Abstract

In order to gain better insight on the fundamental mechanisms governing friction and adhesion at the nanoscale, this thesis examines the friction and adhesion properties and mechanisms on the atomically-thin material, graphene. First, through conducting load dependent measurements of friction on mechanical exfoliated graphene samples, the dependence of the friction behaviour on graphene as a function of number of graphene layers, sliding history, environmental humidity, and air exposure time were examined. A mechanism was proposed to fully explain these experimental observations. Secondly, the finite element method (FEM) was applied to investigate the adhesion between a nanoscale tip and graphene covering a silicon substrate. The simulations, contrary to prior experimental results, showed a slight increase in the pull-off force as layer number increased. In addition, it was revealed that the layer-dependent pull-off forces result from the increasing tip-graphene interactions. This work contributes to gaining better insight on the applications to the lubrication mechanisms of graphene.
Acknowledgments

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<tr>
<th>Symbol</th>
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<tr>
<td>$F_f$</td>
<td>Friction Force</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Coefficient of friction</td>
</tr>
<tr>
<td>$F_n$</td>
<td>Normal Force</td>
</tr>
<tr>
<td>$F_l$</td>
<td>Lateral Force</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Interfacial Shear Stress</td>
</tr>
<tr>
<td>$A$</td>
<td>Contact Area</td>
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<tr>
<td>$F_{adh}$</td>
<td>Adhesion Force</td>
</tr>
<tr>
<td>$R$</td>
<td>Sphere Radius</td>
</tr>
<tr>
<td>$W$</td>
<td>Work of Adhesion</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Surface Energy</td>
</tr>
<tr>
<td>$E_1$</td>
<td>Young’s Modulus</td>
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<tr>
<td>$K$</td>
<td>Combined Young’s Modulus</td>
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<tr>
<td>$G$</td>
<td>Shear Modulus</td>
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<tr>
<td>$v_1$</td>
<td>Poisson’s Ratio</td>
</tr>
<tr>
<td>$U$</td>
<td>Photodiode Differential Signal</td>
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<td>$S$</td>
<td>Sensitivity of Photodetector</td>
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<tr>
<td>$k_n$</td>
<td>Normal Spring Constant</td>
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<td>$k_l$</td>
<td>Cantilever’s Torsional Spring Constant</td>
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<td>$\rho_f$</td>
<td>Density</td>
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<td>$l$</td>
<td>Length</td>
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<td>Height</td>
</tr>
<tr>
<td>$w$</td>
<td>Width</td>
</tr>
<tr>
<td>$Q_n$</td>
<td>Normal Quality Factor</td>
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\(Q_t\)  
Lateral Quality Factor

\(\Gamma_i\)  
Imaginary components of Hydrodynamic Function

\(R_{e,n}\)  
Reynolds Number

\(F_{PO}\)  
Pull-off Force

\(D\)  
Separation Distance

\(H\)  
Vertical Separation Distance

\(z\)  
Vertical Distance between Tip and Graphene

\(w\)  
Vertical Distance between Graphene and Substrate

\(\kappa\)  
Zero-potential Distance

\(\varepsilon\)  
Potential Well Depth

\(\sigma\)  
Interaction Stress between a Pair of Surfaces

\(\sigma_{\text{gra-gra}}\)  
Stress between Graphene and Graphene in Pull-off Direction

\(\sigma_{\text{tip-gra}}\)  
Stress between Tip and Graphene in the Pull-off Direction

\(\sigma_{\text{gra-sub}}\)  
Stress between Graphene and Substrate in Pull-off Direction

\(\sigma_{\text{tip-sub}}\)  
Stress between Tip and Substrate in Pull-off Direction

\(F_a\)  
Additional Force

\(\theta_l\)  
Water Contact Angle during Loading

\(\theta_u\)  
Water Contact Angle during Unloading

\(\gamma_L\)  
Liquid Surface Tension

\(\tau_{\text{water-tip}}\)  
Shear Stress between Water and Tip

\(\tau_{\text{water-graphene}}\)  
Shear Stress between Water and Graphene

\(\tau_{\text{tip-graphene}}\)  
Shear Stress between Tip and Graphene
Chapter 1

Introduction and Motivation

1.1 Introduction to Tribology and Nanotribology

Tribology is a term initially coined in the 1960s [8], and refers to the scientific field encompassing the study of friction, adhesion, lubrication, and wear from a macroscopic scale and practical perspective [9]. Since tribological phenomena, which includes the study and analysis of friction, adhesion, lubrication, and wear, are widely present in our daily lives and industrial production, the study of tribology is of great economic and technological significance. However, tribological problems are often very complex, as tribology is an interdisciplinary field requiring knowledge of various disciplines including physics, chemistry, mechanical engineering, solid mechanics, materials science, rheology, applied mathematics, and reliability. Consequently, the research of the field developed very slowly and most knowledge on tribology is obtained empirically.

Fortunately, with the recent advances of nanoscale instrumentation and associated tools (especially those tip-based microscopes, e.g. atomic force microscopy (AFM)), as well as computational simulations techniques, researchers can access experimental and theoretical investigations that are well described by both techniques at these smaller scales. Developments in thesis techniques have led to the establishment of a new field, known as nanotribology. Nanotribology is a young subject focusing on the investigation of the tribological phenomena occurring at the nanoscale [10]. Most research within the field of nanotribology focuses on the single-asperity contacts between nanoscale tips and flat surfaces. The concept and rationale for studying single-asperity contacts is illustrated in Figure 1.1. The study of nanotribology avoids many complications that occur at the macroscale, and focuses on interacting interfaces at the nanoscale. Consequently nanotribology allows a better scientific understanding of the intrinsic origin and fundamental mechanisms of tribology [11].
Friction is a crucial part of tribology and its behavior at the small scale is quite different from that at the macroscale observed by naked eyes [11]. At the macroscopic scale, friction is widely known to be proportional to the normal load. The friction force linearly increases with the applied normal load is seen in Equation 1.1:

$$F_f = \mu F_n,$$

where $F_f$ denotes the friction force, $\mu$ denotes the coefficient of friction and depends on the properties of the pair of contacting materials, and $F_n$ denotes the normal load. According to the formula, neither the contact area nor the sliding velocity is involved in the determination of friction, suggesting that friction is independent of the contact area between the sliding surfaces (the apparent contact area depicted in Figure 1.1 (a)) as well as the sliding velocity. These laws are referred as the Amonton’s and Coulombs laws of friction [12]. Because they have been working well for years for friction at the macroscale, they are taught in most elementary physics and mechanics courses.

However, with the development of modern physics, it was found that the real contact area between the two sliding surfaces is much smaller than the apparent contact area observed by naked eyes [13]. In Figure 1.1, because of inherent microscopic roughness on every surface, the true
contact area consists of a number of individual tiny asperities. And it is through the deformation of these individual tiny asperities that the applied load is transferred between the two sliding bodies. Bowdon and Tabor would later re-define friction as the product of contact area and interfacial shear stress [13],

\[ F_f = \tau A, \]  

(1.2)

where \( \tau \) is the average interfacial shear stress of the contact and \( A \) is the true contact area. Equation 1.2 indicates the direct dependence of friction force on the true contact area and the interfacial shear stress. At the nanoscale, friction still increases with the normal load, but the increasing trend is nonlinear rather than linear. Furthermore, it was found subsequently that Equation 1.2 proposed by Bowdon and Tabor is consistent with the classical friction laws described by Equation 1.1 at the macroscale, as the real contact area can be shown to increase nearly linearly with load for rough surfaces [14].

1.1.2 Adhesion

Adhesion describes the attractive interactions between two surfaces or particles when the distance between the two materials is small enough, which is typically on the order of nm’s. Two macroscopic objects typically feel very low adhesion forces because the adhesion is very weak at larger separation distances. As the size of particles decreases to microscale and nanoscale dimensions, adhesion forces become significant and their effect cannot be neglected [15]. Therefore, adhesion is a crucial part of Nanotribology.

Adhesion was found to be strongly affected by the surface geometry [16]. In order to avoid the complexity coming from the surface geometry, focus is often placed on single-asperity contacts. The adhesion force existing between two contacting spheres, \( F_{adh} \), was first quantitatively estimated in the Derjaguin approximation in 1934 [17]. The formula was given by

\[ F_{adh} = -2\pi \left( \frac{R_1 R_2}{R_1 + R_2} \right) W_{12}. \]  

(1.3)
In the formula, the negative sign suggests the adhesion force acts as a tensile force for the two spheres, $R_1$ and $R_2$ denote the radii of the two spheres, and $W_{12}$ represents the work of adhesion per unit area, which can be defined as:

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12}, \quad (1.4)$$

where $\gamma_1$ and $\gamma_2$ represent the surface energy of the materials, respectively, and the $\gamma_{12}$ is the interfacial energy between the two surfaces. In the single-asperity contact, $R_1$ is the radius of the sphere tip, and $R_2$ tends to infinity $\infty$.

Subsequently, several contact mechanics theories were proposed. The pioneering work on contact mechanics was done by Hertz in the 19th century [18]. However, no adhesive forces are included in Hertz contact, and only compressive stresses within the solids are considered. Since adhesion is neglected, the Hertz theory is often not applicable for small-scale contact problems. Adhesive forces were first considered by Johnson et al. in 1971 [16], which is regarded as a huge advance. Johnson-Kendall-Roberts (JKR) theory improved the assumption of Hertz model by accounting for the adhesive forces and the associated elastic deformation. A tensile stress was introduced to the Hertzian compressive stress as a result from a short-range adhesive force [16]. The new relationship between the contact area $A$ and the applied load $L$ is seen through the equation:

$$A = \pi \frac{R^{2/3}}{K^{2/3}} \left( L + 3\pi \gamma R + (3\pi \gamma R)^2 \right)^{2/3}. \quad (1.5)$$

Here, $R$ and $K$ are the combined curvature radius and composite elastic modulus of the two contacting materials, respectively. Their definitions are:

$$R = \left( \frac{1}{R_1} + \frac{1}{R_2} \right)^{-1} \quad (1.6)$$
and

\[ K = \frac{4}{3} \left( \frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2} \right)^{-1}. \]  

(1.7)

where \( E_1 \) and \( E_2 \) are the respective Young’s modulus and \( v_1, v_2 \) are the respective Poisson ratios of the materials of the first and second spheres.

As a result, the adhesion force is given by:

\[ F_{adh,JKR} = -3 \pi \left( \frac{R_1 R_2}{R_1 + R_2} \right) W_{12}. \]  

(1.8)

The JKR theory works well for soft materials with low stiffness, but it is not suitable for solids of high elastic modulus. To address this limitation of the JKR theory, a subsequent theory called the Derjaguin-Muller-Toporov (DMT) theory was introduced specifically for rigid materials. The DMT model considers the normal load as the sum of the external applied load and a long-range total adhesive force [19]. Therefore, it can be employed between two materials with high modulus of elasticity, as well as between rigid materials [10]. The DMT area-load relation and the adhesion force-work relation are respectively given by:

\[ A = \pi \frac{R^{2/3}}{K^{2/3}} \left( F_n + 2 \pi \gamma R \right)^{2/3} \]  

(1.9)

and

\[ F_{adh,DMT} = -2 \pi \left( \frac{R_1 R_2}{R_1 + R_2} \right) W_{12}. \]  

(1.10)

The JKR and DMT theories are limiting cases of the contact mechanics behavior. The JKR theory represents the extreme case when the adhesion forces are strong and short-range, whereas the DMT theory represents the extreme case where the adhesion is very low and longer-range. Many contact situations are intermediate between these two extremes, and the transition between these two limits was well discussed [20, 21, 22, 2], as illustrated in Figure 1.2
Figure 1.2: The JKR-DMT transition. The exact dependence of contact area on load predicted by the Johnson-Kendall-Roberts (JKR) theory, Derjaguin-Muller-Toporov (DMT) theory, and an intermediate theory. Curves were plotted in dimensionless units. Negative loads represent attractive forces. The contact area predicted from Hertz model is 0 (no adhesion) when the external load is 0, while contact areas plotted from JKR, DMT, and intermediate are non-zero. Maximum adhesion predicted by the DMT theory, which is a limiting case for rigid materials is higher than the adhesion predicted by the JKR theory, which is a limiting case for highly compliant materials [2].

1.2 Graphene

Graphene is an atomically-thin two-dimensional carbon sheet with a hexagonal packed lattice structure. It is an allotrope of carbon with an $sp^2$ hybridized bonding structure with a molecular bond length of 0.142 nm [23]. The thickness of single-layer graphene is 0.34 nm. Due to its unique structure, especially long-range $\pi$-conjugation, it has many extraordinary properties, including extremely high charge carrier mobility [23], superb thermal properties [24], and high opacity that can be observed by naked eyes [25]. Due to that $sp^2$ bond has a relatively high ratio (1/3) of the strong and stable $\sigma$ bonds, it is a type of very strong bond. The high strength of these $sp^2$ bonds as well as the high density of $sp^2$ bonds in graphene have resulted graphene as the strongest material measured in nature so far [26], with the measurement of the ultimate breaking strength and Young’s
In addition to these impressive physical and mechanical properties, graphene also possesses extraordinary tribological behavior. Friction has been seen to be dramatically reduced once the sliding surface is covered by graphene sheets \[28, 6\]. Owing to its low-friction property and wear resistance abilities \[29\], graphene has been regarded as an excellent candidate for the thinnest solid lubricant \[27\]. In this thesis, a great focus will be placed on those very impressive tribological behaviors.

1.2.1 Graphene Synthesis Methods

There are many graphene synthesis methods. Those methods can be split into top-down approach and bottom-up approaches. Top-down approaches are aimed to break apart the stacked layers of graphite to yield single graphene sheets, such as mechanical exfoliation, electrochemical exfoliation, solvent-based exfoliation, exfoliation of graphene oxide, etc \[30\]. The idea of bottom-up methods is to synthesize graphene from alternative carbon-containing sources. Bottom-up methods include chemical vapor deposition (CVD), epitaxial growth on silicon carbon, etc \[31, 32\].

The various synthesis methods produce graphene with differing size and quality. Mechanical exfoliation and CVD are two of the most popular methods. Mechanical exfoliation, also known as the Scotch tape method or micro-mechanical cleavage, is the best known method of graphene synthesis, as it is the method utilized to first experimentally obtained single-layer graphene by Novoselov and Geim in 2004 \[23\], for which they later won the Nobel Prize for Physics in 2010. By repeatedly peeling off the highly ordered pyrolytic graphite (HOPG) or Kish graphite using a piece of Scotch tape, the colour of graphite becomes less or completely unreflective. The tape attaching with graphite flakes is then pressed on a substrate such as a Si/SiO\(_2\) substrate, such that graphene is deposited on the substrate. The mechanical exfoliation method has a simple procedure and a low requirement for equipment. More importantly, graphene samples obtained by this method have properties very close to theoretical predictions. Despite the fact that the size of graphene obtained
by this method is normally limited, making it difficult to produce large-area graphene, the highest quality as well as the simplest procedures and lowest costs allows mechanical exfoliation method the best option for fundamental research and characterization.

Another commonly used technique is chemical vapor deposition (CVD), where a surface catalyzed process is implemented to allow the direct growth of the graphene films on the substrate surface [33]. In this process, the substrate is placed in a heated furnace and exposed to a mixture of hydrocarbon, hydrogen, and argon. At high temperatures, the hydrocarbon decomposes and the carbon atoms were deposited on the substrate to form the graphene films [33]. The quality of the obtained graphene films are greatly impacted by parameters such as the synthesis temperature, flow rate of gases, and synthesis time. Usually Copper or Nickel substrates are used due to low carbon solubility, as only small amounts of carbon dissolve into the substrate and form single-layer or few-layer graphene on the surface [31]. The biggest advantage of CVD synthesis method is that it can routinely produce single-layer graphene at large scale. Although graphene sheets grown through CVD method normally have more defects compared to the graphene samples obtained mechanically exfoliated, CVD grown graphene has a possibility of reaching low defect densities if the process is well controlled.

