ATOMISTIC-TO-CONTINUUM MODELING OF THE DETACHMENT OF A GRAPHENE SHEET

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ATOMISTIC-TO-CONTINUUM MODELING OF THE DETACHMENT OF A
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Thesis

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ABSTRACT

We study the problem of detachment of a graphene sheet from a rigid substrate. Our study is partially motivated by an interest in the mechanism of unrolling of carbon nanoscrolls. We consider a simplified two-dimensional model that consists of two chains of carbon atoms. One chain representing a substrate is assumed to be fixed while the second chain corresponding to a detachable graphene sheet is unconstrained, except for one endpoint that is assumed to be at a prescribed distance from the substrate. We derive a continuum model of this system by upscaling the corresponding atomistic model. Specifically, we suppose that the distance between the adjacent atoms of the flexible chain is fixed to reflect the strength of covalent bonds. Then the discrete energy of the system consists of two contributions - due, respectively, to deviations of angles between the adjacent bonds from their equilibrium values and to van der Waals interactions. We formally derive an expression for macroscopic continuum energy by expanding the discrete energy in the small parameter equal to the ratio of the interatomic distance to the length of the sheet. The scalar function that describes the equilibrium shape of the graphene sheet can then be determined by solving the variational problem for the macroscopic energy. We conclude by analyzing the solutions of the Euler-Lagrange ODE corresponding to this energy.
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CHAPTER I
INTRODUCTION

1.1 Basic facts about carbon and graphene

The interest in nanotechnology has significantly expanded over the last few decades [20]. Here the prefix “nano” reflects the scale of building blocks of materials and devices in question and originates from the unit of measurement - nanometer (nm) - equal to one billionth of a meter. Some of the current uses of this technology are sunscreens, self-cleaning glass, clothing scratch-resistant coatings, antimicrobial bandages [6], [25], [38], and pollution sensing and prevention [4]. Possible future applications include nanorobots that have dimensions similar to biological cells. These devices can be used for medical procedures, improved cancer treatments, and environmental monitoring for microorganisms [24], [30].

One of the main areas of focus in nanotechnology is carbon-based structures, in particular graphene, carbon nanotubes and nanoscrolls. The simplest of these is a graphene sheet that consists of a single layer of carbon atoms arranged in a repeated hexagonal pattern, where the distance between any two bonded atoms is 0.142 nm [22]. Due to its optical transmittance, electrical and thermal conductivity, graphene has potential uses in a variety of applications from touch screens to smart
In order to understand the fundamental properties of graphene, we now discuss the electronic configuration of carbon atoms. The electrons in carbon orbitals $(1s^22s^22p^2)$ completely fill states $1s$, represented by a sphere around the center of the atom and $2s$—a sphere of bigger radius around the center. Two electrons are in the $2p$-state represented by the three lobes $2p_x$, $2p_y$ and $2p_z$ pointing in orthogonal directions when the atom is isolated as in Figure 1.1.a. Note that one of the three lobes remains empty.

In the presence of other carbon atoms, the electronic orbitals get perturbed and state $2s$ loses one electron to orbital $2p_z$. Orbital $2s$, along with $2p_x$ and $2p_y$ transform into three identical hybrid orbitals $sp^2$, holding only one electron each [39] as in Figure 1.1.b. This phenomena is called hybridization and allows for the three
new lobes to bond with similar lobes from neighboring carbon atoms. Thus each atom makes three strong $\sigma$-bonds around it as in Figure 1.2.a. The unhybridized $2p_z$ orbital stands perpendicular to the surface of the bonded carbon atoms, forming a $\pi$-bond with similar orbitals from other carbon atoms, ensuring that the layer of atoms is flat. The resulting atomic configuration forms a hexagonal lattice of a graphene sheet depicted in Figure 1.2.b.

(a) Six neighboring atoms  
(b) Graphene sheet

Figure 1.2: Structure of graphene.

1.1.1 Nanotubes

Carbon nanotubes (CNT) are of two basic types, single-walled and multi-walled. A single-walled nanotube (SWNT) can be thought of as a graphene sheet rolled up into a cylindrical tube. The tubes have diameters on the order of nanometers, while the lengths can range from a few nanometers to several millimeters [11].

The *chirality* of a nanotube is defined by the direction in which the graphene sheet is rolled with respect to the orientation of the hexagonal lattice in order to
create the tube. Depending on their chirality, CNTs can be classified as \textit{zigzag}, if the axis of the tube is parallel to a lattice direction, \textit{armchair}, if the axis of the tube is orthogonal to a lattice direction, or \textit{chiral}, if neither of the first two cases apply (Figure 1.3).

![Figure 1.3: Chirality of carbon nanotubes. Figures from [13].](image)

Due to the strong covalent bonds discussed in Section 1.1.1, CNTs exhibit exceptional chemical stability, excellent mechanical and thermal conductivity as well as remarkable stiffness paired with light weight. A particularly intriguing electronic property of CNTs is their ability to behave like semi-conductors or metals, depending on their chirality [28]. These characteristics have stimulated intensive theoretical and experimental research on CNTs [41]. Potential applications include transistors, integrated circuits, or logic gates in computers [3].
Typically, nanotubes are grown in a lab by using a chemical vapor deposition method [21]. The CNTs obtained by this technique are not single-walled, but rather multi-walled, i.e., they consist of multiple concentric tubes. Single tubes are obtained by pulling out individual shells from multi-walled nanotubes (MWNT). Studying MWNTs is of independent interest since they retain many of the properties of the SWNTs.

1.1.2 Nanoscrolls

A carbon nanoscroll (CNS) is a graphene sheet curled like a paper towel roll around a cylinder (Figure 1.4). The inner diameter of the CNS has to exceed a certain minimum value to ensure the scroll stability [7], i.e., to prevent the CNS from collapsing.

![Figure 1.4: A carbon nanoscroll. Figure from [42]](image)

Since a CNS is comparable in structure and size to a MWNT, these structures share a number of physical, chemical and optical properties [40]. However, for potential applications, CNS offer several possible advantages. For example, CNS have a tunable size core and a large surface area [33]. Due to the capability of CNS to
change their interlayer space to accommodate energy variations, researchers hope to use CNS for hydrogen storage, as water channels across cell membranes in biology, drug delivery system in a human body, as well as for chemical doping in applications such as capacitors and batteries [7], [34], [36].

An interesting behavior of CNS is that they can act like nano-oscillators with high frequency breathing periodic motion [35] by curling forward and backward around an equilibrium position when subjected to an electric field. A study in [37] suggested that inserting a CNT into a CNS, placing the CNS onto a rigid substrate, and manipulating the surface energy by an electric field transformed the periodic oscillations into a translational rolling motion on the substrate (Figure 1.5). This enables the CNS to be used as a linear actuator or motor.

Figure 1.5: Breathing motion of a CNS. Figures from [33].
CNS can be created in various ways such as rolling a graphene sheet around a CNT [33], hydrogenating a part of a graphene sheet [44], or by using a wedge-based mechanical exfoliation [18]. Chirality in CNS is defined in the same manner as chirality in CNTs (Figure 1.6). Chirality plays a large role in determining the electronic properties of nanoscrolls, similarly to nanotubes [9].

(a) Zigzag  
(b) Armchair

Figure 1.6: Main chiralities of CNS. Figures from [9].

1.2 Modeling of carbon nanostructures

Modeling is a crucial step in predicting the mechanical behavior and equilibrium configuration of carbon nanostructures. We now review both discrete and continuum models of nanotubes and nanoscrolls that have been developed over the past two decades.
1.2.1 Discrete models

Discrete models can be used to predict the atomistic configurations in carbon nanostructures. Typically they are solved numerically. These numerical results can be used to replace an expensive or deficient physical experiments. An adequate numerical model gives a good prediction of an equilibrium configuration or time evolution of a nanostructure.

In molecular dynamics (MD) simulations [2], [12], [43], one has to specify a set of initial conditions, i.e., initial positions and velocities of all atoms in the system, and an interaction potential for deriving the forces between atoms. The evolution of the system in time can be recovered by numerically solving a set of classical equations of motion, usually Newton’s equations for all particles in the system. If the system consists of \( N \) atoms, the force acting on the \( i^{th} \) atom at a given time can be obtained as the gradient of the interatomic potential \( U(r_1, r_2, r_3, \ldots, r_N) \) as a function of the positions of all atoms. Once the initial conditions and forces are known, the equations of motion can be solved numerically. Simulations produce the positions and velocities of all atoms as functions of time, \( r_i(t), v_i(t) \). Some commonly used molecular dynamics software include CHARMM, GROMACS, AMBER, and ADUN [5], [8], [19], [29].

While MD simulations have many advantages, such as the limited data required for input into the model, the high level of detail, and possible discovery of new features that have not been seen in the labs yet, there are significant challenges. In particular, the number of atoms the computer can handle is limited, the time spent
on simulation can be very large, and the possible errors can be difficult to control [1]. In order to address these challenges, continuum models have been developed that attempt to group atoms into larger units.

1.2.2 Continuum models

A nanostructure can be modeled by a continuum model in the form of a body that deforms to achieve equilibrium rather than atoms changing configuration. In [37], the authors study the cross-section of a CNS described as a continuous spiral. They discuss both the dynamics and equilibrium state of CNS, and show that the core size (inner radius) of a CNS can be controlled by changing the effective surface energy through an electric field. The continuum model is supplemented by MD simulations in order to verify the theoretical predictions in [37].

In [26], the authors suggest modeling nanostructures by an equivalent continuum model. The total molecular potential energy for a nano-structured material is calculated as the sum of various energy contributions. Then it is important to choose a suitable representative volume element (RVE) of the nanostructure, which is composed of several atoms. This yields an intermediate model to substitute for the molecular model. The next step is to get an equivalent truss model of the RVE, and view the total energy previously represented as the sum of elastic spring energies between all truss members. The deformation of bonds between the truss elements indicates the displacements of atoms in the system. The final step is to formulate an analytical continuum strain energy to obtain the equivalent continuum properties, or,
when that is not easy, to use numerical tools to determine the continuum parameters. Once the properties of the equivalent continuum model have been determined, the mechanical behavior of larger structures consisting of the nano-structured material may be predicted using the standard tools of continuum mechanics.

1.2.3 Atomistic-to-continuum models

An interesting approach for modeling nanostructures is to obtain a continuum model directly by upscaling a relevant atomistic model. In that process, one may start by computing the energy of interaction between all atoms in the system, then pick a small parameter that decreases as the system size increases. Letting that parameter go to zero and considering one or more terms in a corresponding asymptotic expansion, leads to possible continuum approximation of the energy of the system. A variational problem for this energy determines the system configuration at equilibrium.

Central to this thesis is the following idea. To understand the dynamics of a 3D model of a carbon nanotube or nanoscroll, one could start by examining the cross-section of the 3D model perpendicular to the axis of the tube or scroll. For nanotubes this yields a 2D model for two concentric closed chains of carbon atoms, and for nanoscrolls this yields a 2D spiral chain of atoms. These discrete models could potentially be upscaled to derive 1D continuum models for the deformation of the cross-section.

Next we review [14], [17] in which this atomistic-to-continuum approach is used to explain why the walls of a MWNT polygonize. In this thesis we shall use a
similar approach to study nanoscrolls with a focus on understanding the detachment that may occur at the outer end of the scroll.

In [17], an atomistic model is formulated for the cross-section of a two-walled nanotube in which the cross-section is represented by carbon atoms occupying two closed concentric curves on a fixed distance from each other. Given that the length of these curves is large compared to the distance between any two neighboring atoms on a given curve, the author identifies three different scales (see Figure 1.7). Macroscopically the system appears as a single closed smooth curve. When zooming in at a mesoscopic scale, the two curves look like a single straight line. Microscopically, the system can be visualized as two infinite parallel lines of equidistant atoms [14] and [17].

![Figure 1.7: Cross-section of a two-walled CNT when seen at the macroscale, the mesoscale, and the microscale.](image-url)
The author calculates the total atomistic energy for the system by accounting to the bending energy at the bonds between atoms within the same wall and the van der Waals energy for interactions between atoms from different walls. A more thorough explanation of this construction will be given in Chapter 2. Then the information about various scales in the system is used to derive a continuum model for two curves. This is done by analyzing leading order terms in the expansion of the energy.

The study confirmed that the overall shape of the tube is controlled by the tendency of graphene layers to be arranged in a low-energy A-B stacking (Figure 1.8) as explained in Section 3.1. Since the uniform stacking cannot be maintained over the circumference of the MWNT, the nanotube will tend to polygonize.

