0 = \left(\frac{\bar{E}}{4Q_b}\right)^{1/3}$ as discussed in the previous section. As β^* is increased beyond zero, the real solutions of 4.1.3 show a bifurcation as shown in figure 4.3.(b). The plot shows normalized and non-dimensionalized real roots of 4.1.3 for different substrates. At zero flexoelectric coefficient, there is a repeated root that bifurcates into two branches as the flexoelectric coefficient increases. One branch shows a smaller wavenumber than the purely mechanical case and the other branch shows a larger wavenumber. In addition to that, we investigate 4.1.3 for complex roots to probe the existence of crinkle bifurcation. Figure 4.3.(c1) shows a very interesting picture of the bifurcation landscape. We recall here that our range of interest is $\tilde{u} \in (0, 4.3), \tilde{v} \in (-5, 5)$. As β^*

increases beyond zero, 4.1.3 starts to show complex roots as well in addition to two real roots. However, those roots are out of the physically admissible range. When β^* approaches a critical value that depends on $\bar{E}$, the complex roots begin to appear in our range of interest. This shows the clear

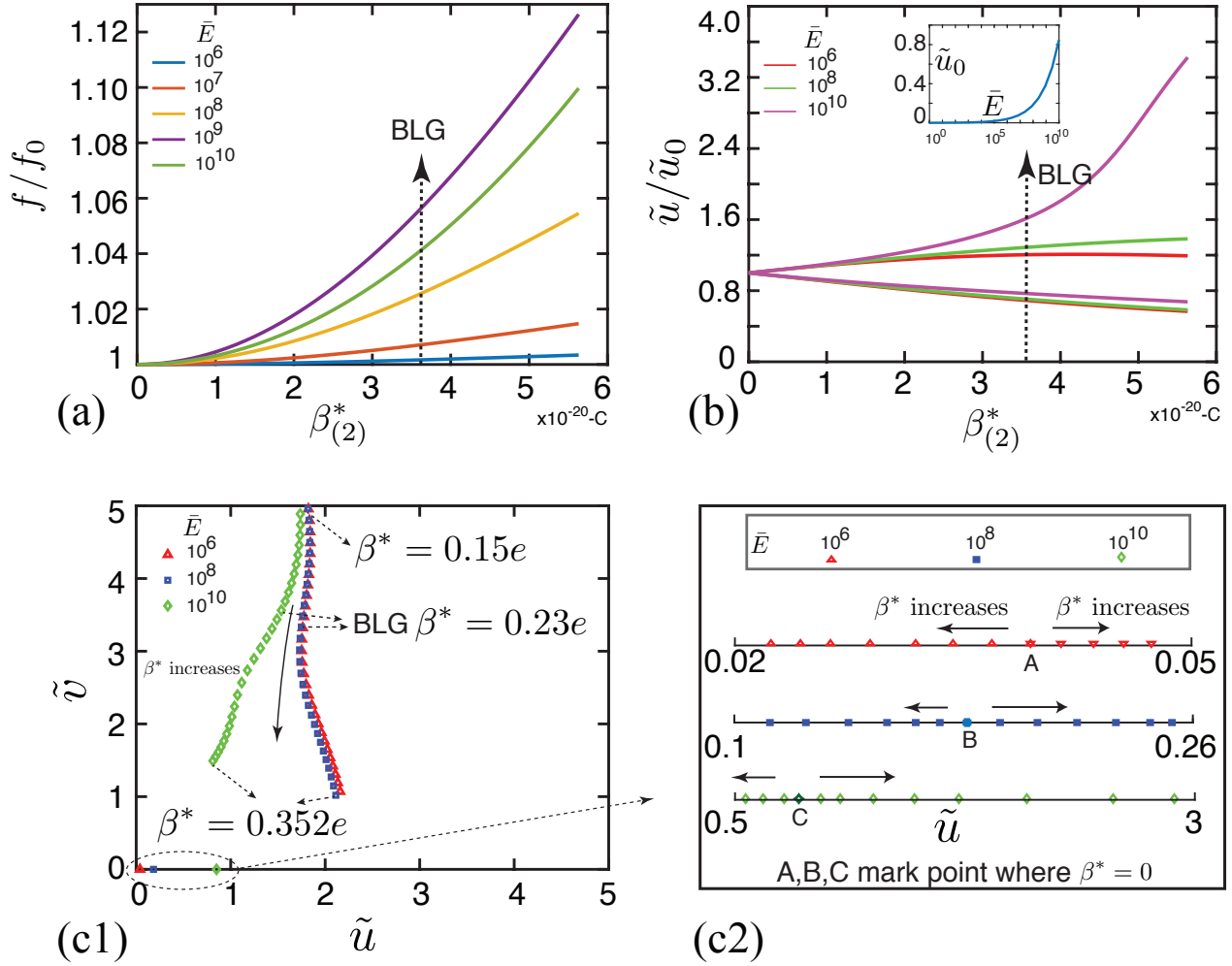


Figure 4.3: (a) Evolution of non-dimensional critical load. (b) Bifurcation of the real wavenumbers with the bifurcation parameter β^* . (c1) Complex wavenumbers and real wavenumbers (c2) given by the solution of 4.1.3 for different substrate stiffness. (c1) shows the existence of crinkle bifurcation for BLG.

existence of crinkle bifurcation for a BLG attached to softer substrate (arrows mark the BLG case). For the range of $\bar{E}$ shown in figure 4.3.(c1) the critical $\beta^* \sim 0.15e$. The flexoelectric coefficient for BLG $\sim 0.23e$. As the flexoelectric coefficient increases beyond graphene's value, $\tilde{u}$

remains more or less constant around ~ 1.8 for $\bar{E} < 10^8$ while $\tilde{\nu}$ decreases, thus making the oscillation persist over a longer width. For higher $\bar{E}$, we note that both $\tilde{u}$ and $\tilde{\nu}$ decrease indicating that wavelength of oscillations and the decay length become wider with increasing flexoelectricity. At the same time, figure 4.3.(c2) shows the evolution of real roots concurrently. We speculate that the post-buckling morphology will display a global periodicity dictated by the real roots (fig. 4.3.(c2)) and locally, the complex roots (fig. 4.3.(c1)) will serve to concentrate the curvature.