1.2.2 Friction Behavior of Graphene

In addition to the excellent lubrication properties, the friction force of graphene exhibits strong dependence on a few of factors. Firstly, the friction of graphene is found to be layer-dependent. Graphene samples generated through various methods (epitaxially grown on SiC [34], mechanically exfoliated on Si/SiO$_2$ [5], and CVD grown on Cu [6]) were extensively observed to show a consistent behavior where friction decreases with increase in the number of graphene layers. This behavior is applicable for graphene sheets having no more than 4 layers [6]. Above 4 layers, the friction seen is consistent to that seen of bulk graphite. The layer-dependent behavior of friction can be explained through two fundamental mechanisms. One of the mechanisms is attributed to a variation in electron-phonon coupling [34]. By examining the properties of epitaxial graphene sup-
ported by the SiC substrate via angle-resolved photo-emission spectroscopy, it was found that the friction contrast between single-layer and bilayer results from the $e$-$ph$ coupling between phonons and electrons suppressed by the extra graphene layer [34]. 1-layer graphene films have much more $e$-$ph$ coupling than 2-layer graphene films, causing the lattice vibrations of 1-layer graphene films are more efficiently damped through the creation of more electronic excitations. However, due to the form of more electron excitation, more friction energy is dissipated in 1-layer graphene films, and therefore, 1-layer graphene films exhibits a higher friction forces. The other mechanism attributes the behavior to a change in the out-of-plane elastic modulus of the graphene film as it becomes thicker, which is also referred to as “pucker effect mechanism” [5]. This proposed mechanism describes the formation of a pucker on the graphene in front of the sliding tip due to the low out-of-plane stiffness of the 2-dimensional graphene. The size of the formed pucker decreases with larger number of graphene layers (or thickness), and a smaller pucker results in a smaller contact area between the tip and the graphene, resulting in a decrease in friction. Currently, there are more experimental and simulation results supporting the pucker mechanism. However, the two mechanisms described above have not yet reconciled and more evidence and investigation is required.

Another unique phenomenon observed on graphene is that the measured friction force is dependent on the previous sliding history between the graphene and the tip [6]. This effect results in a hysteresis between measured friction forces as load is increased and then decreased. For CVD grown graphene supported on Cu, during the unloading process, friction is always seen higher than the loading on the same graphene area [6]. Recently, this friction hysteresis behavior was verified using molecular dynamics (MD) simulations [7]. Among the different proposed mechanisms available for the explanation of the phenomenon [6, 7], the most promising mechanism indicates that the hysteresis behavior is resulted from the presence of water [7]. However, only simulation work has been conducted and further experimental verification on the influence of the water is required.

Moreover, the exposure time of graphene is also regarded as an important impacting factor on
friction. It has been observed that graphene sheets exposed to a laboratory environment for a long time experience lower friction compared with the fresh graphene [35]. A possible explanation for this phenomenon is that long exposure time in the oxidizing air environment develops stronger adhesive force between the graphene layers and substrates. Additionally, the friction of graphene is also observed to be dependent on different supporting substrates. The difference in surface energy for varying substrates, results in different adhesive levels between the substrate and its supporting graphene sheet. Those loosely-bound or suspended graphene films show similar layer dependence on the thickness, whereas this strong dependence of friction on the number of layers is absent when graphene is strongly bonded to the substrate, due to the high surface energy, such as mica [36]. Furthermore, the friction of graphene is seen to change through chemical modification with oxygen, hydrogen, or fluorine. This is attributed to the greater out-of-plane stiffness of oxidized graphene, hydrogenated graphene, and fluorinated graphene sheets [37, 38].

1.2.3 Adhesion Behaviour of Graphene

There are three distinct adhesive interactions that occur during AFM experiments on graphene: an adhesive interaction between the graphene sheets and the moving asperity or tip; an adhesive interaction between the graphene sheets and the supporting substrate; and an adhesive interaction between the interlayers. Normally, focus is placed on the adhesion between the graphene layer and the tip. This adhesive interaction has been reported to be affected by a number of factors, such as surface roughness, humidity, and aging, etc. [39, 40, 41, 42]. In terms of the influence from the humidity, the adhesion was observed to increase with a higher relative humidity environment [41]. Moreover, the tip-graphene adhesion was observed to increase as the sample was exposed to oxygen-containing environments [42]. Furthermore, the sliding history on the graphene surface can also become an important factor when the adhesive interaction between the surface and the tip exceeds the graphene interlayer interaction or the graphene/substrate adhesion [42].

Through contact area, there is one link between friction and adhesion in single asperity experiments: both adhesion and friction are observed to increase with larger contact area [43]. While
friction on graphene has been extensively observed to be layer-dependent, a recent study done by Liu et al. reveals an experimental layer-independence of adhesion on graphene produced with mechanical exfoliation method and supported on both mica and silicon substrates [42]. In their work, different from the layer-dependence of friction, indistinguishable variation on the average pull-off force was measured on different number of graphene sheets between consecutive adhesion measurements, regardless of whether the tip was sliding along the surface before separation or not [42]. This layer-independence of adhesion on graphene is not in agreement with previous expectation from friction experiments and simulations. In fact, despite those discussed findings, only a few studies have explored the adhesion behaviour of graphene, with even fewer focused on the layer-dependence of adhesion [35, 39, 44, 45, 46]. Compared to the studies on friction of graphene, results from recent studies on adhesion on graphene sheets have not produced clear trends (e.g., as a function of the number of FLG layers) and specific mechanisms governing adhesion have not yet been described [47].

1.3 Motivation and Objectives

1.3.1 Friction on Graphene

In order to achieve a wide application of graphene, a full insight of friction properties of graphene is necessary. Currently, friction studies on graphene are not well developed and leaving a number of unknown frictional properties to be explored. Therefore, further load dependence measurements of friction on graphene in different conditions were conducted. As introduced in Section 1.2.2, friction on graphene was recently suggested to be dependent on the sliding history. However, there is no mechanism that can fully explain all the friction hysteresis behaviour and more investigations are required. Since the friction hysteresis behaviour has only been observed on the monolayer CVD grown graphene through experiments [6], more friction experiments performing on graphene obtained from different synthesis methods are required to examine if this particular observation is experimentally reproducible. Furthermore, only the friction hysteresis on
monolayer has been observed, and it is necessary to investigate the friction hysteresis behaviour on few-layer graphene. Moreover, through the verification using MD simulations, the existence of water between the sliding tip and the surface of graphene was suggested to be a key reason for the observed friction hysteresis behaviour [7]. However, no experiments have been conducted to examine the influence from the great reduction in water on the friction hysteresis behaviour, and therefore humidity-dependent friction measurements are required to verify the simulation results.

There are three objectives of the experimental friction study on graphene. The first is to investigate the friction hysteresis behaviour of graphene on mechanically-exfoliated graphene sample having various numbers of layers, and specifically in regards to the dependence between friction hysteresis behaviour and the number of graphene layers. The second objective is to experimentally examine how the friction behaviour of graphene is affected by the presence/reduction of water and verify the role the humidity plays in the friction of graphene. The third objective is to gain a better insight into the fundamentals of friction and to explore more possible factors that could impact friction of graphene.

1.3.2 Adhesion on Graphene

Because both adhesion and friction in single-asperity experiments increase with larger contact area [43], it is hard to provide an explanation for the experimental observation that the adhesion on graphene is independent of the number of graphene layers [5], while friction on graphene with increasing layer thickness has been shown to be reduced [5, 34, 48]. Therefore, motivated by the aforementioned studies on graphene adhesion in Section 1.2.3, in the second part of this work, the dependence of adhesion on the number of graphene layers for a single asperity adhesion was investigated through pull-off simulations solved using finite element method (FEM). Such simulations are motivated because it allows for an exclusive investigation into the dependence of adhesion on graphene surfaces with varying numbers of layers, eliminating external factors, such as humidity, surface roughness, and aging. Moreover, continuum simulations such as those that can be solved through FEM were because relatively large-scale substrates can be included in the FEM model,
whereas other commonly used simulation tool, such as Molecular dynamics (MD) simulations, is
difficult to scale up due to the large number of degrees of freedom involved.

The first objective of the simulation work is to theoretically investigate the dependence of the
adhesion on increased layer thickness of graphene. In addition to that, adhesion behaviour be-
tween the tip and the graphene sheets is also explored, including graphene interlayer interactions,
elastic energy, and the surface energy of supporting substrate. The investigation into the behaviour
and mechanism of adhesion on graphene surface with varying layers may provide additional in-
sight into the layer dependence observed in friction. In addition, a greater understanding of the
mechanisms that affect single asperity adhesion in single and multilayer graphene may help bring
together these currently inconsistent findings.

Overall, friction and adhesion studies on atomically thin graphene are of great significance to
the basic scientific study of atomic scale tribological mechanisms. As a typical atomically-thin
2-dimensional material, the study on graphene can provide insight to other similar 2-dimensional
materials such as BN, MoS$_2$, and contributes to the understanding of the essential laws existing
in tribology. Additionally, gaining insight into the adhesion and friction behaviour of graphene is
desirable for many potential applications of graphene such as the application of coating, thin-layer
microelectromechanical (MEMS) and nanoelectromechanical (NEMS) devices [47].

1.4 Structure

There are five chapters in this thesis. Following this introductory chapter, Chapter 2 provides
a description of the detailed techniques and procedures involved in this work, and is subdivided
into two parts. The first part presents the experimental techniques and procedures involved in the
friction study of graphene in this work, including the approaches to force calibration of AFM can-
tilevers, the methods for data analysis, and the specific experimental procedures for the friction
study. The second part describes the simulation techniques and setup for the investigation of adhe-
sion on graphene, including the theoretical derivation of the interaction expressions as well as the
techniques for the FEM setup. In Chapter 3 and Chapter 4, the respective results for the experimental measurements on friction and the simulation investigation into the adhesion are presented and discussed. Lastly, conclusions and an outlook for future work are provided in Chapter 5.
Chapter 2

Experimental Techniques and Simulation Setup

This chapter is subdivided into two parts. The first part covers the experimental techniques and procedures involved in the friction study of graphene in this work: first, an introduction to atomic force microscopy (AFM), which is an important experimental tool in the field of nanotribology, followed by the approaches for force calibration of AFM cantilevers and the related data analysis involved in this work. Subsequently, experimental procedures for the friction study are presented in details. The experimentation allows the systematic study on the dependence of friction on the various parameters including sliding history, humidity, and exposure times. The experimental results are presented and discussed in Chapter 3.

The second part presents the simulation techniques and setup for the investigation of the adhesion on graphene. Firstly, the finite element modeling (FEM) method is introduced. Then, the detailed description of the proposed FEM model is provided. This includes the theoretical derivation of the interaction expressions as well as the techniques for the FEM setup. The simulation results are presented and discussed in Chapter 4.

2.1 Experimental Techniques for Friction Study on Graphene

2.1.1 Atomic Force Microscopy - An Important Experimental Tool

To gain a better understanding of the origin of friction, it is necessary to experimentally investigate the contacting interfaces at an atomic scale. The atomic force microscopy (AFM) is an important instrument tool and is widely used in the filed of nanotribology. AFM is capable of acquiring high-resolution, three-dimensional surface topographic data, as well as quantitative measurements of adhesion, applied load, and lateral friction force between the tip and the sample. In addition, it has little requirement for sample preparation, material properties, or operation
environment, and thus allows researchers to customize environments such as the temperature and
media for the study of many materials.

A schematic drawing showing the basic principle of the AFM is shown in Figure 2.1. In AFM, a nanoscale tip attached to the free end of the flexible cantilever interacts with the sample surface during scanning, causing deflection of the cantilever beam. Two different types of deflection can occurs. One is the bending deflection due to the interaction in the vertical direction and the other is the torsional deflection due to the lateral force. A laser beam is reflected off the cantilever into a position-sensitive photodiode detector. The detector is split into quadrants (quadrant A, B, C, and D), and both the bending and torsional deflection of the cantilever are captured by the photodiode detector through the change in the position of the reflected laser spot.

Figure 2.1: A schematic shows the basic principle of an AFM [3]. An integrated tip at the end of a cantilever scans across the sample, causing the cantilever to deflect. The cantilever’s bending deflection and torsional deflection are measured by a four-quadrant photodiode through the change in position of the reflected laser spot.

2.1.1.1 Contact Mode

Contact mode is applied to conduct friction measurements in this work. In this mode, the tip is moved across the surface and deflects according to its profile Figure 2.2. Unlike the other modes
such as the tapping mode where only the normal deflection of the cantilever is typically measured, the contact mode is one of the methods that allow the measurement of frictional forces.

There are two distinct modes available in contact mode: constant height mode and constant force mode. In constant height mode, the height of the scanner is fixed during scanning, and the difference between the resulting signal from the detector $U_{((B+D)-(A+C))}$ and the user-specified set point values are the information used to generate images. This mode is preferred when trying to generate atomic-resolution images for atomically flat surfaces, but it is not suitable for scanning samples with large step heights or large roughness surfaces because it requires a small variation in the surface height.

In constant force mode, the set point value, namely the total force applied, is fixed during scanning. The difference between the resulting signal from the detector and the user-specified set point values is called “error signal”. The “error signal” is used as the input in a feedback circuit, and then used to adjust the Z-height piezoelectric ceramic to ensure a constant applied force between the tip and the sample. According to the output of the feedback circuit, the topography, deflection, and friction images of the scanning area are generated.

Figure 2.2: The difference between the deflection value and the user-specified Set Point is called the “error signal”, and the “error signal” is used to adjust Z-height piezoelectric, thus controlling the spatial relationship between the tip and the sample surface. This figure is reproduced from Ref. [3].
2.1.1.2 Setup of the Environmental Chamber for Low Humidity Measurements

In this work, following the load dependence measurements in ambient environment with around 30% relative humidity, the same load dependence measurements were conducted again on the same graphene regions in a low humidity environment (0.1%). The data measured in low humidity act as a comparison to investigate the influence on friction from the presence of water at the interface. To achieve the low humidity measurement conditions, an environmental chamber providing an excellent acoustic isolation and protection from the air movement was used in conjunction with the Agilent 5500 to isolate samples for imaging in a controlled low humidity environment. By introducing dry nitrogen gas to purge the AFM isolated chamber, the humidity can be brought down to 0.1% relative humidity (RH). The simple AFM experimental setup including an environmental control chamber, a humidity sensor, gas tubes, nitrogen (99.998 % pure, class 2.2, Praxair NI 4.8 T) is shown in Figure 2.3.
As seen in Figure 2.3, eight gas ports are included as 4 gas inlets in the front and 4 gas outlets in the back of the chamber. Nitrogen is flowed into the environmental chamber from a regulated cylinder through one of the gas ports at the front of the environmental chamber. The chamber is vented into atmosphere via another gas port on the back of the environmental chamber. When purging the chamber, the flow rate of nitrogen is controlled to approximately 10 ml/s through a gas flow meter to avoid turbulence during scanning. A humidity sensor was placed in the environmental chamber to monitor the variation in the humidity value over the entire experiment. The load
dependence measurements were only performed after the chamber was stabilized at 0.1% RH no less than 15 minutes.

2.1.2 Force Calibration of AFM Cantilevers

The primary objective of AFM measurements in this study is to examine how friction forces change with varying normal load applied between the AFM tip and the sample. Therefore, it is critical to correctly determine the specific values of applied normal forces and measured friction forces. This is complicated in AFM because those signals that the AFM is able to read are in units of voltage. Consequently, conversion and calibration from analog voltage signal provided by the photodetector to the normal and friction forces are required.

All output data are based on the detected normal and lateral deflections of the cantilever. Therefore, determining the related parameters of cantilevers including geometry dimensions and spring constant is a crucial step in the force calibration. Since these parameters vary among AFM cantilevers and manufacturers only provide approximate ranges for these values, each individual cantilever must be measured. In this section, detailed procedure for the calibration of normal load and friction force is presented.

2.1.2.1 Calibration of Normal and Friction Force

As mentioned in the previous section, when the cantilever passes over the sample surface, changes in the position of the laser spot caused by the bending and twisting of the cantilever are recorded by the AFM photodiode detector.