![Figure 1.8: Possible stacking for atoms in different layers](image)

(a) A-B stacking  
(b) A-A stacking

1.3 Motivation

Unlike nanotubes, nanoscrolls have an open topology with two free edges—an inner and an outer edge. Due to bending forces pushing the inner edge against the adjacent wall, this end will not detach from the scroll (See Chapter 2 for further explanation).

On the other hand, there is a set of competing forces on the outer edge of CNS—the
van der Waals force attempts to curl the edge along the scroll, while the bending force attempts to straighten the edge thus possibly creating a detachment (Figure 1.10).

In paper [32], the author shows that intrinsic ripples will occur in freestanding graphene sheets. Thus it is reasonable to expect that the free outer edge of a CNS will wrinkle even at an equilibrium state [37] as in Figure 1.9. Therefore, cross-sections at different points along the axis of a CNS will not be exactly the same. However, these ripples should be small relative to the size of the system of atoms, so that modeling a CNS by its cross-section will be adequate.

![Figure 1.9: The free edge of a nanoscroll [42].](image)

The cross-section of a nanoscroll is represented by carbon atoms sitting on a spiral (See Figure 1.10). One could model the wrapped part of a big nanoscroll in a study similar to [17] because at a microscale, both problems appear as atoms sitting on parallel straight lines, and at a macroscale, they both exhibit polygonization. In
In this thesis, we are interested in the equilibrium shape of the nanoscroll near a point of detachment. We simplify the problem of detachment from a CNS into the problem of detachment of a graphene sheet from a rigid substrate. The physical structure we study and a typical cross-section are shown in Figure 1.11. We also impose boundary conditions along the longitudinal edges of the sheet. The part of the graphene sheet laying on the substrate is fixed. The detaching edge is kept at a fixed height from the substrate.

Figure 1.10: Carbon nanoscroll with detachment.

Figure 1.11: Detachment of a graphene sheet from a substrate.
1.4 Summary of the main results

In this thesis we derive a continuum theory of a system of two chains of atoms of a described initial geometry representing the cross-section of the detachment of a graphene sheet from a rigid substrate. The atoms of the first chain are positioned on a straight rigid substrate while the second chain of carbon atoms is embedded in a curve with one section straight and parallel to the substrate and another section detached from the substrate. Our model is planar and assumes that all bonded atoms are at a constant distance from each other. We start by defining the appropriate energy of the discrete system. There are two contributions to the discrete energy. First, there is a bending energy existing at each atom bonded with two other atoms from the same curve. This energy results from these bonds trying to be linear, thus aiming to straighten the curves. Second, there is van der Waals energy, modeled by a Lennard Jones potential, between pairs of non-bonded atoms, and that is minimized when these atoms are at an optimal distance from each other. The forces associated with these two forces compete to determine the equilibrium configurations of the system.

We define a small parameter as the ratio of the length between two bonded atoms to the length of the curve representing the cross-section of the graphene sheet. From the discrete energy we derive a continuum energy as this parameter goes to zero. The continuum model gives the energy of the system as a function of the shape of the cross-section of the graphene sheet.
From the leading terms in the continuum energy we expect the van der Waals energy to dominate. We write an expression for that energy, and find the shape of the cross-section of the graphene sheet that will minimize it, while ignoring the bending energy. We then add a correction term to that shape, and minimize the total energy taking into consideration the bending energy. The result is a boundary value problem. By analyzing the solution to the corresponding Euler-Lagrange ODE, we discuss what shape of the system will be realized at equilibrium.

We conclude from this work that, when a graphene sheet detaches from a rigid substrate and its free edge is fixed at a prescribed distance from the substrate, the system seeks equilibrium by trying to keep the graphene sheet attached to the substrate for the longest distance possible, thus making the detachment straight and perpendicular to the substrate for the most part. But close to the point of detachment, the sheet detaches smoothly because of the large energy associated with the formation of a sharp angle.

The structure of the thesis is as follows. In Chapter 2, we describe the problem of the detachment of a graphene sheet from a rigid substrate. We consider the interaction of each atom with all other atoms in the system and derive an expression for the energy of the discrete system as a function of the positions of the discrete atoms. After that we extend the atomistic model to get a continuum model of the energy that depends on the function describing the detaching curve. In Chapter 3, we use the leading terms of the continuum energy expression derived in the previous chapter. We first minimize the expression considering the van der Waals energy
alone, then minimize it again by considering the bending energy as well. We derive
the Euler-Lagrange ODE corresponding to the minimum energy. We discuss what
the shape of the system should be in order to achieve equilibrium. In Chapter 4, we
will summarize our results and discuss future work.
CHAPTER II

MODELING THE DETACHMENT OF A GRAPHENE SHEET FROM A RIGID SUBSTRATE

In this chapter we model the problem of detachment of a graphene sheet from a flat rigid substrate. We assume that one edge of the graphene sheet is held at a fixed distance from the substrate. We consider the interaction of each atom with all other atoms in the system to derive an atomistic energy model as a function of the positions of atoms. We then derive a continuum model arising from the atomistic model by taking an appropriate asymptotic limit.

2.1 Problem setup

We consider the model of a graphene sheet partly detached from a rigid substrate. We study the cross-section of the entire setting assuming that the shape is uniform in the direction perpendicular to the cross-section. We model the cross-section as two smooth curves that lie in the same plan (Figure 2.1). Note that this figure is exaggerated to explain the problem setup. Macroscopically, in the region of attachment, the distance is infinitesimally small and the curves coincide on the macroscopic scale.
We assume the curves contain a large number of atoms and define a small parameter $\varepsilon$ to be the interatomic distance $h$ divided by the length $L$ of curve $C_2$. We call $\varepsilon$ a microscale, 1 a macroscale, and $\varepsilon^\gamma$ with $0 < \gamma < 1$, a mesoscale. At the macroscale, we cannot distinguish atoms in the system. We see the entire cross-section as a straight line splitting abruptly at some point. If we zoom in at any area of the system at a mesoscale, we see a straight line either horizontal or at an angle, but we still cannot differentiate between atoms. Finally, at the smaller scale $\varepsilon$, the line in the attachment zone becomes two parallel straight lines at a distance $\lambda \varepsilon$, where $\lambda = O(1)$, endowed with atoms at distance $\varepsilon$ from each other. Figure 2.2 shows the different scales.

Figure 2.1: Cross-section of a graphene sheet detaching from a rigid substrate.
We assume the curve $C_1$ is a horizontal straight line containing $N_1$ atoms where each atom has two adjacent atoms at a distance $h$ from it. We introduce coordinates so that $C_1$ lies on the positive side of the $x$-axis and the first atom on $C_1$ is at the origin. Because $C_1$ models a rigid substrate, we assume that $C_1$ is fixed. We assume that the curve $C_2$ representing the graphene sheet is inextensible, to model the strong covalent bonds between atoms that form the graphene layer. The goal is to determine the equilibrium shape of the curve $C_2$ that minimizes the energy of the system.
The curve $C_2$ in our study is a smooth curve part of which is a straight line parallel to $C_1$ at a distance $\lambda h$ from $C_1$. Beyond a certain point, $C_2$ detaches from $C_1$ (see Figure 2.3). We assume $C_2$ is the graph of a function $\lambda h + \tilde{f}(x)$, where $\tilde{f}(x)$ is twice continuously differentiable, bounded, and nonnegative. In addition, we assume $\tilde{f}'(x)$ is a nonnegative function. The function $\tilde{f}$ is an unknown function that we seek to find by minimizing an appropriately defined total energy.

![Figure 2.3: The geometry of curves $C_1$ and $C_2$ on macroscale.](image)

The curve $C_2$ contains $N_2$ carbon atoms. The first atom on $C_2$ is at distance $k'h$ away from the $y$-axis in the $xy$-plane, where $k' < 1$. Each pair of adjacent atoms of this chain are bonded at a straight line distance $h$ from each other. See Figure 2.4.

Next we write down the total energy of this discrete system of atoms.
2.2 Total energy of the discrete system

The total energy of the system is the sum of the stretching energy, the bending energy, and van der Waals interactions defined by a Lennard-Jones potential [37]. A description of each of these energies follows.

We assume there is a stretching energy between each pair of bonded atoms. The stretching energy between atoms \(j\) and \(j+1\) can be assumed to have the form [27]

\[
\tilde{E}_{sj,j+1} = K(\tilde{r}_{j,j+1} - h)^2,
\]

where \(h\) is the distance between two adjacent atoms on the same curve, if the bond between them is not stretched, \(\tilde{r}_{j,j+1}\) the distance after stretching, and \(K\) is the spring constant (Figure 2.5). We assume that the spring constant \(K\) is very large, which
implies that even for significantly small value of $\tilde{r}_{j,j+1} - h$, the total stretching energy may be large. Since we are looking at the system at equilibrium, we will assume that none of the bonds in the system is stretched, thus $\tilde{r}_{j,j+1} = h$ for all bonds. Then $\tilde{E}_{s,j,j+1} = 0$, and the total stretching energy on $C_1$ and $C_2$ is

$$\tilde{E}_s = \sum_{i=1}^{N_1-1} \tilde{E}_{s,i,i+1} + \sum_{j=1}^{N_2-1} \tilde{E}_{s,j,j+1} = 0. \quad (2.1)$$

Next, we describe the bending energy between two adjacent bonds as a function of the angle $\theta$ formed by these bonds. This energy is minimized if the bonds at each atom are aligned. We describe the bending energy by a smooth function $b(\theta)$ that satisfies $b(\pi) = 0$, $b'(\pi) = 0$ and $b''(\pi) > 0$. Hence the bending energy has a local minimum of zero when two adjacent bonds are aligned. We also assume that $b(\theta)$ is
even about $\theta = \pi$, therefore $b(\pi - \theta) = b(\pi + \theta)$. An example of a graph of a function $b$ that satisfies these hypotheses is shown in Figure 2.6.

![Graph of function $b(\theta)$](image)

Figure 2.6: The general shape of a bending energy function $b(\theta)$.

Now we describe the total bending energy. On $C_1$, all atoms are fixed and the bonds between them are aligned, and therefore their bending energy is zero. The bending energy we calculate is that of the atoms lying on $C_2$. The index $j = 1$ corresponds to the atom closest to the $y$-axis. The angle at atom $j$ between the line joining atom $j$ and atom $j + 1$ and the positive $x$-axis is denoted by $\theta_j$ (Figure 2.8). Thus, the contribution to the total bending energy at atom $j$ is $b(\pi + \theta_j - \theta_{j-1})$, and, with $\tilde{\alpha}$ a scaling factor, the total bending energy for the entire system is

$$
\tilde{E}_b = \tilde{\alpha} \sum_{j=2}^{N_2-1} b(\pi + \theta_j - \theta_{j-1}).
$$

(2.2)
Lastly, we describe the van der Waals energy. We assume that each atom on $C_1$ interacts with each atom on $C_2$ by van der Waals forces. For a pair of atoms, the force associated with this interaction is strongly repulsive when the atoms are closer than $\sigma$—the van der Waals equilibrium distance, 0 when the atoms are $\sigma$ apart, and weakly attractive if the atoms are further apart than $\sigma$. We model this force by starting with a Lennard-Jones type potential [17],

$$g(r) = \left(\frac{1}{r}\right)^{12} - 2\left(\frac{1}{r}\right)^6,$$

where the nondimensional variable $r$ represents the distance between two interacting atoms. The graph of $g$ is shown in Figure 2.7. Note that the derivative of $g$ is $g'(r) = -12\frac{12}{r^{13}} + 12\frac{6}{r^7}$. Thus $g'(1) = 0$, and therefore $r = 1$ is the unique minimum of $g$ with $g(1) = -1$. In addition $g(r) \to \infty$ as $r \to 0^+$, i.e., when atoms approach each other, the repulsive force between them blows up; and $g(r) \to 0^-$ as $r \to \infty$, so that attractive force between two interacting atoms becomes negligible if the atoms are far apart.