As we noted in chapter 2 for the suspended graphene, flexoelectric crinkle parameter governs the existence of crinkles. We expect the parameter to have a similar effect even in the layer-on-substrate case. Figure 4.3 shows that for smaller flexoelectric constants the complex solutions are outside of the range of interest. Speaking in physical terms, the flexoelectric interactions are not strong enough to cause crinkles to form, and the mechanical modality dominates. As the flexoelectricity effect becomes stronger, the system starts to show crinkle bifurcation.

4.3 Future Work

We carried out the onset analysis and predicted the critical wavelength for BLG-on-soft-substrate system in this chapter. In order to comment on the nature of the bifurcation, it is important to analyse the post-buckling evolution as well. Free standing crinkles show a subcritical bifurcation and we expect the substrate stiffness to possibly alter it for certain range of stiffness. A finite element modeling of this system would help characterize the post-buckling evolution accurately and can handle large deformations as well as extensibility and interlayer normal compliance. To the best of our knowledge, such a study has not been previously conducted. This work can also be extended to other 2D materials beyond graphene by carrying out atomistic studies to characterize flexoelectricity

and subsequently analyzing the bifurcation landscape using the machinery developed in this thesis.

Addition of the substrate into the framework, adds another length scale that depends on $\bar{E}$. We already developed a quantum flexoelectric crinkle parameter in chapter 2 that arises out of combination of bending and flexoelectricity-induced stiffness. Another non-dimensional parameter, comprising flexoelectricity and substrate properties can be formulated and subsequently used to study the crinkle-wrinkle transition in the layer-on-substrate case. Lastly, we note that soft-substrates typically demonstrate dielectricity and therefore, a more refined formulation must take into account the dielectric interactions between the layer and the substrate.