Through sensing the laser’s movement between the four quadrants, the detector can measure the normal deflection and torsional deflection. The normal deflection is the differential signal from the photodiode $U_{(A+B)-(C+D)}$ (A, B, C, D are shown in Figure 2.1) and the torsional deflection is the differential signal from the photodiode $U_{(B+D)-(A+C)}$. While the tip is sliding along a surface, both the bending and torsional signals of the cantilever are measured, which are referred to as the applied normal load and lateral force, respectively. To determine the friction force, the difference
between the lateral forces measured while sliding forward and backward was calculated and then averaged [49]. In order to convert the output signals to forces, the Equation 2.1 and Equation 2.2 are given as

\[ F_n = k_n SU_{(A+B)-(C+S)} \]

\[ F_l = \frac{3h}{2l} k_l SU_{(B+D)-(A+C)} \]

where \( k_n \) denotes the normal spring constant of the cantilever, \( k_l \) represents the torsional spring constant of the cantilever. Both \( k_n \) and \( k_l \) are in the unit of N/m. The parameter \( S \) denotes the sensitivity of the photodetector, which is in m/V. These three parameters are discussed further in Section 2.1.2.2 and Section 2.1.2.3

2.1.2.2 Sensitivity of Photodetector

The sensitivity of the photodetector can be determined through taking Force Distance (FD) Spectroscopy measurement. Force distance (FD) spectroscopy, which is also known as the normal force versus distance curve, is one specific mechanical testing operation modes included in an AFM. It is a widely used approach in the study of nanotribology, as it can be used to determine the adhesion force between the AFM tip and the sample, determine the sensitivity of the photodetector, and obtain the deflection value corresponding zero applied load, which is also necessary for normal force calibration. During the FD spectroscopy measurement, the tip is first moved vertically towards the sample and then is moved away from the sample. A schematic curve is depicted in Figure 2.4. Specifically, in the beginning of the approaching process, the tip-sample separation is large so that the cantilever remains in an equilibrium position, thus there is no change in cantilever deflection and the curve is flat (A to B shown in Figure 2.4). In this curve, the cantilever deflection (in V) in the Y-axis can be converted to the normal force interacting between the tip and the sample using equation 2.1 . The scanner extension (in meters) in the X-axis, indicates the vertical displacement of the tip. As the tip approaches the surface further and the tip-sample separation becomes smaller, the cantilever becomes attracted by adhesive forces between the tip
and the sample. Once the attractive force overcomes cantilever’s spring stiffness, the cantilever jumps into the sample, which is shown as a sharp decrease in the measured deflection (B to C). After the tip reaches point C, the cantilever starts to be deflected upwards, as the tip continues moving down and continues contacting the sample surface under the increasing repulsive force, which results in the C-D portion on the curve. When the tip starts retracting, the degree of upwards deflection starts to decrease. Zero deflection occurs when the normal deflection returns to its equilibrium position measured when the tip was far from the surface. Due to the adhesion force from the sample, the tip and sample are still in contact when the tip continues to move upwards and during this process, cantilever starts to be deflected downwards. Consequently, the tip snaps out (F to G) because the tip-sample interaction disappears as the tip-sample separation increases further. The adhesive (negative in magnitude) interaction between the tip and surface can be measured according to the deflection height from F to G. Finally the tip returns to its equilibrium position (G to H) and cantilever recovers to its zero deflection again.

Because the difference between point F to point G gives the maximum adhesion force between the tip and sample, this process is also known as the pull-off measurement. In addition, the slope of the curve (between E and F or between C and D ) obtained when the cantilever was bent gives the sensitivity $S$ of the photodetector, and the corresponding deflection value of the flat portion on the curve is the zero deflection, which will be required for force calibration. It is assumed that the lateral sensitivity and the normal sensitivity of the photodetector are the same [50].
Figure 2.4: A typical force distance spectroscopy curve. When the tip approaches the surface, the cantilever is in an equilibrium position (A) and the curve is flat. As the tip-sample separation gets smaller to point (B), the cantilever snaps into surface at point (C) due to attraction from the sample as well as due to the higher force gradient than cantilever stiffness. Then the cantilever is pushed up to the surface and deflected upwards, which is seen as an increase in the measured force (C to D). Once the tip starts retracting, the deflection starts to decrease gradually and then passes its equilibrium position to point (E). As the tip is moved away further from the surface, it snaps in due to interaction with the surface, and the cantilever is deflected downwards (E to F). Once the tip-sample interactions are terminated due to increased distance, the tip snaps out (F to G), and returns to its equilibrium position (H) [4].

2.1.2.3 Normal Spring Constant and Lateral Spring Constant

In order to perform a force calibration on experimental probes, the experimental normal and lateral spring constants of the probe need to be determined. Due to manufacturing variability, the spring constants between individual cantilevers can vary greatly. Therefore, in order to accurately measure the normal and friction force during AFM measurements, the spring constants for each probe should be experimentally determined.

There are two different types of spring constants. One is the normal spring constant $k_n$, which can be obtained directly. The other one is the lateral spring constant $k_l$, which is usually determined indirectly through the torsional spring constant $k_t$. Two common methods available for the determination of the spring constants $k_n$ and $k_l$, the Sader method [51, 52] and the geometrical method [49, 50, 53], are discussed below.
For the Sader method, the equations used for determining the normal and torsional spring constants $k_n$ and $k_t$ for rectangular, diving-board type cantilevers are given by

$$k_n = 0.1906\rho_f b^2 l Q_n \Gamma^n_i (f_n) f_n^2,$$  

$$k_t = 0.1592\rho_f b^4 l Q_t f_t^2 \Gamma^t_i (f_t).$$

In the two equations, $\rho_f$ is the density of the medium, $b$ the cantilever width, $l$ the length. $f_n$, $f_t$ are the normal and lateral resonance frequency of the cantilever. $Q_n$, $Q_t$ are the normal and the lateral quality factor, respectively. $\Gamma^n_i$ and $\Gamma^t_i$ are the imaginary components of the hydrodynamic function, which depend on the Reynolds number (which is an important dimensionless parameter that gives a measure of the ratio of inertial forces to viscous forces for given fluid flow conditions), $\Re, n = \rho_f f_n b^2/4\eta$, and $\Re, t = \rho_f f_t b^2/4\eta$, where $\eta$ is the viscosity of the medium. Note that the values of $\rho_f$ and $\eta$ for a certain medium are constants, hence the unknowns in the two equations are $f_n$ and $Q_n$. Therefore, in the Sader method, the spring constants $k_n$ and $k_t$ can be calculated from the measurement of the cantilever resonance frequencies $f_n$ and $f_t$ and quality factors $Q_n$ and $Q_t$ in a medium.

In the second method, the spring constants of the cantilever are calculated only from its geometric dimensions and materials properties (using beam bending approximations). The equations are given by

$$k_n = \frac{E w t^3}{4 l^3},$$

$$k_t = \frac{G w t^3}{3 h^2 l},$$

where $E$ is the elastic modulus, and $G$ is the shear modulus of the cantilever material. Parameters $t$, $l$, $w$, $h$ are the cantilever thickness, cantilever length, and the cantilever width, and the height of the tip, respectively [49, 50, 53].

For both methods, the torsional spring constant $k_t$ rather than lateral spring constant $k_l$ is determined. Having the torsional spring constant $k_t$, the lateral spring constant $k_l$ can be obtained.
Based on the fact that the twisting of the cantilever occurs due to the moment from the tip at the end, the conversion between $k_t$ (in N·m) to $k_l$ (in m/N) can be achieved using the equation:

$$k_l = \frac{k_t}{h^2}$$  \hspace{1cm} (2.7)

Likewise, $h$ here represents the height of the tip. The Sader method is preferred in this work because it is the most accurate and reliable [51, 52]. The uncertainty of the results obtained using the Sader method in viscous medium conditions for the rectangular single-beam cantilevers can be as low as 5% [51].

In this work, the obtained normal spring constant $k_n$ is in the range of 0.7 to 0.9 N/m and the lateral spring constant $k_l$ is in the range of 100 to 170 N/m. Geometry dimensions are determined through the means of optical microscopy, and the resonance frequency and the quality factor can be determined by fitting the amplitude-frequency curves (which will be presented in Section 2.1.2.4). In conclusion, using the Sader method [51, 52] and the fit data, the cantilever spring constants were determined to be between in normal bending and lateral twisting, respectively.

2.1.2.4 Measurements of Cantilever Geometry Dimensions

Equation 2.2, 2.5, 2.6, 2.7 require geometric dimensions of the cantilever beam and the tip. Usually accurate dimensions for each individual cantilever are not provided in the manufacturer’s specifications, thus optical microscopy measurements were performed to experimentally determine the geometric specifications of each cantilever. Optical images for a typical cantilever are shown in Figure 2.5.
Figure 2.5: Images for a typical AFM cantilever observed using an optical microscopy. (a) shows a plan view images of the entire length of the cantilever. (b) shows a higher magnification image of (a) near the tip end of the cantilever beam. (c) shows a cross-section view of the entire length of the cantilever. (d) shows a zoomed in cross section image of the cantilever, where the tip is explicitly visible. The scale bar for (a) and (c) are 20 $\mu$m. The scale bar for (b) and (d) is 10 $\mu$m.

For the rectangular cantilevers used in this work, the width $w$, length $l$, and the height of the tip $h$ are approximately 45 - 55 $\mu$m, 445 - 455 $\mu$m, 10 - 15 $\mu$m, respectively.

It is worth mentioning that the precise geometric dimensions of cantilever thickness can be determined using the transmission electron microscopy, or by means of the relation,

$$h = \frac{2\sqrt{12}\pi}{1.875^2} \sqrt{\frac{\rho}{E}} f_n L^2$$

(2.8)

where $\rho$, $E$, $f_n$, and $L$ are the density, Young’s modulus, normal resonance frequency, and length of the tip, respectively [50].
2.1.3 Determination of Resonance frequency and Q-Factor

As seen in the Equation 2.5 and 2.6, the determination of the thermal resonances $f_n$, $f_t$ and quality factors $Q_n$, $Q_t$ are required for calculating the spring constant $k_n$ and $k_l$ of each individual cantilever used in experiments.

An AFM cantilever can be modelled as a simple harmonic oscillator that has free fluctuations in the natural thermal environment. Therefore, thermal noise analysis can be applied to obtain each cantilever’s Q-factor and resonance frequency. By acquiring the data of the normal and lateral fluctuations as a function of the frequency, the resonance frequency $f_n$, $f_t$, as well as Q-factors $Q_n$, $Q_t$ can be fitted by using the equation [50]:

$$A(f) = \frac{A_0}{\sqrt{\left(1 - \left(\frac{f}{f_0}\right)^2\right)^2 + \left(\frac{f}{f_0 Q}\right)^2}}$$

The normal and lateral signals were acquired for 1 s at 2 MHz. A fast Fourier transform (FFT) of the analogue waveform is taken yielding a band width of 1 MHz with 1 Hz spacing between the data points. 10 - 20 more subsequent measurements are acquired and a single FFT is generated through the averaging of all the spectra, in order to reduce noise. To acquire the normal and lateral signals at this high frequency, it is necessary to acquire the lateral frequency response between 150 kHz and 400 kHz. Therefore, a custom designed box was built to access these signals directly from the quadrant detector, before they are filtered by the internal electronics of the AFM.

Once the data have been acquired, fits of the thermal resonance data were performed to obtain the specific normal and lateral resonance frequencies, as well as the corresponding Q-factors. OriginPro 2016 was applied to import and analyze the acquired data. Once FFT of the cantilever deflection curves are plotted, the peaks associated with the normal and lateral thermal resonances can be identified in the graphs. Fits to the selected peaks using the Equation 2.9 are performed. The exact frequency and Q-factors can be extracted from the fits for calibration of $k_n$ and $k_l$. Figure 2.6 shows the fitted curves for the first normal resonance frequency and the first lateral resonance fre-
quency according to the measured normal and lateral frequency-amplitude curves. It is worthy 
mentioning that while the first normal resonance peak is easily identifiable, the first lateral reso-
nance peak is much less obvious. For the cantilever in Figure 2.6, the normal resonance frequency 
\( f_n \) is 17.341 kHz, Q-factor \( Q_n \) is 165, the lateral resonance frequency \( f_l \) is 277.15 kHz and Q-factor 
\( Q_l \) is 198.

![Figure 2.6](image)

Figure 2.6: Typical example for the fitted curves of the first normal resonance frequency and 
lateral resonance frequency of a silicon cantilever with native silicon oxide layer. (a) measured 
(dotted line) and fitted (red line) normal resonance peak and (b) measured (dotted line) and fitted 
(red line) lateral resonance peak.

In experimental measurements, friction data were acquired at a speed of 2 lines per second. 
The resulting imaging data were loaded and analyzed using a customized Matlab code. The normal 
force was determined in the forward scan direction by averaging the data acquired in the region of 
interest. The average friction force was then determined by subtracting the lateral force data in the 
forward direction by the data acquired in the reverse scan direction pixel by pixel. The resulting 
image was averaged and multiplied by 0.5. For both the normal force and friction force data, the 
error bars reported represent the standard deviation in the calculated mean values of the respective 
signal. Before and after each group of load dependence measurements, a force-distance curve 
was acquired to determine the deflection value corresponding zero normal force, and its associated 
drift over the course of the measurement was considered and eliminated when calculating the actual
normal force.

2.1.4 Experimental Procedures for Friction Study on Graphene

2.1.4.1 Sample Preparation

Few-layer graphene samples used in experiments were produced using mechanical exfoliation methods (also widely known as “Scotch tape” method). This synthesis method was used because it has been shown to produce samples having properties of the highest quality, and very close to theoretical predictions. Meanwhile, this method is relatively cost efficient and based on a simple procedure. Moreover, in order to study the dependence of friction of graphene on different layers, samples contain graphene regions with varying number of layers are required, which can be produced through the mechanical exfoliation technique.

The required supplies include bulk graphite (highly oriented highly oriented pyrolytic graphite (HOPG) or Kish graphite), 3M scotch tapes, Si/SiO\(_2\) wafers (525 µm ± 25 µm thick with 300 nm thermal oxide, Silicon Valley Microelectronics, Inc.), ultrasonic cleaner, chemicals including acetone, methanol, and isopropanol, as well as plastic tweezers. The Si/SiO\(_2\) wafers were placed and ultrasonically cleaned in an acetone bath to remove organic contamination. This was performed for 15 minutes. The wafers were then sonicated for 10 minutes in methanol, and finally, ultrasonic cleaning with isopropanol for another 10 minutes. It is preferable to use a dryer or a blower to dry the cleaned wafers, as this improves the evaporation of the organic solvent.

Graphene was obtained by peeling off a graphite crystal by using a piece of Scotch tape. In order to obtain single layers of graphene, the scotch tape method should usually be repeated several times until the colour of graphite is not reflective and the surface is dull. After the repetitive peeling process, the tape with dull graphite flakes were pressed onto a clean Si/SiO\(_2\) substrate by gentling pressing for several seconds. Few layer graphene films along with graphite in varying thickness and size were randomly distributed on the substrate once the tape was then torn off.
2.1.4.2 Sample Characterization

The method would result in flakes with a wide distribution in thickness and size. A simple method was applied to distinguish single-layer and few-layer flakes from other thicker flakes. This method is called optical microscopy (OM) method, which has been widely used as a convenient approach to locate and identify few-layer graphene on Si/SiO$_2$ substrates [54]. It was found that FLG graphene samples deposited on a 300 nm thick film of silicon oxide show different colour contrast depending on its thickness in a standard optical microscope, and the FLG colour contrast on the substrate is distinguishable to trained human eyes [55]. This is because that, in this trilayer system consisting of graphene, 300 nm SiO$_2$, Si layer, the phase differences when the light passes through the media as well as the reflection coefficients for different interfaces can guarantee the reflected light intensity large enough and also to be a function of a number of graphene layers [56]. The optical images of samples from mechanical exfoliation can be seen in Figure 2.7 (a).

![Figure 2.7](image)

Figure 2.7: The mechanical exfoliation method is applied to produce graphene samples. (a) Optical image of a region containing 1 to 3 layers of graphene sheets. Scale bar, 10 $\mu$m. (b) AFM topography image and (c) AFM friction image of the graphene region outlined in the red box.