When taking into account the interaction between all of the atoms from $C_1$ and all of the atoms from $C_2$, the total van der Waals energy of the system is

$$\tilde{E}_w = \tilde{\gamma} \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} g\left(\frac{|\tilde{r}_{1,i} - \tilde{r}_{2,j}|}{\sigma}\right),$$

where $\tilde{\gamma}$ is a scaling factor, $\tilde{r}_{1,i}$ is the position vector of atom $i$ on $C_1$ and $\tilde{r}_{2,j}$ is the position vector of atom $j$ on $C_2$. We note that, if atom $i$ from $C_1$ and atom $j$ from $C_2$ are at distance $\sigma$ from each other, then $\frac{|\tilde{r}_{1,i} - \tilde{r}_{2,j}|}{\sigma} = 1$, and $g$ is minimized. Hence $\sigma$ is the equilibrium distance between non-bonded atoms.
The total energy of the discrete system is the sum of the bending and van der Waals energies which is

$$\tilde{E} = \tilde{\alpha} \sum_{j=2}^{N_2-1} b(\pi + \theta_j - \theta_{j-1}) + \tilde{\gamma} \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} g \left( \frac{|\tilde{\mathbf{r}}_{1,i} - \tilde{\mathbf{r}}_{2,j}|}{\sigma} \right). \quad (2.5)$$

We non-dimensionalize by introducing the rescalings

$$\mathbf{r}_{1,i} = \frac{\tilde{\mathbf{r}}_{1,i}}{L_2}, \quad \mathbf{r}_{2,j} = \frac{\tilde{\mathbf{r}}_{2,j}}{L_2}, \quad \alpha = \frac{\tilde{\alpha}}{\tilde{\gamma}}, \quad E = \frac{\tilde{E}}{\tilde{\gamma}}.$$ 

The non-dimensional total energy becomes

$$E = \alpha \sum_{j=2}^{N_2-1} b(\pi + \theta_j - \theta_{j-1}) + \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} g \left( \frac{|\mathbf{r}_{1,i} - \mathbf{r}_{2,j}|}{\sigma/L_2} \right).$$

We define $\varepsilon = \frac{h}{L_2}$ and $\mu = \frac{\sigma}{\varepsilon L_2}$. The total energy can now be written as

$$E = \alpha \sum_{j=2}^{N_2-1} b(\pi + \theta_j - \theta_{j-1}) + \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} g \left( \frac{|\mathbf{r}_{1,i} - \mathbf{r}_{2,j}|}{\mu \varepsilon} \right). \quad (2.6)$$
2.3 Deriving the continuum approximation of the bending energy

In this section we derive a continuum expression for the bending energy. Let $S_{j-1}$ be the point on $C_2$ with coordinates $(x_{j-1}, \lambda \varepsilon + f(x_{j-1}))$, where atom $j-1$ is positioned. See Figure 2.8. We define similarly points $S_j$ and $S_{j+1}$ corresponding to the position of atoms $j$ and $j+1$ respectively. The shortest distance from $S_{j-1}$ to $S_j$ is $\varepsilon$, so is that from $S_j$ to $S_{j+1}$. Using the distance formula we can write

\[
(x_{j+1} - x_j)^2 + (f(x_{j+1}) - f(x_j))^2 = \varepsilon^2 \tag{2.7}
\]

\[
(x_j - x_{j-1})^2 + (f(x_j) - f(x_{j-1}))^2 = \varepsilon^2 \tag{2.8}
\]

![Figure 2.8: Geometry of three consecutive atoms on $C_2$.](image)
Since $f(x)$ is a smooth function, we can expand it into a Taylor series about $x_j$. Equation (2.7) is now

\[
(x_{j+1} - x_j)^2 + (f(x_j) + f'(x_j)(x_{j+1} - x_j) + O((x_{j+1} - x_j)^2) - f(x_j))^2 = \varepsilon^2
\]

\[
(x_{j+1} - x_j)^2 + (f'(x_j) (x_{j+1} - x_j) + O(\varepsilon^2))^2 = \varepsilon^2
\]

\[
(x_{j+1} - x_j)^2 + (f'(x_j)^2 (x_{j+1} - x_j)^2 + O(\varepsilon^3)) = \varepsilon^2
\]

\[
(x_{j+1} - x_j)^2 \left( 1 + (f'(x_j))^2 \right) = \varepsilon^2 + O(\varepsilon^3).
\]

We define $\Delta x_j = x_{j+1} - x_j$, then

\[
\Delta x_j^2 = \frac{\varepsilon^2}{1 + (f'(x_j))^2} + O(\varepsilon^3).
\]

Using the binomial expansion

\[
\Delta x_j = \left( \frac{\varepsilon^2}{1 + (f'(x_j))^2} + O(\varepsilon^3) \right)^{\frac{1}{2}}
\]

\[
= \frac{\varepsilon}{\sqrt{1 + (f'(x_j))^2}} + O(\varepsilon^3).
\]

(2.9)

We apply Taylor expansion about $x_j$ in equation (2.8), we obtain

\[
(x_j - x_{j-1})^2 + (f(x_j)) - (f(x_j) + f'(x_j)(x_{j+1} - x_j) + O((x_{j+1} - x_j)^2))^2 = \varepsilon^2
\]

\[
(x_j - x_{j-1})^2 + \left( (f'(x_j))^2 (x_{j+1} - x_j)^2 + O(\varepsilon^3) \right) = \varepsilon^2
\]

\[
(x_j - x_{j-1})^2 \left( 1 + (f'(x_j))^2 \right) = \varepsilon^2 + O(\varepsilon^3).
\]

We notice that

\[
x_j - x_{j-1} = \Delta x_j = \frac{\varepsilon}{\sqrt{1 + (f'(x_j))^2}} + O(\varepsilon^2).
\]

(2.10)
Looking at Figure 2.8, the slope of the segment line joining \( S_j \) and \( S_{j+1} \) is
\[
\tan \theta_j = \frac{f(x_{j+1}) - f(x_j)}{x_{j+1} - x_j}
= \frac{f(x_j + \Delta x_j) - f(x_j)}{\Delta x_j}
= \frac{f(x_j) + f'(x_j)\Delta x_j + \frac{1}{2}f''(x_j)\Delta x_j^2 + O((\Delta x_j)^3) - f(x_j)}{\Delta x_j}
= f'(x_j) + \frac{1}{2}f''(x_j)\Delta x_j + O(\varepsilon^2).
\]

By applying the inverse tangent function and expanding into a Taylor series about \( f'(x_j) \), the angle \( \theta_j \) can be written as
\[
\theta_j = \tan^{-1} \left( f'(x_j) + \frac{1}{2}f''(x_j)\Delta x_j + O(\varepsilon^2) \right)
= \tan^{-1} \left( f'(x_j) + \frac{1}{1 + (f'(x_j))^2} \left( \frac{1}{2}f''(x_j)\Delta x_j + O(\varepsilon^2) \right) \right) + O((\Delta x_j)^2) \quad (2.11)
= \tan^{-1} (f'(x_j)) + \frac{1}{1 + (f'(x_j))^2} \frac{1}{2}f''(x_j)\Delta x_j + O(\varepsilon^2).
\]

From Figure 2.8 the slope of the segment line joining \( S_{j-1} \) and \( S_j \) is
\[
\tan \theta_{j-1} = \frac{f(x_j) - f(x_{j-1})}{x_j - x_{j-1}}
= \frac{f(x_j) - f(x_j - \Delta x_j)}{\Delta x_j}
= \frac{f(x_j) - (f(x_j) - f'(x_j)\Delta x_j + \frac{1}{2}f''(x_j)\Delta x_j^2 + O((\Delta x_j)^3))}{\Delta x_j}
= f'(x_j) - \frac{1}{2}f''(x_j)\Delta x_j + O(\varepsilon^2).
\]
And the angle $\theta_{j-1}$ is

$$\theta_{j-1} = \tan^{-1} \left( f'(x_j) - \frac{1}{2} f''(x_j)(\Delta x_j) + O(\varepsilon^2) \right)$$

$$= \tan^{-1} (f'(x_j)) + \frac{1}{1 + (f'(x_j))^2} \left( -\frac{1}{2} f''(x_j) \Delta x_j + O(\varepsilon^2) \right) + O((\Delta x_j)^2) \tag{2.12}$$

$$= \tan^{-1} (f'(x_j)) - \frac{1}{1 + (f'(x_j))^2} \frac{1}{2} f''(x_j) \Delta x_j + O(\varepsilon^2).$$

Using the results from (2.11) and (2.12), the difference between angles $\theta_j$ and $\theta_{j-1}$ can be written as

$$\theta_j - \theta_{j-1} = \frac{f''(x_j)}{1 + (f'(x_j))^2} \Delta x_j + O(\varepsilon^2). \tag{2.13}$$

We replace $\Delta x_j$ by the value from (2.9)

$$\theta_j - \theta_{j-1} = \frac{f''(x_j)}{1 + (f'(x_j))^2} \frac{\varepsilon}{\sqrt{1 + (f'(x_j))^2}} + O(\varepsilon^2) \tag{2.14}$$

$$= \frac{f''(x_j) \varepsilon}{(1 + (f'(x_j))^2)^{3/2}} + O(\varepsilon^2).$$

We define the function $F(x) = \frac{f''(x)}{(1 + (f'(x))^2)^{3/2}}$. Note that $F(x)$ is uniformly continuous on every interval $[x_{j-1}, x_j]$.

The difference between angles $\theta_j$ and $\theta_{j-1}$ is expressed as

$$\theta_j - \theta_{j-1} = F(x_j) \varepsilon + O(\varepsilon^2). \tag{2.15}$$
The total nondimensional discrete bending energy equation (2.6) is

\[ E_b = \alpha \sum_{j=2}^{N_2-1} b(\pi + \theta_j - \theta_{j-1}) \]

\[ = \alpha \sum_{j=2}^{N_2-1} b \left( \pi + F(x_j)\varepsilon + O(\varepsilon^2) \right) \]

\[ = \alpha \sum_{j=2}^{N_2-1} \left\{ b(\pi) + b'(\pi)(F(x_j)\varepsilon + O(\varepsilon^2)) + \frac{b''(\pi)}{2!} \left[ (F(x_j)\varepsilon + O(\varepsilon^2))^2 + O(\varepsilon^3) \right] \right\} \]

\[ = \alpha \sum_{j=2}^{N_2-1} \left\{ \frac{b''(\pi)}{2} \left[ (F(x_j))^2\varepsilon^2 + O(\varepsilon^3) \right] + O(\varepsilon^3) \right\} \]

\[ = \frac{\alpha b''(\pi)}{2} \sum_{j=2}^{N_2-1} \left[ (F(x_j))^2\varepsilon^2 \right] + (N_2 - 2)O(\varepsilon^3). \]

(2.16)

We need the following lemma and theorem to determine the order of \( N_2 - 2 \) in terms of \( \varepsilon \).

**Theorem 1.** The arclength distance between two bonded atoms in chain \( C_2 \) is equal to \( \varepsilon + O(\varepsilon^2) \).

**Proof.** The arclength distance between atoms \( j \) and \( j - 1 \) on curve \( C_2 \) is

\[ s_j - s_{j-1} = \int_{s_{j-1}}^{s_j} ds \]

\[ = \int_{x_{j-1}}^{x_j} \sqrt{1 + (f'(x))^2} dx. \]

(2.17)

By the Mean Value Theorem for Integrals [31], there exists \( \hat{x}_j \in (x_{j-1}, x_j) \) such that

\[ \int_{x_{j-1}}^{x_j} \sqrt{1 + (f'(x))^2} dx = (x_j - x_{j-1})\sqrt{1 + (f'(\hat{x}_j))^2} \]

\[ = (x_j - x_{j-1}) \left[ \sqrt{1 + (f'(x_{j-1}))^2} + \sqrt{1 + (f'(\hat{x}_j))^2} - \sqrt{1 + (f'(x_{j-1}))^2} \right]. \]

(2.18)
Since the function $\hat{G}(x) = \sqrt{1 + (f'(x))^2}$ is smooth and independent of $\varepsilon$ on the domain of $f$, then we can expand $\hat{G}(x)$ about $x_{j-1}$ and get

$$
\hat{G}(\hat{x}_j) - \hat{G}(x_{j-1}) = \hat{G}'(x_{j-1})(\hat{x}_j - x_{j-1}) + O((\hat{x}_j - x_{j-1})^2)
$$

$$
< \hat{G}'(x_{j-1})(x_j - x_{j-1}) + O(\varepsilon^2)
$$

$$
= O(\varepsilon) + O(\varepsilon^2).
$$

Thus, (2.17) becomes

$$
s_j - s_{j-1} = (x_j - x_{j-1}) \left[ \sqrt{1 + (f'(x_{j-1}))^2} + O(\varepsilon) \right]
$$

$$
= (x_j - x_{j-1}) \left[ \sqrt{1 + (f'(x_{j-1}))^2} + O(\varepsilon^2) \right].
$$

(2.20)

Combining this result with equation (2.9), we get

$$
s_j - s_{j-1} = \varepsilon + O(\varepsilon^2)
$$

(2.21)

Thus the arclength distance between two connected atoms on chain $C_2$ is equal to $\varepsilon + O(\varepsilon^2)$.