Chapter 5

Conclusion

5.1 Formation and stability of crinkles

In chapter 2, we investigated crinkles in multilayer graphene. We constructed the MLG phase map of wrinkle versus crinkle. The crinkle phase is more stable than a wrinkle phase for $2L_0 \leq 13.9N\sqrt{(N+1)/Na}$, where $2L_0$, N and a are the whole span, number of layers and the interlayer spacing of a buckling MLG correspondingly. DFT analysis indicates that the curvature of the MLG crinkle ridge (or valley) is localized and highly focused within an approximately 0.15 nm^{-1} for a 3° kink angle, and the curvature vanishes outside of the $\sim 2 \text{ nm}$ boundary layer. A mechanical model of MLG under axial compression undergoes a supercritical interlayer-shear-model buckling to progressively evolve into a crinkle with its curvature localized within a much broader band than those of DFT predictions. The curvature focusing factor, approximately $0.0023 \text{ nm}^{-1}\text{degree}^{-1}$, of the purely mechanical model is much weaker than the DFT prediction, approximately $0.052 \text{ nm}^{-1}\text{degree}^{-1}$. Nevertheless, this long-wavelength mechanical buckling mechanism cooperatively drives MLG crinkle formation with buckling of quantum-flexoelectric dipole-dipole interactions at

the nanoscale. The width of the mechanical crinkle is found to be scaled by the mechanical crinkle parameter, $(\pi/2a\theta_e)\sqrt{Q_b/\mu a}$. Our post-buckling analyses of crinkle reveal that long-range non-local electromechanical interactions in MLG promote concurrent quantum flexoelectric buckling of the interactions at the nanoscale, in addition to the long-wavelength purely-mechanical buckling. The attractive interlayer and intralayer interactions among the electric-charge dipoles, generated by flexoelectricity, lower the total potential energy. For an effective crinkle analysis, we formulate an e-local model for graphene flexoelectricity by lumping together the dielectric and flexoelectric interactions in MLG. The e-local model is calibrated with the DFT results to calculate the effective flexoelectric coefficient $\beta_{(21)}^* = 0.745e$ which is found to be higher than the uc-local polarization constant, $\beta_{(1)}^{(uc)} = 0.11e$, obtained by uniform bending DFT analysis [22]. Our e-local model results of flexoelectricity capture the signatures of the crinkles, i.e. curvature focusing, curvature reversal and FBW characteristic observed in the DFT analyses. The peak curvature of $\sim 0.16 \text{ nm}^{-1}$ for 3° end angle and curvature focusing factor of approximately $0.052 \text{ nm}^{-1} \text{ degree}^{-1}$ are in good agreement with DFT results and are significantly higher than the purely mechanical model. Accounting for flexoelectricity, our linear bifurcation analysis of the e-local model shows that the bifurcation is subcritical with respect to perturbations of complex harmonic modes and happens at a higher critical load of $\tilde{f}_{(2)} = 1.0164$ than the load of purely mechanical model, $\tilde{f}_{(2)}^{mech} = 1.0103$. Our bifurcation analyses reveal existence of two concurrent hierarchical modes of MLG buckling at the onset of buckling. One is a long-wavelength harmonic bifurcation mode, and the other the quantum flexoelectric crinkle mode near the lattice scale. The two modes at the onset of bifurcation lead to the post-buckling crinkle mode of high curvature localization and focusing at the crinkle ridge (or valley) tips. We have uncovered that the quantum flexoelectric crinkle can be formed only if the quantum flexoelectric crinkle parameter is in the range of $1.01 < \pi a Q_b \epsilon_{(2)} / \beta^{*2} < 31.6$. If the parameter value is close to 1.01, the MLG is likely to make spontaneous phase transition from a

sp_2 to a sp_3 structure. On the other hand, if the parameter value is beyond 31.6, the MLG harmonically buckles only with a long wavelength. The quantum flexoelectric crinkle parameter of a bilayer graphene is 3.48, and MLG is found to be an ideal material to form quantum flexoelectric crinkles. The large curvature focusing leads to segregation of charges on the outer surfaces of MLG which are confined within the boundary layer. The polarization density reaches up to $0.12e^{-}nm^{-1}$. This effectively produces a line charge, the magnitude of which can be manipulated by macroscopic deformation. Fine control of this class of surface feature with quantum-flexoelectric charge concentration can be a powerful tool to study selective graphene-surface functionalization, molecular adsorption, self-organization of molecular and other nanoscale electrosensitive systems.

5.2 Flexoelectricity-Dielectricity coupling

In chapter 3, we investigated the thermodynamically motivated constitutive law for flexoelectricity in graphene. The coupling of dielectricity and flexoelectricity was quantitatively analyzed with the thermodynamic framework, while the coupling mechanisms were qualitatively elucidated. We unified the framework for the existing disparate models in uniform curvature and highly localized regimes. We proposed a mathematical formulation for modeling electromechanics in 2-D layered materials. While the existing approach in the literature predominantly employs Maxwell's electric-field-based continuum framework, we applied Legendre transformation of the Maxwell's free-energy potential to another polarization-based one that allows us to construct a free-energy potential for 2D layered materials. Our energetic modeling of the 2D materials with the transformed potential provides computational advantages where the problem can be reduced from solving field quantities for entire space to analyzing nonlocal polarization interactions just over the layers.