After finding regions that may contain few layer graphene sheets, these regions on the sample are scanned using AFM (Keysight 5500 Atomic Force Microscope). Topography image (Figure 2.7 (b)) shows the defined thickness of single and multiple layer graphene. Having the topography images, there are two approaches confirming the precise step height of the graphene samples. One approach is to use a line profile cross a region of interest to determine the height.
A second approach is to use the roughness function to obtain a distribution of all the topographic data collected in one scan frame. The step height would correspond to the distance between peaks in the generated histogram. The height $H$ should be satisfied with $H = 0.34k$ (Unit in nm), where $k$ are the integers, which ranges in value between 1 to 4. The value of $k$ corresponds to the number of graphene layers. In this way, the accurate layer number/thickness of graphene samples can be determined.

Sample preparation was performed in ambient laboratory environment (relative humidity ranges within 20% - 40%, with a temperature of approximately 20°C - 25°C). The regions of interest are those areas having few layer graphene larger than 800 nm.

2.1.4.3 Load Dependence Measurements under Ambient Environmental Conditions

First, force distance (FD) spectroscopy was acquired prior to the load dependence measurement. The objective of taking FD curves is to acquire both the zero deflection value, as shown in Figure 2.4, and the sensitivity of the photodetector for subsequent force calibrations. The sensitivity of the photodetector can be determined by measuring the slope between points E and F (or between C and D) in Figure 2.4. Load dependence measurements were performed after obtaining the FD curve. For the load dependence measurements, friction forces were measured for the graphene area repeatedly first under incrementally increasing applied loads from zero to a predetermined maximum value, and then decreasing the applied load from the maximum value until the tip and sample were finally detached. In other words, the measurement consists of two parts: the initial loading part and the following unloading part. The applied load acting from the tip to the sample is controlled by the Set Point value; hence the loading and unloading can be achieved through changing the Set Point values. During the loading process, the Set Point value was increased incrementally from the initial deflection value by 1 volt. 1 volt is normally considered as the maximum increase in the Set Point value, since 1 volt corresponds to an increase of approximately 100 nN in the applied load and the graphene sample is likely to be worn if the applied load is raised too much. When the maximum Set Point value was reached, the unloading process
was performed by decreasing the Set Point value from the maximum in the same value increment as loading until the adhesive interaction between the tip and the graphene sample is too small to continue conducting the contact scan.

Since there exists drift in zero deflection value over the series of scanning, another FD spectroscopy should be acquired after all measurements are completed. This is to determine the change in the zero deflection value during the entire scanning process. The difference between the initial zero deflection value and the final zero deflection value was considered in the data analysis, to adjust the zero position of the normal force at every point along the measurement.

The friction measurements were performed using AFM (Agilent 5500, Agilent Technologies, Santa Clara, CA, USA) in contact mode. The experiments were performed by using a rectangular cantilever with silicon tip and native silicon oxide layer (Nanosensors, PPT-CONT-50). All the scans shared the same scan direction, sliding speed, scan size, to avoid unwanted influence and error. The images were scanned from the bottom to the top. The sliding speed during these measurements was between 2 and 4 \( \text{nm/s} \). The scan sizes for different graphene areas range from \( 1 \mu m \times 1 \mu m \) to \( 10 \mu m \times 10 \mu m \).

2.1.4.4 Load Dependence Measurements under Low Humidity Environmental Conditions

Humidity is regarded to play a crucial factor in both the magnitude of friction force and the phenomenon of friction hysteresis [7]. The general idea is to first perform the load dependence measurements in the ambient environment, and then perform the same load dependence measurements on the same graphene regions in a dry environmental condition (dry nitrogen) as a comparison. This is aimed to experimentally examine how the friction force and friction hysteresis would change in the great reduction in water in the environment.

Graphene samples were placed in the ambient laboratory air environment to conduct load dependence measurements first, and then introduced into the nitrogen-purged AFM chamber. After that, nitrogen was purged into the AFM environmental chamber. The humidity sensor was placed in the environmental chamber to monitor the variation in the humidity value over the entire exper-
iment. Once the humidity sensor read reaches 0.1% RH, the lowest value has been reached and the load dependence measurements can be conducted after the readout remains stable for over 15 minutes. During the measurements, nitrogen flow rate can be reduced, but it is necessary to keep introducing nitrogen after reaching the lowest humidity. This is because the pressure should be maintained to above atmospheric pressure in the chamber to ensure that the humidity remains as low as possible over the course of the entire experiment. After over 15 minutes exposure in nitrogen, the AFM was operated using the same parameters as in the air to conduct the load dependence measurements.

2.1.4.5 Load Dependence Measurements with Different Exposure Times

Mechanical properties of graphene have been shown to vary significantly with exposure to humid air. A previous study shows a longer exposure time of graphene sample to the air (oxygen) results in a lower friction force [35]. Additionally, even though it is still debated whether graphene is hydrophobic or hydrophilic, but the common assumption is that graphene, as with many other carbon-based materials, is hydrophobic [57]. The exposure time has a strong effect on the presence of water for hydrophobic materials, and it is reasonable to speculate that different exposure times result in different degrees of wetting of graphene. Therefore, conducting load dependence measurements on graphene samples with different exposure times is necessary to investigate the influence of exposure time on the frictional hysteresis behaviour from exposure times. Once the sample was freshly cleaved, the first group of load dependence measurement was conducted immediately within the same day (the exposure time varied from 1 hour to 4 hours). More load dependence measurements were performed on the sample after 2 days, 4 days, and 6 days. During the period, the sample was placed in the lab air condition.

2.1.4.6 Repeatability

All experimental load dependence measurements were conducted with three different AFM tips. Each measurement was conducted on a new graphene sample. Only one respective measurement is shown within this thesis in the subsequent chapters. Although the exact magnitude of the
friction forces vary between the measurements, as a result of tip size and chemistry of the tip apex at the moment of scanning, comparable variances between the Si/SiO\(_2\) substrate and various layers of graphene can be observed. Thus, discussion of the results could be limited to interpreting those variance.

2.2 Simulation Techniques for Adhesion Study on Graphene

2.2.1 Simulations Using Finite Element Method (FEM)

Finite Element Method (FEM) is a method based on the finite element analysis (FEA). The FEA is a powerful computational numerical approach to provide approximate solutions for complex problems. The term finite element was initially introduced by Turner et al. in 1956 [58]. It was originally applied to solve engineering problems such as stress analysis, fluid flow, and heat transfer. Then it has also become an increasingly important tool in the modeling, predicting, and verifying the physical and mechanics phenomena in the research study at the nanoscale.

The basic idea of the FEA is that the domain (which is a continuum structure with a known boundary) can be divided or discretized by a finite number of elements, and these elements are connected at their nodes and along the interelement boundaries. The collection of elements and nodes is called mesh. For each element, the element matrix is developed. These element matrices which are also referred to as the interpolation functions, are defined in terms of the values of the field variables at specific nodes. Through the shared degree of freedom (DOF) for adjacent elements at connecting nodes, the interpolation functions for each element are assembled together to obtain the global system of equations for the entire domain, which can be cast into Equation 2.10. Finally, imposing the boundary conditions to the global matrix and the solution of equations can be obtained:

\[ Ku = F, \]  

where \( K \) is the system stiffness matrix, which is the property of the system, \( u \) is the vector of the
node of displacements, which corresponds to the unknowns of the system, and $F$ is the vector of the nodal forces equivalent to the external forces.

2.2.2 ABAQUS

Most commercial FEM software packages originated in the 1970s. Nowadays there are a number of commercial FEA software available, such as Abaqus, Ansys, Adina, etc. Abaqus is selected as the software used in this work. With the use of (computer aided engineering) CAE software, the software packages can solve problems more quickly because they helps building the model and post-processing the results.

Abaqus is a commercial finite element package developed by Dassault Systems. It is extensively used in both academia and industry to model a wide variety of problems, especially in the deformation and stress analysis of solids. In addition to its wide variety of constitutive models, another key feature is that it provides an interface where users can write their own user-defined subroutines according to their specific cases. This feature significantly widens the application of the FEM. For instance, the nanoscale system investigated in this work is non-continuum and there always exists gaps between bodies, and thus it cannot be described by the conventional continuum approach in-built in Abaqus to describe the contact mechanics between two deformable bodies. However, by means of the user subroutine VUINTER, one can define customized contact constitutive behaviour across the interface between two surfaces if they are not in contact.

Abaqus/Standard and Abaqus/Explicit are two main solvers of Abaqus. Abaqus/Standard employs solution technology ideal for static and low-speed dynamic events where highly accurate stress solutions are critically important, while Abaqus/Explicit is a finite element analysis solver that is particularly well-suited to simulate brief transient dynamics. The ability of Abaqus/Explicit to effectively handle severely nonlinear behaviour such as contact makes it very attractive for the simulation of many quasi-static events. Both Abaqus/Standard and Abaqus/Explicit are supported within the Abaqus/CAE modeling environment for all common pre- and post-processing needs [59].
2.2.3 Model Description

The FEM used in this study mimics adhesion measurements performed in AFM experiments [5, 60, 61]. The FEM model was created using Abaqus/Explicit assuming quasi-static analysis. The FEM and associated subroutine were chosen because the dynamic explicit method is particularly well-suited for analyzing complex contact interactions with possible instability events. The quasi-static loading assumption eliminates the inertial effects result from the dynamic adhesion measurements that are simulated. In our simulation, the quasi-static analysis was achieved by giving the displacement of the tip a very small time increment (which is 0.001 nm/s), so that the kinetic energy of the deforming parts does not exceed 5% of their internal energy throughout most of the process.

We have chosen to model mechanically exfoliated graphene that is supported by a silicon oxide substrate as depicted in Figure 2.8, similar to Refs. [60, 61]. In this model, a rigid tip, half-sphere with a radius of 15 nm is pressed into graphene sheets that are supported by a silicon-oxide substrate. All simulations are conducted in displacement control.

The simulation is performed in three steps. First, the tip approaches the surface vertically with a speed of 0.001 nm/s. In this step, the distance between the tip and the top-most graphene layer decreases from 1.28 nm to 0.28 nm. This first step allows the tip to directly contact the top-most graphene layer and apply a small compressive preload with a value of $F_{\text{tip}}$ (positive values represents compressive load while negative values represents attractive load). In step two, the tip is held at this compressive preload for 50 s. Finally, step three involves withdrawing the tip from the graphene surface in the vertical direction at the same 0.001 nm/s speed. As the tip is withdrawn, the distance between the tip and the topmost graphene layer increases, leading to a reduction in the normal force $F_{\text{tip}}$. Negative values of $F_{\text{tip}}$ indicates attractive/adhesive forces. The maximum attractive force recorded during step three is referred to as the pull-off force, $F_{\text{PO}}$.

In order to improve the computational efficiency, an axis symmetric model was used. The graphene sheets and silicon oxide substrate part were modelled using shell elements SAX1 and
solid elements CAX4R, respectively. An axis symmetric diagram of the model and the boundary conditions used are shown in Figure 2.8 (A). The number of graphene layers (two are shown in Figure 2.8 (A)) were varied from 1 to 4 layers to determine the impact of the number of graphene layers on $F_{PO}$. Translational motion along the $x$-axis and rotational motion around the $y$-axis were constrained. Translational motion along the $y$-direction for the bottom of the substrate was also constrained. The tip only has one degree of freedom in the $z$-direction and its motion was controlled through the parameter $u_z$.

![Diagram of the model](image)

Figure 2.8: Graphical depiction of the two FEM models. A rigid, silicon half-sphere is pressed against the graphene sheets and elastic, silicon substrate through a displacement controlled loading. Dotted line indicates the axisymmetric axis of the model. The graphene sheets and the elastic substrate extend 200 nm laterally from the symmetry axis. (a) A graphical depiction of the graphene sheets in configuration 1, where the graphene sheets are treated as discrete layers that are allowed to slide against each other with zero friction. (b) A graphical depiction of the graphene sheets in configuration 2, where the graphene sheets are modeled as a continuum plate. In both configurations, a hemispherical tip is built for geometry modeling, allowing the separation between the tip atom and the graphene atom “$-h$” varies along different positions on the tip surface. Although the expressions for interaction stresses were calculated assuming the tip had a cylindrical geometry, the impact on the actual interactions is negligible.

Adhesive forces in the simulation were modelled with van der Waals interactions. These forces...
arise from four interactions: tip/graphene, graphene/graphene, graphene/substrate, and tip/substrate. The determination of these forces is depicted in Figure 2.11. The interface interaction forces deduced from van der Waals interactions are implemented in Abaqus using the subroutine VUINTER. The magnitude of these interaction forces are determined using the Lennard-Jones (L-J) potential. The general form of the L-J potential function between a pair of atoms or molecules is

\[
V(D) = 4\varepsilon \kappa^6 \left( \frac{\kappa^6}{D^{12}} - \frac{1}{D^6} \right).
\]  

(2.11)

Given the interaction potential, \(V(D)\), above, the L-J force function, \(P(D)\), is then

\[
P(D) = -\frac{\partial V(D)}{\partial D} = 24\varepsilon \kappa^6 \left( \frac{2\kappa^6}{D^{13}} - \frac{1}{D^7} \right).
\]

(2.12)

To determine the force in the \(y\) or vertical direction, \(F(D)\), the projection of \(P(D)\) on the \(y\)-axis is

\[
F(D) = P(D) \cdot \cos \theta = 24\varepsilon \kappa^6 H \left( \frac{2\kappa^6}{D^{14}} - \frac{1}{D^8} \right).
\]

(2.13)

where \(D\) is the separation distance, \(\theta\) is the projection angle, \(H\) is the separation distance in vertical direction. \(\kappa\) is the zero-potential distance, and \(\varepsilon\) is the depth of the potential well.

The subroutine VUINTER, used to calculate the adhesive interaction forces, requires the expressions of the interaction stress between a pair of surfaces, \(\sigma_{\text{cohesive}}\). Therefore, the vertical interaction force per unit area (dA) subjected from L-J potential between a pair of bodies must be calculated. First, the total vertical interaction force between the tip and graphene is:

\[
\sigma_{g-t} = 2\pi \rho_g \rho_t \int_0^{+\infty} \int_0^{+\infty} F(D) r dr dz,
\]

(2.14)

\[
D = \sqrt{r^2 + H^2},
\]

(2.15)

\[
H = z - h,
\]

(2.16)

where \(z\) is the vertical distance between an arbitrary horizontal plane in the tip and the upper surface.
of graphene, $-h$ is the vertical distance between two bodies. The negative sign before $h$ indicates a gap while a positive value is used to indicate a penetration. Because the force decreases extremely rapid with distance, the integrals $dr$ and $du$ go from 0 to infinity instead of a specific number for convenience, and furthermore, evaluating the integral on semi-space is equivalent to evaluating it over a parallelepiped. A graphical depiction showing the determination of 4 types of interactions is given in Figure 2.9 (a).

Similarly, the vertical interaction stress between the graphene and substrate is given by:

\[
\sigma_{g-s} = 2\pi \rho_g \rho_s \int_0^{+\infty} \int_0^{+\infty} F(D) r dr dw, \tag{2.17}
\]

\[
D = \sqrt{r^2 + H^2}, \tag{2.18}
\]

\[
H = -h + w. \tag{2.19}
\]
where \( w \) is the vertical distance between the lower surface of graphene and an arbitrary horizontal level in the substrate.

For a pair of graphene sheets, the vertical interaction stress is given by:

\[
\sigma_{g-g} = 2\pi \rho_g^2 \int_0^{+\infty} F(D) r dr, \quad (2.20)
\]

\[
D = \sqrt{r^2 + h^2}, \quad (2.21)
\]

\[
H = -h. \quad (2.22)
\]

For the vertical interaction stress between tip and substrate:

\[
\sigma_{t-s} = 2\pi \rho_s^2 \int_0^{+\infty} \int_0^{+\infty} \int_0^{+\infty} F(D) r dr dw dz, \quad (2.23)
\]

\[
D = \sqrt{r^2 + H^2}, \quad (2.24)
\]

\[
H = z - h + w. \quad (2.25)
\]

In all of the previous equations, \( \rho_g \) is the surface density of carbon atoms in graphene, \( \rho_{s-body} \) is the volume density of silicon oxide atoms in the substrate and tip. In the body-to-body interactions, we have neglected any induced curvature from the tip in the calculation of adhesive forces. A graphical representation of the variables used in these equations is shown in Figures 2.9 (A-D).