**Lemma 2.** $N_2 - 1 = O(\varepsilon^{-1})$.

**Proof.** The number of atoms in chain $C_2$ minus one, is equal to the length of the chain—which is 1, divided by the arclength distance between two bonded atoms. According to Theorem 1, that arclength is $\varepsilon + O(\varepsilon^2)$, leading to $N_2 - 1 = O(\varepsilon^{-1})$.

From Lemma 2 we conclude that $N_2 - 2 = O(\varepsilon^{-1})$, and the total bending energy in (2.16) is

$$
E_b = \frac{ab''(\pi)}{2} \sum_{j=2}^{N_2-1} (F(x_j))^2 \varepsilon^2 + O(\varepsilon^2).
$$

(2.22)
Lemma 3. Let $l$ be the $x$-coordinate of the last atom on curve $C_2$. Then we can write

$$
\sum_{j=2}^{N_2-1} (F(x_j))^2 \varepsilon^2 = \varepsilon \int_0^l (F(x))^2 \left[1 + (f'(x))^2\right]^{\frac{1}{2}} \, dx + O(\varepsilon^2).
$$

Proof. We can divide curve $C_2$ into small arcs going from one atom to the following one on the same curve.

$$
\varepsilon \int_0^l (F(x))^2 \left[1 + (f'(x))^2\right]^{\frac{1}{2}} \, dx = \varepsilon \sum_{j=2}^{N_2-1} \int_{x_{j-1}}^{x_j} (F(x))^2 \left[1 + (f'(x))^2\right]^{\frac{1}{2}} \, dx. \tag{2.23}
$$

By the Mean Value Theorem for Integrals [31], there exists $x_j^* \in (x_{j-1}, x_j)$ such that

$$
\int_{x_{j-1}}^{x_j} (F(x))^2 \left[1 + (f'(x))^2\right]^{\frac{1}{2}} \, dx = (F(x_j^*))^2 \left[1 + (f'(x_j^*))^2\right]^{\frac{1}{2}} (x_j - x_{j-1}).
$$

Then (2.23) can be written as

$$
\varepsilon \int_0^l (F(x))^2 \left[1 + (f'(x))^2\right]^{\frac{1}{2}} \, dx = \varepsilon \sum_{j=2}^{N_2-1} (F(x_j^*))^2 \left[1 + (f'(x_j^*))^2\right]^{\frac{1}{2}} (x_j - x_{j-1})
$$

$$
= \varepsilon \sum_{j=2}^{N_2-1} (F(x_j))^2 \left[1 + (f'(x_j))^2\right]^{\frac{1}{2}} (x_j - x_{j-1})
$$

$$
+ \varepsilon \sum_{j=2}^{N_2-1} \left[(F(x_j^*))^2 \left[1 + (f'(x_j^*))^2\right]^{\frac{1}{2}} - (F(x_j))^2 \left[1 + (f'(x_j))^2\right]^{\frac{1}{2}}\right] (x_j - x_{j-1}). \tag{2.24}
$$

Since the function $G(x) = (F(x))^2 \left[1 + (f'(x))^2\right]$ is uniformly continuous on $[x_{j-1}, x_j]$, we have

$$
G(x_j^*) - G(x_j) = o(1)
$$

when $\varepsilon$ is small. This, along with Lemma 2, makes the integral
\[ \epsilon \int_0^l (F(x))^2 \left[ 1 + (f'(x))^2 \right] \frac{1}{2} \, dx = \epsilon \sum_{j=2}^{N_2-1} (F(x_j))^2 \left[ 1 + (f'(x_j))^2 \right] \frac{1}{2} (x_j - x_{j-1}) \]

\[ + \epsilon \sum_{j=2}^{N_2-1} o(1)(x_j - x_{j-1}) \]

\[ = \epsilon \sum_{j=2}^{N_2-1} (F(x_j))^2 \left[ 1 + (f'(x_j))^2 \right] \frac{1}{2} (x_j - x_{j-1}) + o(\epsilon). \]

We use (2.9) to finally write

\[ \epsilon \int_0^l (F(x))^2 \left[ 1 + (f'(x))^2 \right] \frac{1}{2} \, dx = \sum_{j=2}^{N_2-1} (F(x_j))^2 \epsilon^2 + o(\epsilon). \]  

(2.25)

From Lemma 3 the total bending energy in (2.22) is

\[ E_b = \frac{\alpha b''(\pi)}{2} \int_0^l (F(x))^2 \left[ 1 + (f'(x))^2 \right] \frac{1}{2} \, dx + o(\epsilon). \]

We replace \( F(x) \) by its definition, and the total continuum bending energy of the system becomes

\[ E_b = \frac{\alpha b''(\pi)}{2} \int_0^l \left( \frac{f''(x)}{(1 + (f'(x))^2)^{3/2}} \right) \left[ 1 + (f'(x))^2 \right] \frac{1}{2} \, dx + o(\epsilon) \]

(2.26)

\[ = \frac{\alpha b''(\pi)}{2} \int_0^l \left( f''(x) \right)^2 \left( 1 + (f'(x))^2 \right)^{-\frac{3}{2}} \, dx + o(\epsilon). \]

We can also express the bending energy in terms of \( \theta \) and \( s \). \( \theta(s) \) is the function representing the angle made by the tangent to curve \( C_2 \) at the point of arclength \( s \) and the horizontal \( x \)-axis. The arclength unit is \( ds = \sqrt{1 + (f'(x))^2} \, dx \) and the curvature \( \theta'(s) = \frac{f''(x)}{1 + (f'(x))^2} \). The total continuum bending energy is

\[ E_b = \frac{\alpha b''(\pi)}{2} \int_0^l (\theta'(s))^2 + o(\epsilon). \]  

(2.27)
Note that the leading order term in the continuum bending energy expression is of $O(\varepsilon)$.

2.4 Deriving the continuum representation of the van der Waals energy

In this section we derive the continuum van der Waals energy starting from the nondimensional discrete energy given by (2.6)

$$E_w = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} g \left( \frac{|r_{1,i} - r_{2,j}|}{\mu \varepsilon} \right) = \sum_{j=1}^{N_2} \sum_{i=1}^{N_1} g \left( \frac{|r_{1,i} - r_{2,j}|}{\mu \varepsilon} \right). \quad (2.28)$$

The double sum refers to the resultant energy from the van der Waals interactions of each carbon atom located in chain $C_1$ with all atoms on $C_2$. We fix an atom $j$ on $C_2$, and examine the neighborhood $\Lambda_j$ of $j$, defined by a circle of center $P_j$ where $j$ is located, and radius $A = \varepsilon^\frac{a}{20}$. The reason behind choosing this particular value for $A$ will be more clear in the process of approximating some errors during the energy calculation later in our study. At that scale, the curves holding the two chains of atoms appear as two parallel straight lines, the upper one having the direction of the tangent line to the curve at $P_j$.

Let $r_{ij}$ be the distance between atom $j$ on $C_2$ and atom $i$ on $C_1$, i.e., $r_{ij} = |r_{1,i} - r_{2,j}|$. Recall that $\varepsilon << \varepsilon^\frac{a}{20} << 1$.

Looking back at equation (2.28), the total van der Waals energy between atom $j$ from $C_2$ and all atoms on $C_1$ is

$$E_{w_j} = \sum_{i=1}^{N_1} g \left( \frac{r_{ij}}{\mu \varepsilon} \right) = \sum_{i \in \Lambda_j} g \left( \frac{r_{ij}}{\mu \varepsilon} \right) + \sum_{i \notin \Lambda_j} g \left( \frac{r_{ij}}{\mu \varepsilon} \right). \quad (2.29)$$
We then use the definition of $g$ from equation (2.3)

$$
\left| \sum_{i \notin \Lambda_j^A} g \left( \frac{r_{ij}}{\mu \varepsilon} \right) \right| = \left| \sum_{i \notin \Lambda_j^A} \left[ \left( \frac{\mu \varepsilon}{r_{ij}} \right)^{12} - 2 \left( \frac{\mu \varepsilon}{r_{ij}} \right)^6 \right] \right|
\leq \sum_{i \notin \Lambda_j^A} \left[ \left( \frac{\mu \varepsilon}{r_{ij}} \right)^{12} + 2 \left( \frac{\mu \varepsilon}{r_{ij}} \right)^6 \right].$

(2.30)

For $i \notin \Lambda_j^A$, the two corresponding atoms $i$ on $C_1$ and $j$ on $C_2$ are at a distance $r_{ij} > A$, therefore

$$
\sum_{i \notin \Lambda_j^A} g \left( \frac{r_{ij}}{\mu \varepsilon} \right) < \sum_{i \notin \Lambda_j^A} \left[ \left( \frac{\mu \varepsilon}{A} \right)^{12} + 2 \left( \frac{\mu \varepsilon}{A} \right)^6 \right]
= \sum_{i \notin \Lambda_j^A} \left[ \left( \frac{\mu \varepsilon}{\frac{9}{20}} \right)^{12} + 2 \left( \frac{\mu \varepsilon}{\frac{9}{20}} \right)^6 \right]
= \sum_{i \notin \Lambda_j^A} \left[ \left( \frac{\mu \varepsilon}{\frac{11}{20}} \right)^{12} + 2 \left( \frac{\mu \varepsilon}{\frac{11}{20}} \right)^6 \right]
< \sum_{i \notin \Lambda_j^A} \left[ 3 \left( \frac{\mu \varepsilon}{\frac{11}{20}} \right)^6 \right]
= 3\mu^6 \sum_{i \notin \Lambda_j^A} \varepsilon^{\frac{33}{16}}
\leq 3\mu^6 \sum_{i \notin \Lambda_j^A} \varepsilon^{\frac{33}{16}} + 3\mu^6 \sum_{i \in \Lambda_j^A} \varepsilon^{\frac{13}{16}}
= 3\mu^6 \sum_{i=1}^{N_1} \varepsilon^{\frac{33}{16}}
= 3\mu^6 N_1 \varepsilon^{\frac{33}{16}}
= 3\mu^6 \frac{L_1}{L_2} \varepsilon^{\frac{33}{16}}
= 3\mu^6 \frac{L_1}{L_2} \varepsilon^{\frac{23}{16}}
= O \left( \varepsilon^{\frac{23}{16}} \right).
$$

(2.31)
We calculate now the van der Waals energy between the atom at $S_j$ that we fixed on $C_2$, located at $(x_j, \lambda \varepsilon + f(x_j))$, and the atoms on $C_1$ that are in $\Lambda_j^A$.

We call $P_j$ the projection of $S_j$ on $C_1$ i.e., the $x$-axis. $P_j$ is at $(x_j, 0)$. The distance from $S_j$ to $P_j$ is $B_j = \lambda \varepsilon + f(x_j)$. We define $k_j$ so that $k_j \varepsilon$ is the distance between $P_j$ and the first atom on $C_1$ located to the right of $P_j$. Note that $k_j = k = 1 - k'$ in the zone where curves $C_1$ and $C_2$ are still attached. Figure 2.9 summarizes the various definitions we make.

We denote by $J_{jr}$ the number of carbon atoms on $C_1$ that are located in $\Lambda_j^A$ to the right of $P_j$ and by $J_{jl}$ the number of carbon atoms on $C_1$ in $\Lambda_j^A$ to the left of $P_j$. The following calculation is done if there is at least one atom on $C_1$ in the indicated neighborhood, that is where $\{J_{jr}, J_{jl}\} \neq \{0\}$. We will do an energy calculation later in this section for the case where there are no atom from $C_1$ in $\Lambda_j^A$.