The nonlocal model applied to 21 layer, 15 nm span graphene sample produces highly localized

curvature distribution, a signature of the crinkle mode of buckling. These results are in close agreement with DFT and e-local model predictions. The curvature focusing band width was found to be $0.86nm$. We observed noticeable effects of constitutive nonlocality in non-uniform curvature and polarization distributions. In crinkles, the coupling enhanced the curvature reversal, consequently amplifying the polarization reversal as well. The e-local model lumps this constitutive nonlocality into one single parameter and therefore missed out on this detail. The flexoelectric polarization near the crinkle ridge, predicted by our nonlocal model, was found to match with DFT results.

The manifestation of flexoelectric crinkle charges are observed in the form of buckyballs aligning in a straight line on a HOPG surface. Our simplified model of buckyball adsorption along a line charge is captured the underlying physics of the process. We believe that crinkle polarization is a significant outcome which can have far reaching implications in manipulating charged and polarizable molecules. Our DFT analysis shows that enhancement in adsorption of neutral molecules at crinkle ridges depends on the molecular weight and possibly geometry of the molecule as well. The change of physical binding energy of H_2 and O_2 molecules on the crinkle surface is found to be ~ 20 eV and ~ 30 eV respectively, which is approximately 11 – 12% of the total binding energy.

We showed that the nonlocal model is reducible to the uc-local and the e-local models as were introduced in chapter 2. Our calibration test revealed that the e-local model is accurate enough when the curvature is highly localized like in crinkles, while the uc-local is exact in the limit of uniform curvature distribution. Lastly, we investigated the layer-number dependence of flexoelectric coefficients and found that the flexoelectric coefficients increase with number of layers, and saturate to a bulk value.

5.3 Flexoelectric layers attached to softer substrates

In chapter 4, we examine the layer-on-substrate system for onset of bifurcations. While this system has been extensively studied, there are a couple of reasons that make it especially instructive to study. Firstly, most of the studies have focused on single layer graphene. We examine the BLG case as a representative of the general MLG case. Our methodology can be easily extended to the general MLG case. Secondly and most importantly, the role of flexoelectricity in the instability of layer-substrate system has not been received attention previously. As we developed the machinery to handle flexoelectric-dielectric interactions in chapter 2 and 3, we apply that to study how the conventional wrinkling process is affected by the flexoelectric coupling.

From our onset analysis, we find that for small flexoelectric coefficients, the wrinkle bifurcation is the primary instability mode. However, for larger flexoelectric coefficients ($\beta_{(2)}^* > 0.15e$ for bilayer 2D materials) we notice the existence of the crinkle bifurcation. Graphene itself has a flexoelectric coefficient of $\sim 0.23e$ and therefore demonstrates the crinkle bifurcation. In addition to that, larger flexoelectric coefficients also lead to bifurcation in the real roots, i.e. two real wavenumbers - one being larger and other being smaller than the purely mechanical case. We believe that these real roots dictate the global periodicity of the surface pattern with the local morphology being governed by the complex roots.

A finite element analysis of the system would allow for a greater understanding of the post-buckling evolution and throw light on the nature of the bifurcation as well. We propose to carry out matching of the global periodicity and the local decay length with experimental observations to validate the predictions of the model.

5.4 Future Work

This dissertation focused on flexoelectricity and flexoelectricity-induced instability in multi-layer graphene. While this is the first work to discuss the existence of the crinkle buckling mode, the interest in electro-mechanical coupling and 2D materials is growing by the day. For manufacturing of nano-structures, self-assembly is an extremely important tool and crinkles provide a unique way to self-assemble nano-structures using strain-engineering and external electric/magnetic field control. Developing control methodologies is one natural next step in employing crinkles for practical applications. A combination of principles of origami that have been matured in soft-materials and electro-mechanical coupling in graphene, can be envisioned to solve inverse problems of generating programmable surface patterns. In similar vein, extending the work to two dimensional geometry can lead to even more exquisite patterns and instabilities.