Furthermore, the stresses at the interfaces are expressed as follows:

\[
\sigma_{g-g} = 8\pi \rho_g^2 \varepsilon_{c-c} \kappa_{c-c}^6 \left( -\frac{\varepsilon_{g-g}^6}{h^{11}} + \frac{1}{h^5} \right), \quad (2.26)
\]

\[
\sigma_{g-t} = 4\pi \rho_g \rho_t \varepsilon_{g-t} \kappa_{g-t}^6 \left( -\frac{\varepsilon_{g-t}^6}{5h^{10}} + \frac{1}{2h^4} \right), \quad (2.27)
\]

\[
\sigma_{g-s} = 4\pi \rho_g \rho_s \varepsilon_{g-s} \kappa_{g-s}^6 \left( -\frac{\varepsilon_{g-s}^6}{5h^{10}} + \frac{1}{2h^4} \right), \quad (2.28)
\]

\[
\sigma_{t-s} = 4\pi \rho_t \rho_s \varepsilon_{t-s} \kappa_{t-s}^6 \left( -\frac{\varepsilon_{t-s}^6}{45h^9} + \frac{1}{6h^3} \right). \quad (2.29)
\]
For the material systems used in the simulations, the attractive force potential depth ($\varepsilon$) between graphene atoms and graphene atoms $\varepsilon_{g-g}$ is $4.544 \times 10^{-22}$ J ($4.544 \times 10^{-4}$ nN·nm). Potential depth between graphene atoms - tip atoms $\varepsilon_{g-t}$ and graphene atoms - substrate atoms $\varepsilon_{g-s}$ are equal, which is the potential depth between carbon and $\text{SiO}_2$, $1.659 \times 10^{-21}$ J ($1.659 \times 10^{-3}$ nm). The potential depth between tip atoms and substrate atoms $\varepsilon_{t-s}$ is $3.36 \times 10^{-22}$ J ($3.36 \times 10^{-4}$ nm) [62, 63]. The zero potential distance $\kappa_{g-g}$ is 0.34 nm, $\kappa_{g-t}$ and $\kappa_{g-s}$ is 0.31 nm, and $\kappa_{t-s}$ is 0.327 nm [62, 63]. The number of density of atoms for graphene $\rho_g$, tip $\rho_t$, and substrate $\rho_s$ is 36.6 atoms/nm$^2$, 26.56 atoms/nm$^3$, and 26.56 atoms/nm$^3$, respectively.

In both configurations, a hemispherical tip is built in geometry modeling (as shown in Figure 2.8), allowing the separation between the tip atom and the graphene atom “$-h$” varies along different positions on the tip surface. When deriving the expressions of the interaction stresses, the tip was simplified as a cylinder. According to equations 2.26 - 2.29, this simplification to the shape of tip is accurate, because stresses are functions of the term, $-h^x$, which is $x - th$ power of $h$ ($x \geq 9$). As a result, the impact on the actual interactions from the difference caused by the shape of tip would be extremely slight, compared to the influence from the change in $-h$. Therefore, the interaction stresses/forces calculations are accurate, as long as the accuracy of $-h$ is guaranteed.

Deformations in the graphene sheets and substrate are assumed to be purely elastic. Given the thickness of a typical native oxide of $\sim 200$ nm [64], we assume deformations are localized to the oxide, rather than the underlying crystalline silicon in the substrate. Therefore, we have performed the FEM simulations using the elastic properties of $\text{SiO}_2$ in the substrate, which are 60 GPa and a Poisson ratio of 0.3 [65]. The deformation properties of the graphene sheets are more complex. The application of continuum mechanics theory to this study of single layer graphene sheets requires careful choice of the Young’s modulus, Poisson’s ratio, and film thickness when considering out-of-plane deformations and in-plane stretching stiffnesses [66]. Several studies have quoted tensile, in-plane stretching elastic moduli of 1 TPa [67, 68] and a Poisson’s ratio of 0.186 [68]. However, the out-of-plane bending of graphene is more relevant in this study, given
recent reports of the influence of out-of-plane bending of the graphene sheets on friction [69].
We have chosen the Young’s modulus of graphene to be 5.5 TPa, a Poisson’s ratio of 0.19, and a
graphene sheet thickness of 0.066 nm using the criterion to match out-of-plane bending stiffness
determined by Yakobson et al [66]. The distance between successive graphene sheets or planes
was then set to 0.34 nm [70].

The simulations are performed in two configurations, referred to later in the results section as
configuration 1 and configuration 2, as shown in Figure 2.8 (a) and (b), respectively. In configu-
ration 1, we have assumed no friction between the graphene layers. This assumption allows the
graphene layers to freely slide laterally with respect to each other without constraint other than
discrete, adhesive interactions between the individual layers that keep them bound during pull-off
experiments

In configuration 2, the graphene layers are totally constrained to each other, and the graphene
sheets are modelled as a completely continuum elastic material. With this assumption, rather than
having individual layers of graphene, we assume a bulk solid between the tip and substrate. The
continuum solid has the same mechanical properties of graphene, the same interactions between
graphene and tip, the same interactions between graphene and substrate, and the same interactions
between tip and substrate. However, the continuum solid has no L-J interactions between graphene
sheets in this configuration. Therefore, only three interactions are calculated with an increasing
number of graphene layers. These equations are:

\[
\sigma_{i(g-t)} = \sum_{i=1}^{4} 4\pi \rho_g \rho_t \varepsilon_{g-t} k_{g-t}^6 \left( -\frac{k_{g-t}^6}{5(-h+d(i-1))^6} + \frac{1}{2(-h+d(i-1))^4} \right)
\] (2.30)

\[
\sigma_{i(g-s)} = \sum_{i=1}^{4} 4\pi \rho_g \rho_s \varepsilon_{g-s} k_{g-s}^6 \left( -\frac{k_{g-s}^6}{5(-h+d(i-1))^6} + \frac{1}{2(-h+d(i-1))^4} \right)
\] (2.31)

\[
\sigma_{i(t-s)} = 4\pi \rho_t \rho_s \varepsilon_{t-s} k_{t-s}^6 \left( -\frac{k_{t-s}^6}{45h^9} + \frac{1}{6h^3} \right)
\] (2.32)

where \( i \) denotes the number of graphene layers (ranging from 1 to 4), and \( d \) denotes the distance
between the carbon atoms in two adjacent layers, which is 0.34 nm. A change in the number of
layers of graphene is realized by increasing the thickness of this graphene solid between the tip and the silicon substrate. With these two configurations, we believe to have captured the two extreme cases experienced by graphene sheets in adhesion measurements.
Chapter 3

Friction Properties of Few-Layer Graphene

This chapter presents experimental results on friction properties of few-layer graphene (FLG). The objective of this chapter is to gain a better insight into the friction dependence of graphene, as well as the possible underlying mechanisms. This chapter begins with an introduction to previous friction studies on graphene. Subsequently, experimental results on the dependence of friction on the number of graphene layers, sliding history, environmental humidity, and air exposure time are presented. Lastly, the discussion of the experimental results is provided.

3.1 Experimental Results

3.1.1 Layer-dependence of Friction on Graphene

Figure 3.1 shows a plot of the average friction force as a function of normal force for a Si/SiO$_2$ supported graphene region. Figure 3.1 (a) shows a typical topographic image of a 2.5 µm by 2.5 µm mechanically exfoliated graphene sample, covering on an Si/SiO$_2$ substrate. AFM identification indicates that this area contains graphene of different number of layers, varying from 1 to 4. Figure 3.1 (b) is the friction force image of the surface under the maximum normal force (54 nN) during the measurement. In the image, the darker region indicates lower friction, corresponding to the graphene films covering region. The exposed area of the substrate showing a brighter colour at the top right corner of the image exhibits a higher friction. Compared to the topographic image, the colour changes at edges of graphene regions can be observed in the friction force image more clearly.

Load dependence measurements of friction were conducted on this area. Magnitudes of friction forces on the scan area can be quantified according to the forward and backward traces. As mentioned in Chapter 2, the average of the difference between the forward lateral force and the
Figure 3.1: (a) A topographic image of a sample area containing four graphene films having different number of layers. The sample was prepared using mechanical exfoliation. (b) A friction force image (under the normal force of 54 nN) of the same area shown in figure (a). Friction image (b) clearly shows the boundaries of different graphene regions. (c) Friction force as a function of normal force for different number of graphene layers, including 1-layer (black), 2-layer (red), 3-layer (green), and 4-layer (blue) graphene films. The linear fit for each curve is denoted as the dashed line. (d) The comparison between the friction measured on Si/SiO₂ substrate (purple) and on the single layer graphene.
backward lateral force gives the friction force. It is important to have multiple graphene films simultaneously contained in the one scan image, so that the other factors that could possibly influence the measurement of friction, such as tip dimensions, scan speed, and experimental environment, were kept constant in one of any images. Figure 3.1 (c) shows the curves of friction force versus normal force for graphene having different number of layers. 1-Layer graphene film was seen to have significantly higher friction forces than other multilayer graphene films. A monotonic decrease in friction force was observed for the increase in the number of graphene layers from 1 to 4. This unique phenomenon been previously seen in Ref. [5], and was referred as the friction layer-dependent characteristic of graphene.

Another observation is the variation of the coefficient of friction for different number of graphene layers. If these curves of friction versus normal force are regarded to be linear, a linear fit is performed for all the 4 curves in Figure 3.1 (c) and the obtained slopes for the 1-layer, 2-layer, 3-layer and 4-layer are 0.11, 0.05, 0.04 and 0.04, respectively. An increase in the coefficient of friction was seen with decreasing number of graphene layers. Compared with the prominent difference in coefficient of friction between 1-layer and multilayer, the variation between 2-layer, 3-layer, and 4-layer is relatively small. The explanation for this behaviour is discussed in the section afterward.

Figure 3.1 (d) shows the comparison between the friction measured on Si/SiO$_2$ substrate and the friction measured on Si/SiO$_2$ substrate covered by a single layer graphene. Compared to the friction on Si/SiO$_2$ substrate, the friction on graphene covering region is significantly low. As the normal load increases from 0 nN to 54 nN, friction on the Si/SiO$_2$ substrate increases from approximately 5 nN to the 11 nN, while the maximum friction force on the 1-layer graphene is less than 2 nN, which is 5 times lower. Because friction is substantially reduced as the substrate is covered by a graphene film, the lubricating property of graphene as a solid dry lubricant is well supported [34].
3.1.2 Friction Hysteresis on Mechanically Exfoliated FLG Supported on Si/SiO$_2$ Substrate

Figure 3.2 shows the load dependence curves of friction obtained from 3 different graphene samples. Sample 1 contains two graphene films which are respectively 1-layer and 2-layer; sample 2 contains three graphene films which are respectively 1-layer, 2-layer, and 3-layer; sample 3 contains four graphene films, which are respectively 1-layer, 2-layer, 3-layer, and 4-layer. Figure 3.2 (a) and (b) are the topographic and friction force images for the three samples, respectively. Figure 3.2 (c) are the curves of friction force versus normal force plotted from the load dependence measurements. Three load dependence measurements were performed in the ambient laboratory condition using three different AFM cantilevers. Friction forces measured on graphene films with different number of layers share the same phenomenon, showing the friction force during the unloading process is larger than that during the loading process under the same normal load. As shown in the Figure 3.2 (d), the load dependence curve of friction for the supporting Si/SiO$_2$ substrate was plotted. Similar to FLG films, Si/SiO$_2$ substrate also exhibits a friction hysteresis between loading and unloading. In addition to CVD copper-supported 1-layer graphene, the friction hysteresis is also observed on few layer (within 4 layer) mechanically exfoliated Si/SiO$_2$ supported graphene as well as the Si/SiO$_2$ substrate, suggesting that friction hysteresis is more likely to be a common behaviour extensively shared by a variety of materials in the ambient environment.

The second observation from the friction load dependence measurements of friction (Figure 3.2 (c)) is that the thickness of graphene has no strong impact on the friction hysteresis behaviour. This is concluded by comparing the magnitude of hysteresis (the difference in hysteresis between the loading curve and the unloading curve) between different graphene regions having different layers. According to the graphene hysteresis curves shown in Figure 3.2 (c) (sample 1 - sample 3), the magnitude of friction hysteresis does not vary significantly for graphene film with different number of layers. However, a noticeable larger hysteresis on the Si/SiO$_2$ substrate than the graphene hysteresis is observed. This observation indicates that the magnitude of friction hysteresis is independent of the thickness of one material but varied from different materials.
Figure 3.2: (a) Topographic images of graphene samples containing (from left to right) 1 to 2 layers (sample 1), 1 to 3 layers (sample 2), and 1 to 4 layers (sample 3). (b) Friction images scanned by AFM on the same areas. Samples are supported by the Si/SiO$_2$ substrate. 1L, 2L, 3L, 4L indicate graphene with thickness of one, two, three, and four layers. (c) Load dependence curves for different number of graphene layers in the same scan areas. Films having the same thickness are represented in the same colour (1-layer: black, 2-layer: red, 3-layer: green, 4-layer: blue) for both loading curves (hollow) and unloading curves (solid). (d) Load dependence curves of the Si/SiO$_2$ substrate (violet) are added in the friction force versus normal load curves.
3.1.3 Environmental Humidity Influence on Friction

Figure 3.3 summarizes the results acquired from load dependence measurements under different humidity conditions on an area of $4 \mu m \times 4 \mu m$ containing both 1-layer and 3-layer graphene films. Measurements were first conducted under the ambient condition with relative humidity (RH) at 24% and then followed by moving the sample to an nitrogen-purged environment condition at 0.1% RH. The condition with relative humidity at 0.1% can be regarded as an extremely dry environment, almost free of water.

3.1.3.1 Humidity Influence on Magnitude of Friction Force

Figure 3.3 (a) and (b) are the respective topographic and friction force images (normal force $= 85$ nN) of a sample. Figure 3.3 (c) shows the friction force as a function of the normal load during loading and unloading under two different humidity conditions for both 1-layer and 3-layer graphene films. For both graphene films, friction forces are remarkably higher in the ambient environment at 24% RH than those in an extremely dry environment at 0.1% RH. A comparison between the results obtained under the two humidity conditions is presented in Figure 3.3 (c). Under 24% RH condition, as the normal load changes within the range from 0 nN to 90 nN, the measured friction force varies from 0.35 nN to 0.7 nN for 1-layer graphene and from 0.3 nN to 0.5 nN for 3-layer graphene. However, under the same range of normal loads, the measured friction at 0.1% RH for the two graphene films varies around 0 nN and 0.1 nN, respectively. As expected, friction forces monotonically increase with increasing normal force at 0.1% RH. However, it is worthy noting that 1-layer graphene shows negative friction forces as the normal force is less than 30 nN, and that friction forces on the 3-layer graphene were calculated to be negative even when the maximum normal load of 90 nN is applied.

3.1.3.2 Humidity Influence on Layer-dependence of Friction

As shown in Figures 3.3 (c) and (d), under the condition of 0.1% RH, the friction measured on 1-layer graphene is larger than that on 3-layer graphene. Combined with the previous observation
Figure 3.3: Friction force versus normal load curves for the sample in different humidity conditions. Figures (a) and (b) are the topographic and friction force images of the sample (under 85 nN), respectively. 1L and 3L denote 1-layer and 3-layer graphene films, respectively. Boundaries of graphene films are outlined with white lines. Figure (c) shows the load dependence of friction on the area containing loading (solid) and unloading (hollow) for 1-layer (square) and 3-layer (circle) graphene films in ambient environment with relative humidity at 24% (black) and under an extremely dry condition with 0.1% relative humidity (blue). Figure (d) exclusively presents the load dependence of friction in the extremely dry condition with relative humidity at 0.1%. Two tests were performed continuously on the same area. Test 1 (blue) was followed by test 2 (red) without withdrawing the tip. Figure (e) compares the load dependence of friction on Si/SiO₂ substrate under the condition with 24% RH (black) and 0.1% RH (blue).
presented in Section 3.1.1, it was suggested that friction forces measured on graphene decrease as the number of graphene layers increases under both ambient humidity and extremely dry conditions. Therefore, the conclusion can be drawn that the mechanism for the layer-dependent property of graphene is independent from water, and that the characteristic is not affected by the great reduction in water.