We use the local integer variable $p$ to designate a particular atom on $C_1$. The coordinates of the place of $p$ on the $xy$-plane are then given by the ordered pair
We set $p = 0$ for the first atom on $C_1$ found to the right of $P_j$, and continue counting positively each additional atom to the right. $p$ will have negative values to specify atoms located to the left of $P_j$. Hence $p = -1$ is the closest atom to $P_j$ from the left side. Using the distance formula, the space $r_{pj}$ between atom $j$ on $C_2$ and atom $p$ on $C_1$ is

$$r_{pj} = \sqrt{B_j^2 + (k_j \varepsilon + \varepsilon p)^2}. \quad (2.32)$$

Next (2.29), we calculate the summation of the interactions within the neighborhood $\Lambda_j^A$

$$\sum_{i \in \Lambda_j^A} g \left( \frac{r_{ij}}{\mu \varepsilon} \right) = \sum_{p \in \Lambda_j^A} g \left( \frac{r_{pj}}{\mu \varepsilon} \right) = \sum_{p=-J_j}^{J_j-1} g \left( \frac{r_{pj}}{\mu \varepsilon} \right) = \sum_{p=-\infty}^{\infty} g \left( \frac{r_{pj}}{\mu \varepsilon} \right) + \text{error}_5 + \text{error}_6, \quad (2.33)$$

where $\text{error}_5 = \sum_{p=-\infty}^{J_j-1} g \left( \frac{r_{pj}}{\mu \varepsilon} \right)$, and $\text{error}_6 = \sum_{p=-J_j}^{\infty} g \left( \frac{r_{pj}}{\mu \varepsilon} \right)$.

We now estimate $|\text{error}_6|$. For $p = J_{jr}$, the corresponding atom falls outside $\Lambda_j^A$, so that $r_{J_{jr}j} > A = \varepsilon \frac{a}{2b}$. And the van der Waals energy between atom $J_{jr}$ and atom $j$ on $C_2$ is
\[
\left| g \left( \frac{r_{J_{jr,j}}}{\mu \varepsilon} \right) \right| = \left| \left( \frac{\mu \varepsilon}{r_{J_{jr,j}}} \right)^{12} - 2 \left( \frac{\mu \varepsilon}{r_{J_{jr,j}}} \right)^6 \right|
\leq \left( \frac{\mu \varepsilon}{r_{J_{jr,j}}} \right)^{12} + 2 \left( \frac{\mu \varepsilon}{r_{J_{jr,j}}} \right)^6
\leq \left( \frac{\mu \varepsilon}{A} \right)^{12} + 2 \left( \frac{\mu \varepsilon}{A} \right)^6
\leq \left( \frac{\mu \varepsilon^{11}}{\mu} \right)^{12} + 2 \left( \frac{\mu \varepsilon^{11}}{\mu} \right)^6
\leq 3 \left( \frac{\mu \varepsilon^{11}}{\mu} \right)^6
= 3 \mu^6 \varepsilon^{33}.
\]

(2.34)

For \( p > J_{jr,j} \), we know that \( r_{pj} > A \), which means \( \frac{\mu \varepsilon}{r_{pj}} < \mu \varepsilon^{11} \frac{\mu}{\mu} < 1 \). We calculate the other terms in the summation of \( |error6| \)

\[
\left| \sum_{p=J_{jr,j}+1}^{\infty} g \left( \frac{r_{pj}}{\mu \varepsilon} \right) \right| = \left| \sum_{p=J_{jr,j}+1}^{\infty} \left[ \left( \frac{\mu \varepsilon}{r_{pj}} \right)^{12} - 2 \left( \frac{\mu \varepsilon}{r_{pj}} \right)^6 \right] \right|
\leq \sum_{p=J_{jr,j}+1}^{\infty} \left[ \left( \frac{\mu \varepsilon}{r_{pj}} \right)^{12} + 2 \left( \frac{\mu \varepsilon}{r_{pj}} \right)^6 \right]
\leq 3 \sum_{p=J_{jr,j}+1}^{\infty} \left( \frac{\mu \varepsilon}{r_{pj}} \right)^6.
\]

We use the last result and replace \( r_{pj} \) by the value from (2.32) for \( p > J_{jr} \), and \( g \left( \frac{r_{pj}}{\mu \varepsilon} \right) \) by the result from (2.34) for \( p = J_{jr} \). We get

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\[ |\text{error6}| = \sum_{p=J_{jr}+1}^{\infty} g \left( \frac{r_{pj}}{\mu \varepsilon} \right) + g \left( \frac{r_{J_j r}}{\mu \varepsilon} \right) \]
\[ \leq 3 \sum_{p=J_{jr}+1}^{\infty} \left( \frac{\mu \varepsilon}{\sqrt{B_j^2 + (k_j \varepsilon + \varepsilon p)^2}} \right)^6 + 3 \mu^6 \varepsilon^{\frac{33}{10}} \]
\[ = 3 \mu^6 \sum_{p=J_{jr}+1}^{\infty} \left( \frac{1}{\sqrt{B_j^2 + (k_j + p)^2}} \right)^6 + 3 \mu^6 \varepsilon^{\frac{33}{10}} \quad (2.35) \]
\[ \leq 3 \mu^6 \sum_{p=J_{jr}+1}^{\infty} \frac{1}{(B_j / \varepsilon^2 + (k_j + p)^2)^3} + 3 \mu^6 \varepsilon^{\frac{33}{10}}. \]

We define \( b_j \) by \( B_j / \varepsilon \), and \( a \) by \( A / \varepsilon = \varepsilon^{-\frac{11}{20}} \). The distance from \( P_j \) to the intersection of \( \Lambda_j^A \) with the \( x \)-axis on the right is \( \sqrt{A^2 - B_j^2} \) by the Pythagorean theorem, and holds \( J_{jr} \) atoms at a distance \( \varepsilon \) from each other. That can be translated into \( \left\lfloor \sqrt{A^2 - B_j^2} \right\rfloor = (J_{jr} + 1) \varepsilon \), or \( \left\lfloor \sqrt{a^2 - b_j^2} \right\rfloor = (J_{jr} + 1). \)

Equation (2.35) is now
\[ |\text{error6}| \leq 3 \mu^6 \sum_{p=J_{jr}+1}^{\infty} \frac{1}{(b_j^2 + p^2)^3} + 3 \mu^6 \varepsilon^{\frac{33}{10}} \]
\[ = 3 \mu^6 \sum_{p=\left\lfloor \sqrt{a^2 - b_j^2} \right\rfloor}^{\infty} \frac{1}{(b_j^2 + p^2)^3} + 3 \mu^6 \varepsilon^{\frac{33}{10}}. \quad (2.36) \]
We perform a change of variables \( q = p - \left\lfloor \sqrt{a^2 - b_j^2} \right\rfloor \), and error6 becomes

\[
|\text{error6}| \leq 3\mu^6 \sum_{q=0}^{\infty} \frac{1}{\left( b_j^2 + \left( \left\lfloor \sqrt{a^2 - b_j^2} \right\rfloor + q \right)^2 \right)^3} + 3\mu^6 \epsilon^{\frac{33}{10}}
\]

\[
\leq 3\mu^6 \sum_{q=0}^{\infty} \frac{1}{\left( b_j^2 + \left( \left\lfloor \sqrt{a^2 - b_j^2} \right\rfloor \right)^2 + 2q \left\lfloor \sqrt{a^2 - b_j^2} \right\rfloor + q^2 \right)^3} + 3\mu^6 \epsilon^{\frac{33}{10}}
\]

\[
\leq 3\mu^6 \sum_{q=0}^{\infty} \frac{1}{\left( b_j^2 + \sqrt{a^2 - b_j^2} \right)^2 + 2q \left\lfloor \sqrt{a^2 - b_j^2} \right\rfloor + q^2 \right)^3} + 3\mu^6 \epsilon^{\frac{33}{10}}
\]

\[
= 3\mu^6 \sum_{q=0}^{\infty} \frac{1}{\left( b_j^2 + \sqrt{a^2 - b_j^2} \right)^2 + 2q \left\lfloor \sqrt{a^2 - b_j^2} \right\rfloor + q^2 \right)^3} + 3\mu^6 \epsilon^{\frac{33}{10}}
\]

\[
(2.37)
\]

In this last expression, the sum can be estimated by an integral in the usual way associated with the Integral Test from Calculus. In addition, from the definition of \( a \) we conclude that \( a^{-6} = \epsilon^{\frac{33}{10}} \). Estimate (2.37) becomes

\[
|\text{error6}| \leq 3\mu^6 \int_0^{\infty} \frac{dq}{(a^2 + q^2)^3} + 6\mu^6 \epsilon^{\frac{33}{10}}.
\]

In this last expression, the sum can be estimated by an integral in the usual way associated with the Integral Test from Calculus. In addition, from the definition of \( a \) we conclude that \( a^{-6} = \epsilon^{\frac{33}{10}} \). Estimate (2.37) becomes

\[
|\text{error6}| \leq 3\mu^6 \int_0^{\infty} \frac{dq}{(a^2 + q^2)^3} + 6\mu^6 \epsilon^{\frac{33}{10}}.
\]
We apply the change of variables $q = a \tan \theta$, so $dq = a \sec^2 \theta$

\[
|\text{error6}| \leq 3\mu^6 \int_0^{\frac{\pi}{2}} \frac{a \sec^2 \theta d\theta}{(a^2 + a^2 \tan^2 \theta)^3} + 6\mu^6 \varepsilon^{\frac{33}{10}}
\]

\[
= 3\mu^6 \int_0^{\frac{\pi}{2}} \frac{a \sec^2 \theta d\theta}{(a^2 + a^2 \tan^2 \theta)^3} + 6\mu^6 \varepsilon^{\frac{33}{10}}
\]

\[
= 3\mu^6 \int_0^{\frac{\pi}{2}} \frac{\sec^2 \theta d\theta}{(\sec^2 \theta)^3} + 6\mu^6 \varepsilon^{\frac{33}{10}}
\]

\[
= \frac{3\mu^6}{a^5} \int_0^{\frac{\pi}{2}} \frac{d\theta}{\sec^4 \theta} + 6\mu^6 \varepsilon^{\frac{33}{10}}
\]

\[
= 3\mu^6 \varepsilon^{\frac{11}{4}} \int_0^{\frac{\pi}{2}} \frac{d\theta}{\sec^4 \theta} + 6\mu^6 \varepsilon^{\frac{33}{10}}
\]

\[
= O \left( \varepsilon^{\frac{11}{4}} \right) + O \left( \varepsilon^{\frac{33}{10}} \right)
\]

\[
= O \left( \varepsilon^{\frac{11}{4}} \right).
\]

We next estimate the second error of Equation (2.33),

\[
|\text{error5}| = \sum_{p=-\infty}^{-J_{j_l} - 1} g \left( \frac{r_{p,j}}{\mu \varepsilon} \right)
\]

\[
= \sum_{p=-\infty}^{-J_{j_l} - 1} g \left( \sqrt{B_j^2 + (k_j \varepsilon + \varepsilon p)^2} \right) \mu \varepsilon
\]

\[
= \sum_{p=J_{j_l} + 1}^{\infty} g \left( \sqrt{B_j^2 + (k_j \varepsilon - \varepsilon p)^2} \right) \mu \varepsilon
\]

\[
= \sum_{p=J_{j_l} + 1}^{\infty} g \left( \sqrt{B_j^2 + (-k_j \varepsilon + \varepsilon p)^2} \right) \mu \varepsilon
\]

\[
= \sum_{p=J_{j_l}}^{\infty} g \left( \sqrt{B_j^2 + (k_j \varepsilon + \varepsilon p)^2} \right) \mu \varepsilon
\]

\[
= \sum_{p=J_{j_l}}^{\infty} g \left( \sqrt{B_j^2 + (k_j \varepsilon + \varepsilon p)^2} \right)
\]

\[
\leq O \left( \varepsilon^{\frac{11}{4}} \right),
\]

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where $k'_j = 1 - k_j$ and where the final inequality in (2.39) follows from estimates similar to those of (2.35) and (2.38). \textit{error}5 is of the same size of \textit{error}6.

The equation of the van der Waals energy of the discrete system from (2.28), (2.31) and (2.33) can be written as

\[
E_w = \sum_{j=1}^{N_2} \left[ \sum_{p=-\infty}^{\infty} g \left( \frac{r_{pj}}{\mu \varepsilon} \right) + O \left( \varepsilon^\frac{11}{4} \right) \right]
\]

\[
= \sum_{j=1}^{N_2} \sum_{p=-\infty}^{\infty} g \left( \frac{r_{pj}}{\mu \varepsilon} \right) + O \left( \varepsilon^\frac{7}{4} \right)
\]

\[
\rho \sum_{j=1}^{N_2} \sum_{p=-\infty}^{\infty} g \left( \frac{\sqrt{(\lambda \varepsilon + f(x_j))^2 + (k_j \varepsilon + \varepsilon p)^2}}{\mu \varepsilon} \right)
\]

\[
\rho \sum_{j=1}^{N_2} \sum_{p=-\infty}^{\infty} g \left( \frac{\sqrt{\left( \lambda + \frac{f(x_j)}{\varepsilon} \right)^2 + (k_j + p)^2}}{\mu} \right)
\]

\[
= \sum_{j=1}^{N_2} G \left( \lambda + \frac{f(x_j)}{\varepsilon}, k_j \right),
\]

where $G$ is defined as $G \left( \lambda + \frac{f(x_j)}{\varepsilon}, k_j \right) = \sum_{p=-\infty}^{\infty} g \left( \frac{\sqrt{\left( \lambda + \frac{f(x_j)}{\varepsilon} \right)^2 + (k_j + p)^2}}{\mu} \right)$.