The flexoelectric surface charges generated by the curvature localization hold tremendous potential in being able to manipulate charged and polarizable macromolecules and more controlled experiments need to be carried out to explore the dynamics of adsorption. Another important area is the manipulation of material properties- electric, magnetic, band-gap control and so on - using strain control. We demonstrated that the effective flexoelectric response of graphene depends strongly on the morphology and number of layers. Same holds true for the dielectric response as well. How the geometry affects other physical properties and potentially the quantum behavior, needs to be explored further.

While the focus has been mostly on graphene in this dissertation, this work provides the background for investigating other 2D materials as well, for instance hBN, MOS_2 etc. Coupling of piezoelectricity, flexoelectricity and dielectricity in non-centrosymmetric materials can lead to

new electromechanical instabilities and may provide more desirable response for certain applications. We hope that this work serves as an impetus to explore the landscape of electromechanical instabilities in 2D materials and how they can be leveraged for enhanced functionality whether it be for tunable surface properties, molecular adsorption, superior structural properties and so on.

Appendix A

Phase map analysis of multi-layer graphene

To delineate the different modalities of deformation we construct the phase map as shown in fig 2.1d by comparing the critical load of crinkle versus wrinkle formation for N-layered sandwich structures. Employing the notation in section 2.2.2, the potential energy for the wrinkle mode arising from bending and compression/extension of layers is given as

$$\Pi_{overall} = N \int_{-L_0}^{L_0} \frac{Q_b}{2} \kappa^2 ds + 2 \int_{-L_0}^{L_0} \frac{Y^{(2D)}}{2} \left(\sum_{m=1}^{(N-1)/2} \epsilon_m^2 \right) ds - f \int_{-L_0}^{L_0} (1 - \cos \theta) ds \quad (\text{A.0.1})$$

where $\epsilon_m = \pm m\alpha\kappa$ represents the strain in the m th layer away from the central layer by distance ma and N is odd. From (A.1.1), the critical buckling load for end angles prescribed as $\theta(\pm L_0) = \pm \theta_e$ is calculated to be,

$$f_{cr}^{(wrinkle)} = \pi^2 \frac{Q_b N}{4L_0^2} + \pi^2 \frac{Y^{(2D)}}{48L_0^2} a^2 N(N^2 - 1) \quad (\text{A.0.2})$$

Expression of (A.1.2) is found to be the same for even number of layers. In contrast to the wrinkling, the critical buckling load for mechanical wrinkle, as already discussed in section 2.2.2, is given as,

$$f_{cr}^{(mech.crinkle)} = \mu(N-1)a + \pi^2 \frac{Q_b N}{4L_0^2} \quad (A.0.3)$$

For the mechanical crinkle to be favorable over wrinkle, in the parameter space of L_0 and N , we must have $f_{cr}^{(mech.crinkle)} < f_{cr}^{(wrinkle)}$. This gives,

$$2L_0 \leq \pi N \sqrt{\frac{Y^{(2D)}a}{12\mu} \left(\frac{N+1}{N} \right)}, \quad (A.0.4)$$

and for MLG material properties,

$$2L_0 \leq 13.9N \sqrt{\left(\frac{N+1}{N} \right) a}, \quad (A.0.5)$$

which is the blue curve in fig. 2.1d. The asymptotic limit of large N is marked by broken orange curve. The critical load for flexoelectric crinkle formation is found to be even lower than mechanical crinkle formation as discussed in section 2.3. Thus, the phase boundary presented in fig.2.1d is referred to as a lower bound for flexoelectric crinkle formation.

Appendix B

Comparison of e-local and uc-local model predictions

Figure B.1 shows the comparison of curvature distribution predicted by two different models : the uc-local model (Red curve) and the e-local model (blue curve). The former uses $\beta_{(1)}^{(uc)} = 0.11e$ obtained from uniform bending DFT study [7] while the latter employs $\beta_{(21)}^{(*)} \sim 0.745e$ which was obtained by calibrating a single case (3°) to our DFT result for highly non-uniform bending of MLG. The pronounced differences in distribution because of non-local coupling effects of dielectricity and electric field become significant.