3.1.3.3 Humidity Influence on Hysteresis Behaviour

Figure 3.3 (c) - (e) shows that humidity has a strong impact on the layer-dependent friction hysteresis behaviour. As shown in the figures, the normal load versus friction force curve for loading is significantly higher than the curve for unloading in the 24% RH; however, the two curves surprisingly overlap at 0.1% RH. Furthermore, the absence of friction hysteresis in the 0.1% RH not only occurs to the FLG films but also occurs to the Si/SiO₂ substrate. Given that water is the only variable in the conditions for the two group of experiments, the hypothesis can be made that having water is a necessity for both graphene and the Si/SiO₂ substrate to exhibit the hysteresis behaviour of friction.

3.1.4 Aging Influence on Friction

Figure 3.4 (a - d) show the variation of measured friction forces on different exposure times. The sample 3 shown in the Figure 3.3 was used in this experiment. It was measured for 4 times after exposure to the air environment for 3 hours, 24 hours, 48 hours, and 144 hours, respectively.
Figure 3.4: Curves of friction force versus normal load for the same sample plotted with different exposure times. (a) The results measured immediately within 3 hours after the fresh sample was prepared. The dependence of friction forces with normal force measured on the area for (b) 20 hr (red), (c) 48 hr (blue) and (d) 144 hr (magenta), respectively.

3.1.4.1 Aging Influence on Friction Magnitude

Figure 3.4 shows the variation of friction forces of graphene films on increasing exposure times. Measurements were performed using the same AFM tip. It can be clearly observed that friction forces on both 1-layer and 3-layer graphene films decrease with aging.
3.1.4.2 Aging Influence on Friction Layer-Dependence

Figure 3.4 (a) - (d) commonly show that friction forces on 1-layer graphene are always observed to be higher than those on 3-layer graphene, suggesting that the aging of graphene has no impact on the friction layer-dependence behaviour. However, the difference in the magnitude of friction between different layers decreases with increasing exposure times. This phenomenon could be a result of increased adhesion between the graphene and the substrate with increased exposure time. The longer the exposure is, the stronger the sample is adhered by the substrate, causing the layer-dependent out-of-plane deformation less prominent. As a consequence, friction is less layer-dependent.

3.1.4.3 Aging Influence on Friction Hysteresis

Figure 3.4 (a) - (d) show that the difference between the loading and unloading curves (or the magnitude of the hysteresis) changes with increasing exposure time. As shown in Figure 3.4 (a), the loading and unloading curves for each freshly-prepared graphene film do not overlap. Figure 3.4 (b) and (c) shown the results obtained after 24-hour exposure and 48-hour exposure, respectively. At the beginning, the loading curve is higher than the unloading curve when the normal loads are relatively small. As the load increases, the loading and unloading curves intersect and then switch places when the normal loads vary around relative high values. However, after 144 hours exposure to the air, as shown in Figure 3.4 (d), the magnitude of friction hysteresis is dramatically reduced and there is only a small difference between loading and unloading curves.

3.1.4.4 Absence and Presence of Friction Hysteresis

Friction hysteresis can be observed in most load dependence experiments. However, some of the freshly-cleaved graphene samples did not show the friction hysteresis, but the hysteresis arose after 1 day exposure. In contrast to this seemingly inconsistence on graphene, the Si/SiO$_2$ substrate always exhibited hysteresis even when the behaviour was absent on the graphene covered regions. A typical result is shown in Figure 3.5 (a). As shown, the friction hysteresis was absent when the load dependence measurements was conducted on the sample immediately, less than 3 hours after
it was prepared. For the freshly-cleaved sample, the friction forces are lower during unloading. However, when conducting repeated measurements on the same sample after its 4-day exposure to the ambient environment, the friction hysteresis between loading and unloading was observed, as shown in Figure 3.5 (b).

Figure 3.5: Load dependence of friction curves showing the influence of ambient exposure time on the presence of friction hysteresis. (a) Topographic and (b) friction force images for the scanning area under 60 nN. (c) The load dependence of friction curve for the freshly-cleaved sample. (d) Friction hysteresis on the area when the sample was exposed to air for 4 days is observed. Black denotes single layer graphene and red denotes 3-layer graphene. Squares represent data for freshly-cleaved sample and circles represent data obtained from sample with 4-day air exposure.

To summarize, this section presented the results obtained in friction loading dependence mea-
measurements on few layer graphene films as well as the substrates. Observations were categorized into friction load-dependence, hysteresis, humidity, and aging. These phenomena and proposed mechanism will be discussed in the following Section 3.2.

3.2 Discussion

3.2.1 Layer-dependence of Friction on Graphene

Friction on few-layer graphene was observed to decrease with increasing number of layers. As introduced in Section 1.2.2, the layer-dependence of friction on graphene has been extensively investigated in previous studies and two different mechanisms have been proposed for the explanation of the property [5, 34]. One of the mechanisms was proposed by Filleter et al in [34]. By examining the properties of epitaxial graphene supported by the SiC substrate via angle-resolved photo emission spectroscopy, they stated that the friction contrast between single-layer and bilayer is resulted from the coupling between phonons and electrons suppressed by the extra graphene layer [34]. Subsequently, an alternative and perhaps more widely accepted mechanism, was proposed by Lee et al in 2010 [5]. It was suggested that, because graphene is an atomically-thin flexible material with a lower out-of-plane stiffness than its in-plane stiffness, it easily deform locally out-of-plane. During sliding, a pucker is formed in front of the nanoscale tip. This mechanism is referred to as the “pucker effect mechanism” and a schematic drawing of the puckering effect is given in Figure 3.6. This mechanism was successfully applied to explain many layer-dependence observations, including the mechanically-exfoliated graphene films covering on Si/SiO$_2$ and CVD grown graphene supported by Cu foil [5, 6]. In the pucker effect mechanism, the out-of-plane stiffness, which increases as a function of the thickness of graphene films (the number of graphene layers), is the main source of the layer-dependence behaviour, as it determines how much the graphene films pucker. In other words, the variation of the size of pucker results in the same change in the contact area between tip and graphene.

Furthermore, according to the friction theory from Bowdon and Tabor ($F_f = \tau A$), friction is the
product of the contact area $A$ and the interfacial shear stress $\tau$. In the pucker effect mechanism, it is believed that the interfacial shear stress is constant and the change in the contact area plays the dominant role for the change in friction. Therefore, the decrease in tip-graphene contact area arising from the increasing number of graphene layers causes a decrease in friction. In this way, the observed layer-dependent phenomena of graphene films can be well understood.

### 3.2.2 Friction Hysteresis on Mechanically Exfoliated FLG Supported on Si/SiO$_2$ Substrate

It is observed from Figure 3.1 that the friction force measured during the unloading process was always higher than the values obtained under the same normal load during the loading process. This indicates that the friction between the tip and the graphene films measured at each moment is affected by the sliding history of system. The dependence of sliding history of friction is referred to as “load-dependent friction hysteresis” [6]. Load-dependent friction hysteresis behaviour on graphene was first observed on single layer CVD-grown graphene deposited on copper foils in experiments [6]. Subsequently, the same behaviour was reproduced in MD simulations [7]. In our study, in contrast with previous works available in the literature, the graphene synthesis method and supporting substrate were changed and the friction hysteresis behaviour was initially investigated on mechanical-exfoliated graphene samples supported by Si/SiO$_2$ substrate. Moreover, other than...
single layer graphene, few-layer graphene samples ranging from 1-layer to 4-layer were examined simultaneously, allowing us to explore any possible impact from the difference in the number of layers on the friction hysteresis.

There are two proposed mechanisms available to explain the load-dependent friction hysteresis behaviour. The first mechanism was proposed based on the out-of-plane deformation as well as the pucker effect of graphene [6], while the second mechanism attributes the hysteresis to the presence of water in the sliding interface [7]. The first mechanism is depicted in Figure 3.7. Specifically, because of the small out-of-plane stiffness, a local pucker forms in front of the nanoscale tip when tip is sliding during the loading process (as described in Section 3.2.1). Furthermore, during the unloading process after that, the relaxation of the formed pucker (the deformed graphene films) will be inhibited by adhesive force between the tip and the deformed graphene film. As a result, the contact area under a certain applied load value during unloading would be larger than the contact area corresponding to the same applied load during loading. Therefore, there exists a difference in contact area under the same applied load between loading and unloading. The difference in contact area leads to the difference in friction, thus causes the hysteresis phenomenon [6].

A most recent study carried out theoretical MD simulations to explore the possible underlying mechanism [7]. The simulated data showed that the load-dependent friction hysteresis behaviour is present in the case where water is present between the tip and the sample, while the friction
hysteresis is absent in vacuum. Therefore, the friction hysteresis was regarded to be a consequence of the presence of water between the sliding tip and the graphene samples. Since the first mechanism failed to explain this phenomenon, the new mechanism based on the presence of water was proposed (referred to from now on as “water mechanism” in this thesis) [7]. As shown in Figure 3.8, when the tip is sliding on the graphene surface in the humid air, the tip does not contact with the graphene surface directly. Instead, because of the presence of water, water intercalates between the AFM tip and the surface. During the loading process, the water meniscus between the tip and surface swells and is squeezed out under increasing applied load, resulting in an increasing water-surface contact angle increases; while during the unloading process, the water meniscus shrinks under decreasing applied load, resulting in a decreasing water-surface contact angle. Due to the fact that the shrinking motion of the water during unloading will be impeded and pinned by the surface, water-surface contact angle is a smaller than that during loading under the same applied load [71]. Furthermore, given that the hysteresis of water-surface contact angle is assumed to directly result in a hysteresis of the water-graphene contact area, the increase in contact angle leads to the increase in water-graphene contact area. In this way, the friction, which is linked to water-graphene contact area, is explained to exhibit the load-dependent friction hysteresis [7]. Essentially, this mechanism indicates that the friction hysteresis originates from the hysteresis of the contact angle between the water and the graphene surface.

This mechanism has only been examined through MD simulations, and there are currently no experimental results available to prove it. The friction measurements in different humidity conditions performed in this work (Section 3.1.3) act as the experimental verification of the mechanism, which will be discussed in the following Section 3.2.3.

3.2.3 Influence from Environmental Humidity

3.2.3.1 Humidity Influence on Friction Hysteresis

A strong support for the water mechanism comes from the absence of friction hysteresis in the extremely dry condition, as shown in Figure 3.3 (c) and (d). No friction hysteresis was observed in
Figure 3.8: MD simulation snapshots of the tip sliding (from the right to left) on the graphene surface with the presence of water. The contact angles $\theta_{\text{front}}$ and $\theta_{\text{back}}$ during loading are larger than the corresponding $\theta_{\text{front}}$ and $\theta_{\text{back}}$ during unloading. Figure is reproduced from Ref. [7].

dry nitrogen, which reveals that the presence of friction hysteresis in humid air resulted from the presence of water between the tip and the surface, and that the absence of the friction hysteresis in dry conditions is because that the removal of water between tip and surface.

The water effect mechanism has been discussed in Section 3.2.2. The mechanism is proposed to explain the friction hysteresis of graphene, and it can be further extended to interpret the similar observation on the Si/SiO$_2$ substrate, as seen in Figure 3.3 (e). Owing to the essence of the mechanism is the presence of water, both the Si/SiO$_2$ substrate and the tip are able to absorb sufficient amount of water from humid air [72]. Under the humid air condition, it is the absorbed water on the Si/SiO$_2$ surface that causes friction hysteresis. Under the dry condition, the substrate exhibits no hysteresis because of the great reduction in water. A similar behaviour can be expected shown on a large range of materials that are able to absorb sufficient amount of water from air.

3.2.3.2 Humidity Influence on Friction Layer-dependence

As shown in Figure 3.3 (c) and (d), the friction forces are influenced by the number of layers of graphene in both dry and humid environments. As discussed in Section 3.2.2, the pucker effect mechanism currently has the most published experimental and simulation mechanistic support for
the observed layer-dependence of friction for dry lubrication of graphene under ambient conditions. However, the influence of water, or the presence of a water film on the topmost graphene layer, has not been considered to be a contributing factor in this friction mechanism. For example, it could be rationalized that the water layer can effectively increase the thickness of the graphene film and influence the out-of-plane stiffness of the overall graphene system, if the graphene and water act as a single elastic body. However, as the layer dependence of graphene is unaffected by humidity in Figure 3.3 (c) and (d), the water is likely to have little influence on the out-of-plane stiffness of graphene. In other words, the layer-dependence of contact area is independent of the humidity.

3.2.3.3 Co-presence of Friction Layer-dependence and Hysteresis

As shown in Figure 3.4 (a), both the layer-dependence and hysteresis of friction are present in humid air. The conclusion can be drawn that the pucker effect and the presence of water between the tip and graphene cannot be separated. We proposed a revised friction mechanism to support the observed co-presence of layer-dependence and hysteresis friction behaviour. The revised mechanism also provides supports for the observed friction behaviour in both dry and humid environments. Exposed to humid air, both the tip and the graphene sample absorb water molecules on their respective surfaces [73, 74, 57], which are demonstrated as two thin water layers in Figure 3.9 (a). When the tip is brought into contact with the surface, water condenses on and between the two surfaces forms a meniscus or capillary bridge around the contact resulting from capillary condensation [71], as shown in Figure 3.9 (b). When the tip begins to slide on the graphene film, a pucker in the graphene is formed and the pucker is covered by a formed capillary bridge (Figure 3.9 (c)).
Figure 3.9: A schematic drawing showing the possible mechanism. In the humid air: (a) Before the tip is approached to the sample, the tip and sample are separated. A layer of water film covers the AFM tip (which is made of silicon oxide) and a layer of water covers the graphene film. Due to the difference in hydrophilicity, water film on the tip is thicker than the water film on the graphene. Tip, water, and graphene are represented in gray, blue and orange, respectively. (b) Tip and graphene are brought into contact, resulting in two layer of water films attached on the two surfaces merging together and forming a meniscus between the tip and the surface. (c) Graphene formed a pucker when the tip sliding (from the left to the right) on the graphene surface, covered by the water meniscus.

The mechanism for friction hysteresis under humid conditions can be described as in Figure 3.10. When sliding, the water meniscus formed between the tip and the surface can be squeezed out under increasing normal loads during loading process, and pinned to the graphene surface to prevent the meniscus from shrinking under decreasing normal loads during unloading process. Consequently, under the same magnitude of applied normal load, the contact angle $\theta_l$ between the water and the sample during swelling motion is significantly larger than the contact angle $\theta_u$ during the shrinking motion. This phenomenon is known as the contact angle hysteresis [10]. A consequence of this contact angle hysteresis is that an additional shear force is required to be applied to initiate the sliding motion the water meniscus during unloading (shrinking) [10], resulting in higher friction forces during unloading. This is where the friction hysteresis behaviour comes from. Furthermore, the additional force per unit length of the water meniscus perimeter needed to initiate motion $F_a$ can be calculated using,

$$F_a = \gamma_L (\cos \theta_l - \cos \theta_u),$$

where $\gamma_L$ is the liquid surface tension [75]. Here, the difference in the tip-water angle is consid-
ered to effect the interfacial shear stress, rather than having significant impact on the tip-graphene contact area. The hysteresis of the water-surface contact angle leads to the hysteresis of interfacial shear stress and thus the observed friction hysteresis behaviour.

![Figure 3.10](image)

Figure 3.10: A schematic drawing showing the contact angle hysteresis between loading and unloading. Under the same magnitude of applied normal load, (a) the water-sample contact angle of the meniscus during loading (swelling) $\theta_l$ is larger than (b) the contact angle during unloading (shrinking) $\theta_u$. The smaller water-sample contact angle during unloading requires additional shear force to initiate the sliding motion, causing hysteresis of friction. Tip, water, and graphene are represented in the colour of gray, blue and orange, respectively.