We will need the following lemma to pass to the continuum limit in the last summation.

\textbf{Lemma 4.} Let $l$ be the $x$-coordinate of the last atom on curve $C_2$. Then we can write

\[
\sum_{j=1}^{N_2} G \left( \lambda + \frac{f(x_j)}{\varepsilon}, k_j \right) = \frac{1}{\varepsilon} \int_0^l \sqrt{1 + (f'(x))^2} \ G \left( \lambda + \frac{f(x)}{\varepsilon}, k(x) \right) dx + O(1).
\]
Proof. Assume that
\[
\varepsilon \sum_{j=1}^{N_2} G \left( \lambda + \frac{f(x_j)}{\varepsilon}, k_j \right) = \int_0^1 \sqrt{1 + (f'(x))^2} G \left( \lambda + \frac{f(x)}{\varepsilon}, k(x) \right) dx + \text{error} \\
= \int_0^1 G \left( \lambda + \frac{f(x)}{\varepsilon}, k(x) \right) ds + \text{error}.
\] (2.41)

We can divide curve \( C_2 \) into small arcs going from one atom to the following one on the same curve. We can write
\[
\int_0^1 G \left( \lambda + \frac{f(x)}{\varepsilon}, k(x) \right) ds = \sum_{j=2}^{N_2} \int_{s_{j-1}}^{s_j} G \left( \lambda + \frac{f(x)}{\varepsilon}, k(x) \right) ds.
\] (2.42)

By the Mean Value Theorem for Integrals [31], there exists \( s_j^* \in (s_{j-1}, s_j) \) such that
\[
\int_{s_{j-1}}^{s_j} G \left( \lambda + \frac{f(x)}{\varepsilon}, k(x) \right) ds = G \left( \lambda + \frac{f(x(s_j^*))}{\varepsilon}, k(x(s_j^*)) \right) (s_j - s_{j-1}),
\]
then (2.42) can be written as
\[
\int_0^1 G \left( \lambda + \frac{f(x)}{\varepsilon}, k(x) \right) ds = \sum_{j=2}^{N_2} G \left( \lambda + \frac{f(x(s_j^*))}{\varepsilon}, k(x(s_j^*)) \right) (s_j - s_{j-1}),
\] (2.43)
and the error in (2.41) is
\[
\text{error} = \varepsilon \sum_{j=1}^{N_2} G \left( \lambda + \frac{f(x_j)}{\varepsilon}, k(x_j) \right) - \sum_{j=2}^{N_2} G \left( \lambda + \frac{f(x(s_j^*))}{\varepsilon}, k(x(s_j^*)) \right) (s_j - s_{j-1})
\]
\[
= \varepsilon G(\lambda, k) + \sum_{j=2}^{N_2} G \left( \lambda + \frac{f(x_j)}{\varepsilon}, k(x_j) \right) \varepsilon
\]
\[
- \sum_{j=2}^{N_2} G \left( \lambda + \frac{f(x(s_j^*))}{\varepsilon}, k(x(s_j^*)) \right) (s_j - s_{j-1})
\]
\[
\approx \varepsilon G(\lambda, k) + \sum_{j=2}^{N_2} \left[ G \left( \lambda + \frac{f(x_j)}{\varepsilon}, k(x_j) \right) - G \left( \lambda + \frac{f(x(s_j^*))}{\varepsilon}, k(x(s_j^*)) \right) \right] (s_j - s_{j-1}).
\] (2.44)
We note that in the interval \([s_{j-1}, s_j]\), \(k(x(s))\) remains the same to an \(o(\varepsilon)\) error,

\[ k(x(s^*_j)) = k(x(s_j)) + o(\varepsilon). \]

And we can write

\[
G \left( \lambda + \frac{f(x(s_j))}{\varepsilon}, k(x(s_j)) \right) - G \left( \lambda + \frac{f(x(s^*_j))}{\varepsilon}, k(x(s^*_j)) \right)
= G \left( \lambda + \frac{f(x(s_j))}{\varepsilon}, k(x(s_j)) \right) - G \left( \lambda + \frac{f(x(s^*_j))}{\varepsilon}, k(x(s_j)) + o(\varepsilon) \right)
= G \left( \lambda + \frac{f(x(s_j))}{\varepsilon}, k(x(s_j)) \right) - G \left( \lambda + \frac{f(x(s^*_j))}{\varepsilon}, k(x(s_j)) \right) + o(\varepsilon)
\]

and

\[
+ o(\varepsilon) \frac{d}{dk} \left[ G \left( \lambda + \frac{f(x(s^*_j))}{\varepsilon}, k(x(s_j)) \right) \right].
\]

But \(G\) is periodic in \(k\), then \(\frac{d}{dk} G \left( \lambda + \frac{f(x(s^*_j))}{\varepsilon}, k(x(s_j)) \right)\) is bounded and

\[
G \left( \lambda + \frac{f(x(s_j))}{\varepsilon}, k(x(s_j)) \right) - G \left( \lambda + \frac{f(x(s^*_j))}{\varepsilon}, k(x(s^*_j)) \right)
= G \left( \lambda + \frac{f(x(s_j))}{\varepsilon}, k(x(s_j)) \right) - G \left( \lambda + \frac{f(x(s^*_j))}{\varepsilon}, k(x(s_j)) \right) + o(\varepsilon).
\]

Since \(G\) is continuous on \([s_{j-1}, s_j]\) and differentiable on \((s_{j-1}, s_j)\), with continuous partial derivatives, then by the Mean Value Theorem [31], there exists \(\hat{s}_j \in (s^*_j, s_j)\) such that

\[
G \left( \lambda + \frac{f(x(s_j))}{\varepsilon}, k(x(s_j)) \right) - G \left( \lambda + \frac{f(x(s^*_j))}{\varepsilon}, k(x(s^*_j)) \right)
= \frac{d}{ds} \left[ G \left( \lambda + \frac{f(x(\hat{s}_j))}{\varepsilon}, k(x(\hat{s}_j)) \right) \right] (s_j - s^*_j) + o(\varepsilon).
\]

Moreover, \(\frac{d}{ds} \left[ G \left( \lambda + \frac{f(x(\hat{s}_j))}{\varepsilon}, k(x(\hat{s}_j)) \right) \right]\) is bounded, then

\[
G \left( \lambda + \frac{f(x(s_j))}{\varepsilon}, k(x(s_j)) \right) - G \left( \lambda + \frac{f(x(s^*_j))}{\varepsilon}, k(x(s^*_j)) \right) = O(\varepsilon) + o(\varepsilon) = O(\varepsilon).
\]
We use (2.8), the error from (2.44) becomes

\[
error = \varepsilon G(\lambda, k) + \sum_{j=2}^{N_2} O(\varepsilon)(s_j - s_{j-1}) = O(\varepsilon).
\] (2.49)

In (2.41), we divide by \(\varepsilon\), we end up with

\[
\sum_{j=1}^{N_2} G\left(\lambda + \frac{f(x_j)}{\varepsilon}, k(x_j)\right) = \frac{1}{\varepsilon} \int_0^1 G\left(\lambda + \frac{f(x(s))}{\varepsilon}, k(x(s))\right) ds + O(1)
\]

\[
= \frac{1}{\varepsilon} \int_0^l \sqrt{1 + (f'(x))^2} \ G\left(\lambda + \frac{f(x)}{\varepsilon}, k(x)\right) \ dx + O(1).
\] (2.50)

Note that the leading order term is of \(O(\varepsilon^{-1})\). 

Following Lemma 4, the continuum expression for the van der Waals energy in (2.40) is

\[
E_w \simeq \frac{1}{\varepsilon} \int_0^l \sqrt{1 + (f'(x))^2} \ G\left(\lambda + \frac{f(x)}{\varepsilon}, k(x)\right) \ dx.
\] (2.51)

2.5 Total continuum energy of the system

Combining the results in (2.6), (2.26), (2.27) and (2.51), the continuum model of the total effective energy of the system becomes

\[
E \simeq \varepsilon \frac{a b''(\pi)}{2} \int_0^l (f''(x))^2 \left[1 + (f'(x))^2\right]^{-\frac{3}{2}} \ dx
\]

\[
+ \frac{1}{\varepsilon} \int_0^l \sqrt{1 + (f'(x))^2} \ G\left(\lambda + \frac{f(x)}{\varepsilon}, k(x)\right) \ dx,
\] (2.52)

where \(G\left(\lambda + \frac{f(x)}{\varepsilon}, k(x)\right) = \sum_{p=-\infty}^{\infty} \frac{1}{\mu} \ g\left(\sqrt{\left(\frac{\mu}{\varepsilon} - k(x) - p\right)^2 + \left(\frac{\mu}{\varepsilon}\right)^2}\right)\),

subject to \(\int_0^l \sqrt{1 + (f'(x))^2} \ dx = 1\) and \(f(l) = 1 - m\).
The first condition comes from the length of curve $C_2$ being 1, and the second constraint is the result of holding the last atom from that chain at a height $1 - m$. Note that the bending energy term in (2.52) can be written as function of the curvature, i.e., $\varepsilon \frac{\alpha b''(\pi)}{2} \int_0^1 (\theta'(s))^2 \, ds$, as shown in (2.27).
CHAPTE III

THE EULER-LAGRANGE ODE AND NUMERICAL RESULTS

The system we model in this thesis is at equilibrium, therefore its energy is minimal. The function \( f(x) \) that describes the shape of the curve \( C_2 \) can be determined by minimizing the energy in (2.52). Recall that the first term in that expression—representing the bending energy—is of \( \mathcal{O}(\varepsilon) \), whereas the second term—representing the van der Waals interactions—is of \( \mathcal{O}(\varepsilon^{-1}) \) with an error of \( \mathcal{O}(1) \) as in (2.50). That implies that the first term has little to no impact on the equilibrium of the system, compared to the second term, or even the correction to that one. But we cannot neglect the bending energy term for the reason we discuss in the following section.

3.1 The shape of curve \( C_2 \) that minimizes the van der Waals energy

We assume that curves \( C_1 \) and \( C_2 \) are at the optimal equilibrium distance \( \lambda \varepsilon \) from each other in the zone where they are attached. Recall that at a microscale level, these curves appear as two infinite parallel chains of atoms. The lower chain is fixed. Each atom \( j \) from the upper curve experiences pushing and pulling van der Waals forces exerted by all atoms from the lower chain, trying to put that atom at an equilibrium distance. In order for that to happen, the sum of the horizontal components of these forces to the right of the atom on \( C_2 \) has to equal the sum of
the horizontal components of forces from the left side. This will happen when atom 
$j$ is in a horizontally symmetrical position with respect to the atoms on curve $C_1$.

![Diagram](image)

(a) Unstable equilibrium, $k = 0$
(b) Stable equilibrium, $k = 0.5$

Figure 3.1: Optimal $k$.

Figure 3.1 shows the two symmetrical geometries for the stacking, thus two
possible equilibrium positions. One of these positions is when atom $j$ from $C_2$ is
directly on top of one of the atoms on the bottom, i.e., $k = 0$. The other equilibrium
position is when atom $j$ is horizontally in the middle of two atoms on the bottom,
i.e., $k = 0.5$. The equilibrium in Figure 3.1.a is unstable, because atom $j$ will move
away from the equilibrium after a small horizontal disturbance, whereas it is stable in
Figure 3.1.b, because atom $j$ will always return to the equilibrium if slightly moved
horizontally from that position. We use MATLAB [23] to generate a plot (Figure 3.2)
showing that the minimum van der Waals energy is for $k = 0.5$. We assume in our
problem that the stacking in the attached zone looks like Figure 3.1.b and $k = 0.5$. 
Figure 3.2: For a fixed $\lambda$, the minimum van der Waals energy is at $k = 0.5$.