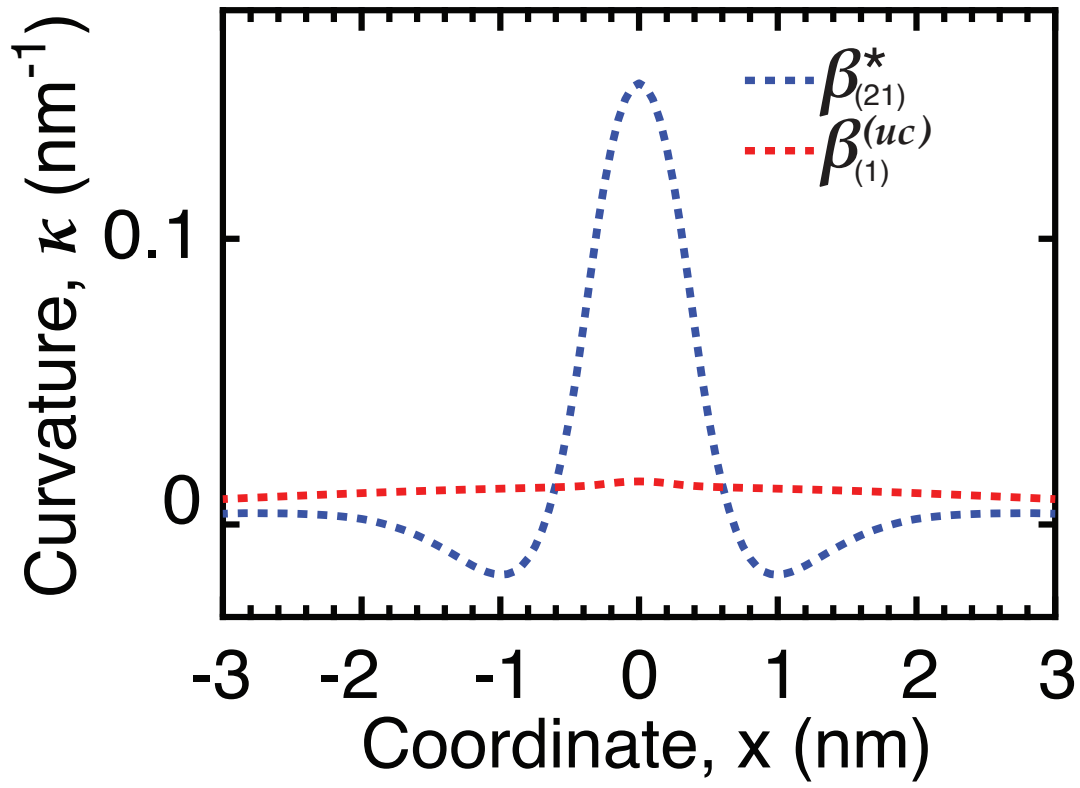


Figure B.1: Curvature distribution near a crinkle ridge of 21-layer MLG predicted by 21-layer e-local (blue) and single-layer uc-local (red) flexoelectric models; $2L_0 = 15\text{nm}$

Appendix C

Inter C_{60} spacing on crinkle ridge

The potential energy of the buckyballs on a crinkle ridge or valley (Fig. 3.(b2)) per unit spacing, can be formulated as,

$$\psi(l) = \frac{1}{4\pi\epsilon l} \left\{ Qq \int_{-\infty}^{\infty} \frac{1}{\sqrt{(h+d)^2 + x^2}} - \frac{1}{\sqrt{h^2 + x^2}} \right\} dx + \frac{1}{4\pi\epsilon l} 2Q^2 \sum_{i=1}^{\infty} \left(\frac{1}{il} - \frac{1}{\sqrt{d^2 + i^2 l^2}} \right). \quad (\text{C.0.1})$$

Simplifying (B.1) gives

$$\frac{\Phi(l)}{Q^2} = \frac{4\epsilon\psi(l)}{Q^2} = \frac{-2q/Q}{l} \ln \frac{(h+d)}{h} + \frac{2}{l^2} \sum_{i=1}^{\infty} \frac{1}{i} \left(1 - \frac{1}{\sqrt{(d/il)^2 + 1}} \right) \quad (\text{C.0.2})$$

The function $\Phi(l)$ can now be minimized to find the optimal inter-buckyball spacing. We assume $q/Q = 0.5$, $h = d = 1 \text{ nm}$ for this calculation, and $\Phi(l)$ is plotted in Fig. 3.(b3).

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