Therefore, the combination of the pucker effect, the scenario of tip sliding on the graphene sample during the load dependence measurement is depicted as follows: When a tip is brought into contact with a graphene sample and begins sliding on it in a humid environment, a pucker is formed and a water meniscus is formed on the graphene pucker. During the loading process, both the size of the pucker gets larger and the water-surface contact angle of the meniscus get larger, which leads to an increase in tip-graphene contact area and an increase in sliding interfacial shear stress, respectively. As a result, friction force increases with increasing normal load. As the load decreases, the surface tension caused by the cohesion within the water holds back the shrinking of the water, and the interaction between the water and surface also inhibits the pucker from releasing. Consequently, under the same normal force, the lower friction force during unloading comes from a larger interfacial shear stress as well as a larger tip-surface contact area.
3.2.3.4 Humidity Influence on Friction Magnitude

Figure 3.3 (c) and (d) show an offset between the humid and dry measurements of friction on graphene, when comparing with the same number of layers. Considering that water is the only variable in the conditions for the two groups of experiments, the conclusion can be drawn again that the intercalation and amount of water at the tip-sample contact have an impact on the friction behaviour.

This phenomenon can also be interpreted based on the mechanism shown in Figure 3.9. When the tip is brought into contact with the surface and sliding on the surface, the water attaching on the two surfaces will come together and form a meniscus in the narrow gap between AFM tip and the graphene surface. The formation of water meniscus introduces the meniscus force, which includes the capillary force and the adhesive forces between the water and the tip/sample, into the sliding system. The meniscus force acts as the additional shear resistance force between the tip and the graphene surface. Increased forces are consequently required to overcome the increased resistance when the tip is sliding on the surface, resulting in a higher friction force between the tip and the graphene surface. However, under 0.1% RH achieved by blowing nitrogen, the water is removed between the the tip and the graphene. The great reduction in water causes the lack of the additional resistance that comes form the water meniscus, and therefore, friction in the dry condition is remarkably reduced.

To explore how the water meniscus causes an additional friction force, the influence of water meniscus on both contact area and shear stress is examined. The mechanism of a tip sliding on a graphene sample in the extremely dry environment is illustrated in Figure 3.11. Exposure to dry environment, a very small amount of water is adsorbed on the tip and the graphene surface. When the tip is sliding on the surface, the stress between the tip and graphene \( \tau_{\text{tip–graphene}} \) contributes to the friction, which is illustrated as the black dashed line in Figure 3.11 (a). However, the shear stresses differs when the tip is sliding on the sample in humid air. The existence of the meniscus between the tip and the sample results in two different types of shear stress mutually
contributing to the friction, the shear stress between tip and water $\tau_{water-tip}$ and the shear stress between water and graphene surface $\tau_{water-graphene}$ (shown in Figure 3.11 (b)). The increased friction could be resulted from the fact that the total of $\tau_{water-tip}$ and $\tau_{water-graphene}$ is larger than $\tau_{tip-graphene}$ ($\tau_{water-tip} + \tau_{water-graphene} > \tau_{tip-graphene}$). On the other hand, it is also likely that larger water meniscus causes larger contact area, and further it is the change in contact area that responsible for the increased friction under humid conditions. Namely, the contact area in a humid environment (the area covered by the green dashed line in Figure 3.11 (b)) is larger than that in a dry environment (the area covered by the black dashed line in Figure 3.11 (a)), which results in a higher friction force. More investigation is required to have a better understanding of how the presence of water increases the friction force.

It is important to observe the fact that the magnitude of friction is highly dependent on the presence of water. Despite that it remains unclear how the existence of water increases the friction force and more investigation is required, two contributions of the observation are clear. First, water in the air plays a crucial role in friction measurements on graphene. Secondly, as a convincing supplement to the simulation findings, strong experimental supports for the water mechanism are provided.

Figure 3.11: A schematic drawing showing the contact angle hysteresis between loading and unloading. Under the same magnitude of applied normal load, (a) the water-sample contact angle of the meniscus during loading (swelling) $\theta_l$ is larger than (b) the contact angle during unloading (shrinking) $\theta_u$. The smaller water-sample contact angle during unloading requires additional shear force to initiate the sliding motion, causing hysteresis of friction. Tip, water, and graphene are represented in the colour of gray, blue and orange, respectively.
In summary, friction of graphene is observed to be humidity-dependent. In the dry condition, although the friction of graphene still exhibits the layer-dependence property, the magnitude of friction is reduced remarkably. In addition, the behaviour of load-dependent friction hysteresis is observed to be humidity-dependent and is absent in extremely dry condition. The observed phenomena covered in this work can be explained by the revised mechanism. However, more experiments should be conducted to further verify those assumptions involved in the mechanism.

3.2.4 Influence from Exposure Time

3.2.4.1 Influence on the Magnitude of Friction

As shown in Figure 3.4, friction decreases with increasing exposure time in air. This could be due to two possible reasons. The first reason is the decrease in the wettability of graphene with aging [74]. Wettability of a surface is very sensitive to contamination on the surface and airborne hydrocarbon moleculars ambient air are a common source of contamination. Thus, when the graphene samples were exposed to ambient air, graphene adsorbs the airborne hydrocarbons in the ambient air and forms contaminants on its surface [74]. The formation of these contaminants causes graphene to be more hydrophobic and the wettability of the graphene samples decreases. As discussed in the previous section, friction decreases as the amount of water between the tip and the sample reduces. Therefore, friction would reduce with longer exposure times. However, the decrease in the wettability normally occurs in a quite short time [74]. Consequently, this reason can only explain the decrease in the friction force at the beginning of air exposure, but not the subsequent decrease in friction with further exposure to the air.

The first reason emphasizes a reaction on the surface of graphene samples, the second reason considers a change in the adhesion between the graphene and the supporting substrate. Specifically, the reduction on friction is due to the increase in graphene-substrate adhesion with its aging. A study shows exposure to air can cause the occurrence of oxygen chemisorption on the graphene surface and the increase in surface oxygen has a strong impact on the adhesive properties [35]. Graphene samples with a longer exposure time have a higher amount of surface oxygen, which
leads to a larger adhesion force between the graphene and the substrate [35]. A higher adhesive force resulting in a stronger bond between the graphene and the substrate could cause a decrease in out-of-plane deformation and thus forming a smaller pucker. According to the discussed pucker effect mechanism, a smaller formed pucker would result in a lower friction force.

Unlike the fact that the wettability varies by the exposure times within only 1 day and then stays at the bottom level steadily, the impact from the exposure time on the adhesive force can work for a much longer time. A study showed that the adhesion between graphene and the supporting substrate enhanced considerably with exposure time increasing from 144 hours to 336 hours [35]. With a continuous increase in the exposure time, the adhesion between graphene and substrate continues to increase, causing a decreasing in out-of-plane deformation. Therefore, the second reason might be the main contribution to the decreasing friction with exposure time.

The explanation for the observation in this work is still unclear, and the variation of the magnitude of friction hysteresis requires more investigation. The only conclusion can be drawn is that the exposure time has some effects on the magnitude of friction hysteresis.

3.2.4.2 The Presence and Absence of Friction Hysteresis

Figure 3.5 shows that the friction hysteresis occurred after 1-day sample exposure to the air. Given the hydrophobility of graphene materials, the phenomenon can be attributed to the insufficient amount of water on the freshly-cleaved graphene films when the first load dependent measurement was performed. Compared to the limited 3-hour exposure, 144-hour exposure time to air allowed graphene films to absorb sufficient amount of water on its surface, and therefore it exhibited the friction hysteresis when the sample was measured again 4-days later.

The exposure to air for graphene could cause a change in the amount of water on the graphene surface, the absorption/deposition of contaminants on the surface, and the adhesion between graphene and the substrate. The impact of the air exposure includes but are not limited to the above. Therefore, the friction of graphene is believed to be dependent on the air exposure time.
3.3 Conclusions

In summary, this chapter reveals that the friction on graphene varies as a function of number of graphene layer, relative humidity in experimental environment, sliding history, and exposure times. Firstly, the layer-dependence of friction is reproduced in both humid air and dry nitrogen environment. The pucker effect mechanism can explain why this friction layer-dependent characteristic is independent from different humidity conditions. Secondly, in humid air, load-dependent friction hysteresis behaviour was extensively observed on different layer of graphene films and their Si/SiO$_2$ substrate, whereas all hysteresis behaviour is absent in 0.1% RH environment. Water existing between the tip and the graphene surface was proven to be an extremely important factor causing the friction hysteresis behaviour. Thirdly, combing the pucker effect and the water effect, a mechanism combining the pucker effect mechanism and the water mechanism was proposed.
Chapter 4

Adhesion between Nanoscale Tips and Two-Dimensional Films

This chapter presents finite element method (FEM) simulation results on the adhesive contact between a nanoscale tip and graphene sheets supported by a silicon substrate. The results were obtained based on the modeling described in Chapter 2. As mentioned, in order to capture all the cases experienced by the graphene layers, two extreme configurations of graphene were considered in the FEM simulations: one was modeled with discrete layers that were allowed to slide laterally with respect to each other; and one was modeled with a continuum elastic shell with effective in-plane and bending stiffness. In this chapter, adhesion behaviour of the two configurations is provided and discussed. The goal of this work is to understand experimental AFM pull-off force measurements that indicate no layer dependence, whereas sliding friction experiments do.

Firstly, this Chapter presents the simulation results. For models with different number of layers in both configurations, the variation of normal force with the tip-graphene separation and the variations of the contact area with the normal force are provided. In particular, the dependence of pull-off forces on different number of graphene layers is listed. This is followed by a discussion of layer dependence of adhesion on graphene films, as well as the influence from the configuration. Furthermore, the adhesion of suspended graphene will be discussed, examining the how the absence of substrate would impact the adhesion behaviour of graphene films.

4.1 Simulation Results

4.1.1 Force versus Tip-sample Separation Curves

Figure 4.1 (a) shows the variation of the normal force with increasing tip-graphene separation distance following the application of a compressive pre-load for simulations in configuration 1. The tip-sample separation in x-axis are defined as the distance (which was denoted as the variable $-h$ in
Chapter 2.2.3) between the lowest point on the tip and the highest point on the graphene sample; the normal force in y-axis is extracted from the vertical net force acting on the tip, which is a result from the equations 2.26 - 2.32. The variance in the force curves for simulations containing 1-4 layers of graphene can also be distinguished in Figure 4.1 (a). The inset of Figure 4.1 (a) shows a zoomed in image of the minima of the various force versus distance curves. An increasingly negative value in the minima of the normal force is observed in the force distance curves with increasing the number of graphene layers. Given that the simulations are performed in displacement control, the value of the pull-off force $F_{PO}$ is the largest negative value recorded during the simulation. To better identify the key parameters, including the pull-off force, work of adhesion, and the tip-sample separation at $F_{PO}$, the results have been summarized in Table 4.2. The work of adhesion was calculated using the Derjaguin approximation [17]. Table 4.2 shows that the pull-off force and work of adhesion both increase with the number of graphene layers, while the tip-sample separation at $F_{PO}$ decreases very slightly with increasing number of graphene layers.

![Figure 4.1](image)

Figure 4.1: Force-distance curves measured on graphene layer thickness that varies from 1-4 layers in pull-off simulations in (a) configuration 1 and (b) configuration 2. The insets highlight the variance in the minima of the force distance curves. The colour scheme is as follows: colours denote the number of graphene layers. black, red, blue, and green represents 4-layer (4L), 3-layer (3L), 2-layer (2L), and 1-layer (1L), respectively.
Table 4.1: Pull-off forces, work of adhesion, and tip-graphene separation at $F_{PO}$ for simulations conducted in configuration 1 with 1 - 4 layers of graphene in the contact.

<table>
<thead>
<tr>
<th>Pull-off Force $F_{PO}$</th>
<th>Work of Adhesion</th>
<th>Tip-Sample Separation at $F_{PO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Layer 14.1 nN</td>
<td>0.150 J/m$^2$</td>
<td>0.299 nm</td>
</tr>
<tr>
<td>2-Layer 15.7 nN</td>
<td>0.166 J/m$^2$</td>
<td>0.299 nm</td>
</tr>
<tr>
<td>3-Layer 16.1 nN</td>
<td>0.171 J/m$^2$</td>
<td>0.296 nm</td>
</tr>
<tr>
<td>4-Layer 16.3 nN</td>
<td>0.173 J/m$^2$</td>
<td>0.296 nm</td>
</tr>
</tbody>
</table>

Figure 4.1 (b) shows the variation of the normal force with increasing tip-graphene separation distance following the application of a compressive pre-load for simulations containing 1-4 layers of graphene in configuration 2. Similarly, the inset of Figure 4.1 (b) shows a zoomed in image of the minima of the various force curves shown, highlighting the small variations observed between configuration 1 and 2. The values of the pull-off force, work of adhesion, and tip-sample separation at $F_{PO}$ have been summarized in Table 4.2. Again, the work of adhesion was calculated using the Derjaguin approximation [17]. The trends observed in the pull-off force and work of adhesion increase with increasing number of graphene layers, as they did in configuration 1. However, the tip-sample separation at $F_{PO}$ also increase significantly with increasing number of graphene layers in the contact in configuration 2, as opposed to configuration 1. There is also a slightly greater increase in the pull-off force and associated work of adhesion with three and four layers of graphene in configuration 2 than was observed in configuration 1.

Table 4.2: Pull-off forces, work of adhesion, and tip-graphene separation at $F_{PO}$ for simulations conducted in configuration 2 with 1 - 4 layers of graphene in the contact.

<table>
<thead>
<tr>
<th>Pull-off Force $F_{PO}$</th>
<th>Work of Adhesion</th>
<th>Tip-Sample Separation at $F_{PO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Layer 14.1 nN</td>
<td>0.150 J/m$^2$</td>
<td>0.298 nm</td>
</tr>
<tr>
<td>2-Layer 15.9 nN</td>
<td>0.169 J/m$^2$</td>
<td>0.311 nm</td>
</tr>
<tr>
<td>3-Layer 17.3 nN</td>
<td>0.184 J/m$^2$</td>
<td>0.314 nm</td>
</tr>
<tr>
<td>4-Layer 18.0 nN</td>
<td>0.191 J/m$^2$</td>
<td>0.310 nm</td>
</tr>
</tbody>
</table>

4.1.2 Contact Area versus Normal Force

The variation of the contact area with normal force during a pull-off simulation is shown in Figure 4.2 (a) for configuration 1 and Figure 4.2 (b) for configuration 2. Specifically, the contact
area between the tip and the topmost graphene layer is shown in Figure 4.2. The contact area is calculated from the sum of all the area associated with the graphene nodes that are in contact with the tip. The decisions about which nodes are in contact are made based on whether their smallest relative position is less than a cut-off gap distance, which is assumed to be 3 nm. In other words, an element of the topmost layer graphene was assumed to be in contact with the tip once the distance between any node of the element and the tip is less than 3 nm. The variation of contact area with normal force varies little in configuration 1, compared with configuration 2, where there is some variation between the various cases simulated. In configuration 2, the greater adhesion observed for 4 layers of graphene also resulted in a higher contact area at pull-off than was observed for 1 layer of graphene.

![Figure 4.2](image)

**Figure 4.2**: Contact area versus pull-off force graphs in (a) configuration 1, where graphene layers were not confined and (b) configuration 2, where the graphene layers were laterally confined. The colour scheme is as follows: colours denote the number of graphene layers. Green, blue, red, black represents 1-layer, 2-layer, 3-layer, and 4-layer, respectively.

### 4.2 Discussion

Results from two types of pull-off simulations have been shown in the previous Section 4.1. Configuration 1 where the graphene layers were not laterally confined and free to move. Configuration 2 where the graphene layers were laterally confined. In each configuration, the layer
dependence of graphene was simulated by changing the number of graphene layers between the tip and substrate from 1 layer of graphene to 4. The analysis of the simulation data will be organized in this section as follows. First, the rationale for the observed layer dependence of the pull-off force will be discussed. Second, the variance between the two configurations in terms of the influence of confining the layers has on pull-off force measurements will be presented. Finally, we will use the simulation to understand the adhesive behaviour of suspended graphene.