In the configuration we choose, the distance between atom $j$ on curve $C_2$ and the closest atom from curve $C_1$ is $\bar{\mu}\varepsilon$ which is slightly smaller than the van der Waals equilibrium distance $\mu\varepsilon$ between two stand-alone atoms, described in Section 2.2, due to the additional atoms on curve $C_1$ trying to pull on atom $j$. The van der Waals energy between curves $C_1$ and $C_2$ in the attached zone is at a minimum for a distance $\lambda\varepsilon$ between the two curves that is smaller than $\bar{\mu}\varepsilon$, as shown in Figure 3.3.
The van der Waals energy term in (2.52) is minimal for a function $f(x)$ such that $\lambda \varepsilon + f(x) = \lambda \varepsilon$, therefore $f(x) \equiv 0$ for the longest possible interval in $x$. The length of that interval is controlled by the constraint we impose on the last atom in chain $C_2$, to be at a fixed height $1 - m$ from the $x$-axis, allowing the curve to collapse on that axis for a distance $m$. Here we consider the $x$-axis to be the line holding the attached part of curve $C_2$. Note that the shift in this case is $k(x) \equiv k$. The shape of this van der Waals minimizing curve is given by Figure 3.4. The minimum van der Waals energy is

$$E_{\text{min}} = \frac{m}{\varepsilon} G(\lambda, k).$$

(3.1)

Figure 3.3: The general shape of $G(t, 0.5)$ for $\mu = 0.6$ showing a minimum at $t \simeq 0.33 < \mu$. We pick $\lambda = 0.33$. 
Figure 3.4: The graph of $f(x)$ that minimizes the van der Waals energy.

But this shape creates a sharp right angle at $x = m$, which is energetically expensive. Looking at the expression in (2.52), $f''(m) = \infty$ causes the bending energy to blow up. Thus we cannot neglect that term. Instead, we assume that the energy-minimizing curve slightly deviates from the curve in Figure 3.4. To describe this deviation, we consider a correction to the detached part of curve $C_2$ of the form

$$x = m + \varepsilon^w g(y),$$

instead of $x = m$. The new point of detachment is at $x = m + \varepsilon^w g(0)$. Our goal in this chapter is to calculate the parameter $w$, representing the size of the deviation of the actual curve from the one drawn in Figure 3.4, and determine how $g(y)$ perturbs the shape of $C_2$ from Figure 3.4 in order for the system to reach equilibrium. We assume that $g$ is twice differentiable so that the bending energy remains finite.
3.2 Size of the correction

In this section we find the order $w$ of the correction to the shape that minimizes the van der Waals energy. To do so, we transform the expression of the bending energy into a form that contains the parameter $w$.

Due to the large difference in the orders of magnitude for the bending and the van der Waals energies calculated in (2.52), we predict that the equilibrium shape of curve $C_2$ is close to the shape in Figure 3.4, therefore we expect $\varepsilon^w$ to be small. That implies that the correction to the function $y(x)$ is big over a small interval in $x$. In order to get a small correction to the function representing the curve $C_2$, we switch the axes of the coordinate system (Figure 3.5.a). The corrected shape of curve $C_2$ is represented in Figure 3.5.b.

(a) The shape minimizing van der Waals energy.  
(b) The shape minimizing the total energy.

Figure 3.5: The graph of $x$ as a function of $y$ without and with correction.
The bending energy from (2.52) can be written as

\[ \varepsilon \frac{ab''(\pi)}{2} \int_0^1 (\theta'(s))^2 ds. \]  \hspace{1cm} (3.3)

If we describe the curve by \( x = m + \varepsilon^w g(y) \), then

\[ ds = \left[ 1 + \left( \frac{dx}{dy} \right)^2 \right]^{\frac{1}{2}} dy = \left[ 1 + \varepsilon^{2w} (g'(y))^2 \right]^{\frac{1}{2}} dy. \]

Also, the curvature can be written as

\[ \kappa(y) = \frac{d^2 x}{dy^2} \left[ 1 + \left( \frac{dx}{dy} \right)^2 \right]^{\frac{3}{2}} \]
\[ = \varepsilon^w \frac{g''(y)}{[1 + \varepsilon^{2w} (g'(y))^2]^{\frac{3}{2}}}. \]  \hspace{1cm} (3.4)

Now we can apply the change of variables to (3.3)

\[ \int_0^1 (\theta'(s))^2 ds = \int_0^{1-m} \varepsilon^{-4w} (g''(y))^2 \left[ 1 + \frac{1}{\varepsilon^{2w} (g'(y))^2} \right]^{-\frac{5}{2}} \varepsilon^w g'(y) dy \]
\[ = \int_0^{1-m} \varepsilon^{-4w} (g''(y))^2 \varepsilon^{5w} (g'(y))^5 \left[ \varepsilon^{2w} (g'(y))^2 + 1 \right]^{-\frac{5}{2}} \varepsilon^w g'(y) dy \]
\[ = \int_0^{1-m} \varepsilon^{2w} (g''(y))^2 \left[ \varepsilon^{2w} (g'(y))^2 + 1 \right]^{-\frac{5}{2}} dy. \]  \hspace{1cm} (3.5)

We introduce two new variables \( z \) and \( h \) such that \( z = \varepsilon^{-w} y \) and \( h(z) = g(y) \). In this case

\[ dz = \varepsilon^{-w} dy, \quad g'(y) = \varepsilon^{-w} h'(z), \quad g''(y) = \varepsilon^{-2w} h''(z). \]  \hspace{1cm} (3.6)
The integral in (3.5) becomes
\[
\int_0^1 (\theta'(s))^2 \, ds = \int_0^{1-m} \varepsilon^{-2w} \varepsilon^{-4w} (h''(z))^2 \left[ (h'(z))^2 + 1 \right]^{-\frac{3}{2}} \varepsilon^w \, dz
\]

(3.7)

\[
= \varepsilon^{-w} \int_0^{1-m} (h''(z))^2 \left[ 1 + (h'(z))^2 \right]^{-\frac{3}{2}} \, dz.
\]

Since the corrected graph of \( f \) is expected to be close to the graph corresponding to the minimum van der Waals energy, then the expression can be similarly written, but replacing \( m \) by \( m + \varepsilon^w g(0) \), i.e., the energy in (3.1) becomes
\[
E = \frac{m + \varepsilon^w g(0)}{\varepsilon} G(\lambda, k).
\]

The total continuum energy derived in (2.52) can be written as
\[
E = \frac{1}{\varepsilon} G(\lambda, k) (m + \varepsilon^w g(0)) + \varepsilon \frac{\alpha b''(\pi)}{2} \int_0^1 (\theta'(s))^2 \, ds
\]

\[
= E_{\text{min}} + \varepsilon^{-1} G(\lambda, k) g(0) + \varepsilon \frac{\alpha b''(\pi)}{2} \int_0^{1-m} \varepsilon^{-w} (h''(z))^2 \left[ 1 + (h'(z))^2 \right]^{-\frac{3}{2}} \, dz
\]

\[
= E_{\text{min}} + \varepsilon^{-1} G(\lambda, k) h(0) + \varepsilon^{1-w} \frac{\alpha b''(\pi)}{2} \int_0^{1-m} (h''(z))^2 \left[ 1 + (h'(z))^2 \right]^{-\frac{3}{2}} \, dz.
\]

(3.8)

The total length of curve \( C_2 \) is 1. It consists of the length of the part attached to \( C_1 \), i.e., \( m + \varepsilon^w g(0) \), and the detached part. The element of the arc length of the detached part is
\[
ds = \left[ 1 + \left( \frac{dx}{dy} \right)^2 \right]^\frac{1}{2} \, dy,
\]
where \( x \) is defined as \( m + \varepsilon^w g(y) \). The length of \( C_2 \) is
\[
1 = m + \varepsilon^w g(0) + \int_0^{1-m} \left[ 1 + \varepsilon^{2w} (g'(y))^2 \right]^\frac{1}{2} \, dy
\]

(3.9)

\[
= m + \varepsilon^w h(0) + \varepsilon^w \int_0^{1-m} \left[ 1 + (h'(z))^2 \right]^\frac{1}{2} \, dz,
\]

which implies that
\[
h(0) + \int_0^{1-m} \left[ 1 + (h'(z))^2 \right]^\frac{1}{2} \, dz = \frac{1 - m}{\varepsilon^w} = \int_0^{1-m} \varepsilon^{-w} \, dz.
\]

(3.10)
We can write this condition on the function $h$ as

$$h(0) = \int_{0}^{1 \pm \frac{m}{w}} \left\{ 1 - \left[ 1 + (h'(z))^2 \right]^{\frac{1}{2}} \right\} dz. \quad (3.11)$$

Due to the smooth detachment of curve $C_2$ from $C_1$, the tangent line to $h$ at $z = 0$ is vertical. That means that $h'(0^+) \to \infty$. Next, we discuss how different values of $w$ can affect the energy of the system. We determine the value $w$ should have if the energy of the system is minimized.

3.2.1 Case where $w < 1$

We assume that $w < 1$. As $\varepsilon \to 0$, $\varepsilon^{w-1} \to \infty$. Inspecting (3.8), we can tell that the van der Waals energy blows up, while the bending energy is very small. This does not present a minimum energy for our problem. In addition, the upper limit of the integral in (3.11) goes to 0 as $\varepsilon \to 0$, making $h(0) \simeq 0$. Thus a sharp angle is formed. That does not represent a minimum of the energy due to the effect a sharp angle has over the bending energy. Therefore $w \geq 1$.

3.2.2 Case where $w > 1$

We assume that $w > 1$. In this case $\varepsilon^{1-w} \to \infty$ and $\frac{1 - \frac{m}{\varepsilon^w}}{\varepsilon^w} \to \infty$, as $\varepsilon \to 0$. The bending energy term in (3.8) goes to $\infty$ and the system is not at a minimum of the energy.

3.2.3 Case where $w = 1$

We set $w = 1$. As $\varepsilon \to 0$, $\frac{1 - \frac{m}{\varepsilon^w}}{\varepsilon^w} \to \infty$. The upper limits in the integrals of (3.8) and (3.11) are $\infty$. We get
\[ h(0) \simeq \int_0^\infty \left\{ 1 - \left[ 1 + (h'(z))^2 \right]^{\frac{1}{2}} \right\} dz. \quad (3.12) \]

In order for this to be integrable, then \( [1 + (h'(z))^2]^{\frac{1}{2}} \simeq 1 \) for \( z \) large. That means that \( h'(z) \to 0 \) as \( z \to \infty \).

We change the variable \( z \) in the previous equation into arclength \( \hat{s} \). \( \hat{s} = 0 \) corresponds to \( z = 0 \) and \( \hat{s} \to \infty \) as \( z \to \infty \). Let \( \psi(\hat{s}) \) be the function describing the angle made by the tangent to the graph of \( h \) with the horizontal \( z \)-axis, at the point of arclength \( \hat{s} \) (Figure 3.6). We can write (3.12) as

\[
\begin{align*}
 h(0) & \simeq \int_0^\infty \left\{ 1 - \left[ 1 + (h'(z))^2 \right]^{\frac{1}{2}} \right\} dz \\
 & = \int_0^\infty dz - \int_0^\infty \left[ 1 + (h'(z))^2 \right]^{\frac{1}{2}} dz \\
 & = \int_0^\infty \cos(\psi(\hat{s})) \, d\hat{s} - \int_0^\infty d\hat{s} \\
 & = \int_0^\infty (\cos(\psi(\hat{s})) - 1) \, d\hat{s}. \quad (3.13)
\end{align*}
\]

Figure 3.6: \( \psi(\hat{s}) \) is the angle made by the tangent to the graph of \( h(z) \).
Also \( h'(0^+) \to \infty \) and \( h'(z) \to 0 \) as \( z \to \infty \) imply that \( \psi(0) = \frac{\pi}{2} \) and \( \psi(\hat{s}) \to 0 \) as \( \hat{s} \to \infty \). We use the curvature form of the last term in (3.8). We combine it with (3.13), we get

\[
E \simeq E_{\min} + \int_0^\infty \left[ G(\lambda, k) \left( \cos \left( \psi(\hat{s}) \right) - 1 \right) + \frac{\alpha b''(\pi)}{2} \left( \psi' \right)^2 \right] d\hat{s}, \tag{3.14}
\]

subject to \( \psi(0) = \frac{\pi}{2} \) and \( \psi(\hat{s}) \to 0 \) as \( \hat{s} \to \infty \).

3.3 The Euler-Lagrange equation and shape of the correction

Now we seek functions \( \psi \) that minimize the total energy (3.14). This means minimizing the functional

\[
E_1[\psi] \simeq \int_0^\infty \left[ G(\lambda, k) \left( \cos \left( \psi(\hat{s}) \right) - 1 \right) + \frac{\alpha b''(\pi)}{2} \left( \psi' \right)^2 \right] d\hat{s}
= \int_0^\infty L(\hat{s}, \psi(\hat{s}), \psi'(\hat{s})) d\hat{s}, \tag{3.15}
\]

subject to the constraints

\[
\psi(0) = \frac{\pi}{2}, \tag{3.16}
\]

\[
\psi(\hat{s}) \to 0 \text{ as } \hat{s} \to \infty.
\]

From (3.15), we get the Euler-Lagrange equation [15]

\[
0 = \frac{\partial L}{\partial \psi} - \frac{d}{d\hat{s}} \left( \frac{\partial L}{\partial \psi'} \right)
= -G(\lambda, k) \sin(\psi) - \frac{d}{d\hat{s}} \left[ \frac{\alpha b''(\pi)}{2} \psi' \right]
= -\sin(\psi) G(\lambda, k) - \alpha b''(\pi) \psi'', \tag{3.17}
\]

or

\[
\psi'' = -\frac{G(\lambda, k)}{\alpha b''(\pi)} \sin(\psi). \tag{3.18}
\]
We multiply both sides of (3.18) by $\psi'$ and integrate, which gives

$$
\frac{1}{2} (\psi')^2 = \frac{G(\lambda, k)}{\alpha b''(\pi)} \cos(\psi) + \text{constant}
$$

(3.19)

From (3.16), as $\hat{s} \to \infty$, $\psi'(\hat{s}) \to 0$ and $\psi''(\hat{s}) \to 0$. Therefore the constant in (3.19) is equal to $-\frac{G(\lambda, k)}{\alpha b''(\pi)}$, and

$$
(\psi')^2 = 2 \frac{G(\lambda, k)}{\alpha b''(\pi)} \cos(\psi) - 2 \frac{G(\lambda, k)}{\alpha b''(\pi)}

= -4 \frac{G(\lambda, k)}{\alpha b''(\pi)} \left[ \sin^2 \frac{\psi}{2} \right].
$$

(3.20)

Note that $G(\lambda, k) < 0$ (Figure 3.3). We also use the constraint in (3.16) to conclude that $\psi$ is decreasing, thus $\psi' < 0$. We can write now

$$
\psi' = -2 \sqrt{\frac{G(\lambda, k)}{\alpha b''(\pi)}} \sin \frac{\psi}{2}.
$$

(3.21)

Then, by separation of variables

$$
\frac{d\left(\frac{\psi}{2}\right)}{\sin \frac{\psi}{2}} = -\sqrt{-\frac{G(\lambda, k)}{\alpha b''(\pi)}} d\hat{s},
$$

(3.22)

and by integrating both sides,

$$
\ln(\tan \frac{\psi}{4}) = -\sqrt{-\frac{G(\lambda, k)}{\alpha b''(\pi)}} \hat{s} + C.
$$

(3.23)

From (3.16), $\psi(0) = \frac{\pi}{2}$, then $C = \ln \left(\tan \frac{\pi}{8}\right)$, and (3.22) becomes

$$
\tan \frac{\psi}{4} = e^{-\sqrt{-\frac{G(\lambda, k)}{\alpha b''(\pi)}} \hat{s} + \ln(\tan \frac{\pi}{8})}

= e^{-\sqrt{-\frac{G(\lambda, k)}{\alpha b''(\pi)}} \hat{s}} \tan \frac{\pi}{8}.
$$

(3.24)

This leads to the solution

$$
\psi(\hat{s}) = 4 \tan^{-1} \left( \tan \frac{\pi}{8} e^{-\sqrt{-\frac{G(\lambda, k)}{\alpha b''(\pi)}} \hat{s}} \right).
$$

(3.25)
We perform a reverse change of variables using $h'(z) = \tan(\hat{s})$ and $dz = \cos(\hat{s})d\hat{s}$ (Figure 3.6) to get the ODE

$$\hat{s}' = \frac{d\hat{s}}{dz} = \frac{1}{\cos(\hat{s})}$$

$$= \frac{1}{\cos \left[ 4 \tan^{-1} \left( \tan \left( \frac{\pi}{8} \right) e^{-\sqrt{-G(\lambda,k)} b''(x)} \right) \right]}$$

subject to $\hat{s}(0) = 0$.

We use ode45 MATLAB solver [23] to solve this ODE and get $\hat{s}(z)$ numerically. We get an array of values for $z$ and the corresponding array of arclength values $\hat{s}$. Since $h(z) = \int_0^z \tan(\hat{s}(\gamma))d\gamma$, and $h(0) = \int_0^\infty (\cos(\hat{s}) - 1) d\hat{s}$, we use the numerical integration in MATLAB to create an array of values for $h$. We then revert to the variables $y$ and $g$ using $z = e^{-1}y$ and $g(y) = h(z)$.

![Graphs](attachment:graphs.png)

(a) $y$ as a function of $x$. \hspace{1cm} (b) Zooming on the detachment.

Figure 3.7: Graph of $y(x)$ for $m = 0.7$ using MATLAB.
Finally, using \( x = m + \varepsilon g(y) \), we get \( x \) as a function of \( y \). Figure 3.7 gives the shape that curve \( C_2 \) takes in order to have minimum energy. Note that at a macroscale, the detachment of curve \( C_2 \) appears close to a right angle (Figure 3.7.a), but at a smaller scale (Figure 3.7.b) we see that the curve is smooth.
CHAPTER IV

CONCLUSION

In this thesis we modeled the cross-section of the detachment of a graphene sheet from a rigid substrate. We derived a continuum expression for the energy of the system. We distinguished two main energies, the bending energy and the van der Waals energy. The bending energy tries to straighten all the bonds in the discrete system and prevent the formation of sharp angles in the continuum model. The van der Waals energy tries to keep the graphene sheet attached to the substrate, but is restricted by the boundary constraint that the edge of the graphene sheet is held at a prescribed distance from the substrate.

Our goal was to find the shape of the cross section that minimizes the total energy. After deriving an expression for the continuum energy, our approach was to follow two steps. First, we minimized the energy that has the leading term contribution to the total continuum energy—that is the van der Waals energy—while ignoring the bending energy. We sketched the shape of the curve that corresponds to this minimum. The second step was to add a correction to that shape while taking into account both the van der Waals and bending energy. We analyzed the size and shape of the correction that minimizes the total energy of the system. By solving analytically the corresponding Euler-Lagrange ODE in (3.17), and solving numeri-
cally the ODE in (3.26), we deduced that the graphene sheet will try to lay on the rigid substrate for the longest distance possible, and will detach smoothly from the substrate when the edge is held at a prescribed distance from the substrate.

Another approach that can be done is to combine both steps of energy minimizing into a single step. One could minimize both the van der Waals and bending energy in (2.52) by deriving the corresponding Euler-Lagrange ODE. By solving that ODE analytically or numerically, one can generate the shape of the cross-section of the detachment at equilibrium.
BIBLIOGRAPHY


APPENDICES
APPENDIX A

THE MATLAB CODE TO PLOT THE GRAPH OF $E_S(r)$

```matlab
%The stretching energy \( E_s = K(r-h)^2 \)

K=1e4; %K is the spring constant

r=-10:0.01:10; %r is the distance between two bonded atoms after stretching

h=1; %h is the distance between two bonded atoms if the bond is not stretched

E=K*(r-1).^2;

plot(r,E,'-')

xlabel('r', 'FontSize', 14)

ylabel('\( E_s(r) \)', 'FontSize', 14)

ylabel('E_s(r)', 'FontSize', 14)
```
APPENDIX B

THE MATLAB CODE TO PLOT THE GRAPH OF $b(\theta)$

```matlab
% Bending energy at an atom with two bonds

tht=0:0.00001:2*pi;  % tht is the angle between the two adjacent bonds

y=abs(tht-pi).^1.02./(((tht-pi).^2-4*pi^2/9).^2+1)+0.1./(pi^2-(tht-pi).^2);

plot(tht,y,'.-');
axis([-1 2*pi+0.1 0 6]);
xlabel('\theta','FontSize',15)
ylabel('b(\theta)','FontSize',15)
```
APPENDIX C

THE MATLAB CODE TO GENERATE THE PLOT OF $g(r)$

```matlab
% The Lennard Jones potential $g(r) = (1/r)^{12} - 2(1/r)^{6}$

r = 0.01:0.0001:4; % r is the nondimensional distance between two atoms

temp = 1./r;

g = temp.(12) - 2.* (temp.(6));

plot(r, g, '.-')

axis([-1.1 4 -2 10])

xlabel('r', 'FontSize', 14)

ylabel('g(r)', 'FontSize', 14)
```

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APPENDIX D

THE MATLAB CODE TO PLOT $G(t, 0.5)$

%The graph of $G(t, k)$, for $k=0.5$ fixed
m=10000;
mu=0.6; % mu is the van der Waals equilibrium distance between two atoms
k=.5; % k is the horizontal shift between two atoms from different curves
t = linspace(0,4,m);
G = zeros(m,1);
for th=1:m
    for p=-1000:1000
        temp=mu/sqrt((t(th)).^2+(k+p).^2);
        G(th) = G(th)+temp.^12-2*temp.^6;
    end
end
plot(t,G,'.-')
xlabel('t','FontSize',14)
ylabel('G(t,0.5)', 'FontSize', 14)
APPENDIX E

THE MATLAB CODE TO FIND $k$ THAT MINIMIZES THE ENERGY

% This code finds the horizontal shift $k$ that gives the smallest minimal
% van der Waals

m=101;
k = linspace(0,1,m);
Gmin_vect = zeros(m,1);
k_minG = 0;
for th=1:m
    Gmin_vect(th) = Gmin(k(th));
    if Gmin(k(th))<Gmin(k_minG)
        k_minG = k(th);
    end
end
plot(k,Gmin_vect,'LineWidth',2)
xlabel('k','FontSize',14)
ylabel('G(\lambda,k)','FontSize',14)
k_minG
APPENDIX F

THE MATLAB CODE TO PLOT $f(x)$

% The code used to plot $f(x)$
% All measures are nondimensional
clc;

alph = 1; % alph is the scaling factor of the bending energy
bdp_pi = 1; % bdp is b"(pi)
G_lamb_k = Gmin(0.5); % G_lamb_k is the minimum van der Waals energy with
% respect to k and lambda
M = sqrt(-G_lamb_k/alph/bdp_pi);

n = 100000;

e = 0.01; % e is epsilon, the distance between two bonded atoms
ylast = 0.3; % ylast is the height at which the last atom in chain C2 is held
m = 1-ylast;

zmax = ylast/e; % zmax is the value of z of the last atom on chain C2
z = linspace(0,zmax,n);

options = odeset('RelTol',1e-8,'AbsTol',1e-8);

[T,SH] = ode45(@(t,sh) rhs(t,sh,M),z,0,options);

S_HAT = SH(:,1);
P = tan(psip(S_HAT(2:end),M));

T = T(2:end);
h = cumtrapz(T,P);
Q = cos(psip(S_HAT(2:end),M))-1;
h0 = trapz(T,Q);  % h0 gives h(0)
h = h+h0;
g = h(2:end);
y = e*T(2:end);
x = m + e*g;
x_first_max = (m + e.*g(1))/e-1;
x_first = linspace(0,x(1),x_first_max);
y_first = y(1)*ones(x_first_max,1);
plot(x_first,y_first,'LineWidth',3)  % plots C2 in the attached zone
hold on
plot(x,y,'LineWidth',3)  % plots C2 in the detached zone
xlabel('x','FontSize',14)
ylabel('y','FontSize',14)

function Gmin = Gmin(k)
%function used to find the minimum energy for a specific k
m=1000;
mu=0.6;
t = linspace(0,4,m);
G = zeros(m,1);
for th=1:m
    for p=-1000:1000
        temp=mu/sqrt((t(th))^2+(k+p)^2);
        G(th) = G(th)+temp.^12-2*temp.^6;
    end
end
end

Gmin = min(G(:));
end

function rhs = rhs( t,y,k )

% rhs of the ODE to solve for arclength \( s_{\hat{\text{h}}} \)

rhs = 1/cos(psip(y,k));
end

function psip = psip( s,M )

% angle made by \( h \) as function of arclength \( s_{\hat{\text{h}}} \) and parameter \( M \)

psip = 4*atan((tan(pi/8))*exp(-M*s));
end