4.2.1 Layer Dependence of Adhesion on Graphene Films

In both configurations examined, the simulation results indicate that graphene adhesion exhibits a layer-dependent property, increasing with the number of graphene layers between the tip and substrate. In previous experimental work of a single asperity silicon AFM tip used to measure pull-off forces on silicon surfaces covered by graphene, a complete layer independence in the pull-off force was measured [60]. However, the experimental error quoted in this study was approximately 10%-20% in the value of the pull-off force and associated work of adhesion, typical of most AFM measurements. The variance in the pull-off force observed in the two configurations simulated in this study is much smaller than the experimental error. The average value obtained for the work of adhesion from all simulations is 0.17 ± 0.01 J/m², which is within the error range of 0.23 ± 0.11 J/m² given in Ref. [60]. Again, as mentioned Section 4.1.1, work of adhesion was calculated using the Derjaguin approximation. However, the work of adhesion results from the FEM simulations are lower than that observed in blister tests, which was 0.45 ± 0.02 J/m² for single layer graphene and 0.31 ± 0.03 J/m² for multilayer graphene, both on a silica substrate [61]. Koneig et al. acknowledged that their work of adhesion was higher than other studies, and suspected that the high adhesion was a result of the graphene being capable of conforming to substrate roughness, which is why adhesion decreased with multilayer graphene. Given that the substrates are perfectly flat in the simulations, we should expect lower pull-off forces. Finally, roughness has been observed to reduce adhesion [76, 77] while the presence of a water meniscus has been observed to increase adhesion [41]. These contributions are present in the aforementioned
studies, and have a stronger influence on the pull-off force measurement than the small variance observed in the simulations.

To gain greater insight into the physical origins of layer dependence of graphene in the FEM simulations, we examined the contribution of elastic strain energy and the influence of the Lennard-Jones potential on the pull-off force. First, we examined the contribution of elastic strain energy on the pull-off force by dramatically increasing the Young’s modulus of the substrate and graphene in the out-of-plane direction to 550 TPa, the highest elastic constant that can be entered currently in the ABAQUS software. The in-plane modulus of graphene, as well as the other parameters remained unchanged. Thus, in these simulations, the substrate and/or graphene was essentially rigid, or rigid to out-of-plane deformation in the case of graphene. Figure 4.3 summarizes the results from these simulations. In every graph of Figure 4.3, the dashed lines indicate the original data given in Section 4.1 (rigid tip, deformable graphene/substrate) and the solid lines indicate either a rigid tip and substrate (Figures 4.3 (a) and (b), configuration 1 and 2, respectively) or a completely rigid system (Figures 4.3 (c) and (d), configuration 1 and 2, respectively). Figure 4.3 shows that although the repulsive forces have much higher slopes when the substrate and/or complete system are rigid, the attractive sections of the force curves do not vary substantially. Furthermore, the pull-off force magnitude and tip-sample separation at pull-off remain unchanged with the changing elastic constant. Finally, in all cases examined in Figure 4.3, an increase in the pull-off force with the number of graphene layers is observed in each case. We therefore conclude that elastic deformation does not substantially contribute to the observed layer dependence of the pull-off force in the simulations.
Figure 4.3: Normal force vs tip-sample separation curves simulated on graphene layer thickness varying from 1-4 layers in pull-off simulations on rigid substrate or models (solid lines) and elastic models (dashed lines). The elastic models show the same data from Section 4.1. Solid lines correspond to models conducted a rigid tip and substrate and elastic graphene layers in configuration 1 (a) and configuration 2 (b). Completely rigid models (rigid tip, substrate and graphene) are represented by the solid line curves given in (c) and (d) for configuration 1 and 2, respectively.

Next, we examine the contribution of the peak attractive energy on the pull-off force. In the previous simulations, the peak attractive energy between carbon-silicon oxide (the tip-graphene interaction) is approximately 5 times higher than silicon oxide-silicon oxide (the tip-substrate interaction), which are $1.659 \times 10^{-21}$ J and $3.36 \times 10^{-22}$ J, respectively. Additionally, there are also slight differences in the zero potential distance $\kappa$ and the number of density of atoms $\rho$ that were used in calculating the cohesive stresses. As a result, the pre-factor in front of the bracketed in
Equation 2.29, corresponding to $4\pi p_{SiO_2}^2 \varepsilon \kappa^6$, is 99 times higher than pre-factor in Equation 2.28, corresponding to $4\pi p_{gra}p_{SiO_2} \varepsilon \kappa^6$. To confirm a layer dependent pull-off force primarily resulting from the LJ peak interaction strength, simulations were conducted where the scaling constants used in Equation 2.28 and 2.29 were exchanged. Figure 4.4 (a) and (b) show the force curves for these simulations, where the tip-graphene pre-factor is now 100 times weaker than the tip-substrate interaction for configuration 1 and 2, respectively. Here, the pull-off force decreases dramatically when more than one layer of graphene is present, and continues to be reduced slightly from 2-4 layers. This opposing trend, compared with the previous simulations, indicates that the slight increase in the pull-off force observed as the number of layers was increased from 1-4 layers was a result of the higher peak interaction strength and the associated pre-factor used when determining the cohesive stress between the tip and graphene, compared with the tip and substrate. Additionally, the same trends with respect to the layer dependence of graphene are observed in both configurations in Figure 4.4 (a) and (b). Therefore, the layer dependence observed in the adhesion FEM simulations results from the presence of graphene near the tip in the contact zone having a larger cohesive stress than that of the silicon substrate. With increasing layers of graphene, a larger amount of adhesive material (in comparison with the substrate) is placed close to the tip. The smaller distance between the tip and the graphene, compared with the tip and the substrate, combined with the larger cohesive between the tip and graphene results in the greater pull-off force with increasing number of graphene layers. Should a material with the same cohesive stress as the substrate be placed in the contact, no change in the pull-off force would be observed with an increase in the amount of layered material in the contact.
4.2.2 Influence of FEM Configuration on Pull-Off Force

In this section, the influence of applying either configuration 1 (discrete layers) or configuration 2 (continuum layers) to the study of graphene adhesion is examined. As shown in Figure 4.1 and summarized in Tables 4.1 and 4.2, the two configurations yield the same marginal result in terms of the work of adhesion and pull-off force. Therefore, the confinement of the layers does not impact the magnitude of the adhesive forces measured in the FEM simulations. However, there is a small impact on the configuration of the simulations in terms of the contact area between the tip and the sample. Figure 4.5 (a) summarizes Figure 4.2, showing only the portion of the force curve from the maximum applied repulsive force until pull-off. Additionally, the contact area versus normal force curve generated for 1 layer of graphene has been eliminated, as it is the same for the two configurations. What becomes apparent in Figure 4.5 (a), particularly for 3 and 4 layers of graphene, is that the contact area variation for the continuum simulations is slightly shifted downwards and to the left compared with those in configuration 1. Figure 4.5 (b) and (c) are snapshots of graphene layers adhered by the tip at the pull-off point. It can be seen that the delamination of configuration 1 between the graphene layers and the substrate is larger than that
of configuration 2, leading to configuration 1 a larger contact area. The difference in delamination suggests that the continuum model has a greater resistance to out-of-plane deformation, which appears slightly stiffer to the indenting tip, compared with the discrete model.

Figure 4.5: (a) Contact radius versus pull-off force graphs in configuration 1 and configuration 2. The colour scheme is as follows: colours denote the number of graphene layers. Green, blue, red, and black represents 1-layer, 2-layer, 3-layer, and 4-layer, respectively. Solid lines and dashed lines denote configuration 1 and configuration 2, respectively. 2-Layer graphene models in (b) configuration 1 and (c) configuration 2 at pull-off force point were shown as an example. Colours denote the magnitude of Mises stress. Red and black represent the maximum and minimum values, respectively.

4.2.3 Suspended Graphene Adhesion Simulations

Finally, we examine the adhesive properties of suspended graphene using the model shown in Figure 4.6 (a) for configuration 1. Suspended graphene is created by cutting a cylindrical hole with the radius of 10 nm and the depth of 34 nm in the middle of substrate beneath the tip, effectively removing any adhesive interaction from the substrate to the graphene layers. Many experimental studies have examined the properties of suspended graphene with a limited number of layers present in the contact zone. The influence of the substrate becomes less relevant in these simulations, as the substrate is too far to influence the tip. Therefore, the interaction and layer dependence of adhesion on graphene can be studied in greater detail. Additionally, the change in mechanical
stiffness between the two simulation configurations is likely to be very important, as the substrate will not be able to impart additional stiffness to the suspended graphene sheets.

![Diagram of FEM model](image)

Figure 4.6: (a) Schematic of the FEM model used to investigate the pull-off forces on suspended graphene. Normal force versus tip-sample separation curves measured on suspended graphene 1-4 layers films in pull-off simulations in (b) configuration 1 and (c) configuration 2.

Figure 4.6 (b) and (c) show the force distance curves obtained from the suspended graphene simulations in configuration 1 and 2, respectively. The results extracted from these simulations are summarized in Table 4.3 and 4.4. Here, one can observe that the increase in the pull-off force and associated work of adhesion, again determined using the Derjaguin approximation [78], increases more significantly for the suspended graphene than observed on the supported graphene.

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Figure 4.7: Snapshots of 4-layer suspended graphene FEM models in (a) configuration 1 and (b) configuration 2 at their respective pull-off points. Colours denote the magnitude of Mises stress. Red and black represent the maximum and minimum values, respectively.

Additionally, the confined layers show a greater increase in the pull-off force and work of adhesion with the number of graphene layers than the discrete layers. Figure 4.7 (a) and (b) are the snapshots of the FEM simulations of 4-layer suspended graphene in configuration 1 and 2, respectively. Examination of the snapshots of the FEM simulations shows that the discrete layers show a lower pull-off force because the layers delaminate as the tip pulls up on the graphene sheets, increasing the distance between the topmost and bottom most layers. This layer delamination is prevented when confining the layers in configuration 2, and thus the entire graphene film can contribute to the adhesive interaction during the entire pull-off process.

Table 4.3: Pull-off forces, adhesion work, and tip up moving distance for simulations conducted on suspended graphene films in configuration 1

<table>
<thead>
<tr>
<th>1-Layer</th>
<th>2-Layer</th>
<th>3-Layer</th>
<th>4-Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.7 nN</td>
<td>10.2 nN</td>
<td>10.9 nN</td>
<td>11.3 nN</td>
</tr>
<tr>
<td>0.092 J/m²</td>
<td>0.108 J/m²</td>
<td>0.116 J/m²</td>
<td>0.120 J/m²</td>
</tr>
<tr>
<td>0.328 nm</td>
<td>0.325 nm</td>
<td>0.324 nm</td>
<td>0.322 nm</td>
</tr>
</tbody>
</table>
Table 4.4: Pull-off forces, adhesion work, and tip up moving distance for simulations conducted on suspended graphene films in configuration 2

<table>
<thead>
<tr>
<th>Layer</th>
<th>Pull-off Force $F_{PO}$</th>
<th>Work of Adhesion</th>
<th>Tip-Sample Separation at $F_{PO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Layer</td>
<td>8.7 nN</td>
<td>0.092 J/m$^2$</td>
<td>0.328 nm</td>
</tr>
<tr>
<td>2-Layer</td>
<td>12.3 nN</td>
<td>0.131 J/m$^2$</td>
<td>0.309 nm</td>
</tr>
<tr>
<td>3-Layer</td>
<td>16.2 nN</td>
<td>0.172 J/m$^2$</td>
<td>0.309 nm</td>
</tr>
<tr>
<td>4-Layer</td>
<td>17.7 nN</td>
<td>0.188 J/m$^2$</td>
<td>0.315 nm</td>
</tr>
</tbody>
</table>

4.3 Conclusions

FEM simulations of adhesive pull-off measurements were conducted for graphene films supported by a silicon oxide substrate in two configurations: configuration 1 where layers were laterally unconstrained to shear stresses, and configuration 2 where layers were totally constrained together. The FEM simulations showed that the work of adhesion compares well with the values determined from AFM experiments. However, a very small increase in the work of adhesion was observed in FEM simulations that was not observed in experiments possibly due to the experimental uncertainty. Our simulations reveal that the higher cohesive stresses calculated for the tip-graphene interaction, compared with the tip-substrate interaction resulted in the simulated layer dependence in the work of adhesion. A comparison between the two configurations showed little difference in the magnitude of the pull-off forces observed, but when the layers were confined, the resulting surface was slightly stiffer than the when the layers were discrete. Finally, suspended graphene was shown to exhibit a stronger layer dependence in the work of adhesion compared with supported graphene sheets, particularly in when the graphene layers were confined and prevented from delaminating from each other.
Chapter 5

Concluding Remarks and Future Work

5.1 Friction Behavior of Graphene

5.1.1 Conclusions

Friction properties of graphene were studied through the load dependence measurements using AFM. Variations of the friction of graphene on the number of graphene layers, the environmental humidity, sliding history, and exposure times were explored. First, independent from aging and humidity conditions, the layer-dependence of friction was widely reproduced. This extensive observation of friction layer-dependence provided strong support for the feasibility of pucker effect mechanism, where the change in out-of-plane stiffness was considered as the main reason. Second, experimental AFM load-dependent friction measurements capturing the hysteresis in the friction forces between loading and unloading on graphene lubricated $\text{SiO}_x$ substrates were successfully performed. In humid air, this behaviour was widely observed on different layers of mechanically-exfoliated graphene films, as well as the on the supporting Si/$\text{SiO}_2$ substrate. However, the friction hysteresis was absent under dry nitrogen condition. This contrast suggests that water existing between the tip and the graphene surface was an extremely important source causing the hysteresis behaviour of the friction. A significant reduction in friction forces at 0.1% RH compared with those obtained under humid environments provided further support that humidity has an important effect on friction. Third, there was no significant difference in the magnitude of the hysteresis between different number of graphene layers being observed, suggesting that the hysteresis behaviour is layer-independent. A combined pucker and water meniscus enhancement of friction was proposed resulting from the observations made for these two observations. The load-dependent hysteresis of the water-graphene contact angle caused the hysteresis of the interfacial shear stress subjected
by the sliding tip, and thus further leading the friction hysteresis. Lastly, the aging of the sample, resulting from an exposure of the graphene coated surfaces to the ambient lb atmosphere was investigated. The evolution of the measured friction forces with time which was associated with the amount of absorbed water, deposited contaminants, as well as the change in adhesion from the supporting substrate.

5.1.2 Future Work

First, since the water absorbed on graphene surface is assumed to be the reason for friction hysteresis behaviour, the friction hysteresis behaviour should be less likely observed on a highly hydrophobic material. Therefore, a further verification of the assumption can be conducted by using those highly hydrophobic materials. Hexagonal Boron nitride (h-BN), another typical 2-dimensional material known to be superhydrophobic [79, 80] is an excellent option. Moreover, in order to explain those observed phenomena, the load-dependent hysteresis of the water-surface angle is assumed to cause the load-dependent hysteresis interfacial shear stress. Experimental and theoretical work is required to support the assumption. Furthermore, different substrates with different surface energies can provide different adhesive forces when supporting graphene films. It has been observed that the layer-dependent behaviour is absent on graphene when it was strongly-adhered on mica, which has a high surface energy [36]. Motivated by that, it might be interesting to see how the friction hysteresis would be affected through replacing the substrate with mica. Lastly, the friction study on graphene is at an early stage and the dependence of friction on those parameters discussed in the thesis has only been investigated qualitatively. In order to achieve a better application of these “magic” materials, more study is desirable to gain the quantitative dependence on those parameters.
5.2 Adhesion Behaviour of Graphene

5.2.1 Conclusions

Adhesion properties of graphene were investigated by constructing simulations solved though FEM. Specifically, by mimicking the pull-of adhesion performed in AFM, the dependence of adhesion behaviour of graphene on the number of graphene layers, the graphene configurations, the absence of substrate were examined. Simulations showed a slight increase in the pull-off force and effective work of adhesion as layer number increased, but this small enhancement was within the experimental error. Layer-dependent pull-off forces did not vary with the elastic strain in the system, but were influenced by the greater cohesive stresses for tip-graphene interactions, compared with tip-substrate interactions. Two configurations of graphene were used in the FEM simulations: one was modeled with discrete layers that were allowed to slide laterally with respect to each other; and one was model with a continuum elastic shell with effective in-plane and bending stiffnesses. The change in the two simulation conditions resulted in the continuum model having a greater resistance to out-of-plane deformation than the discrete model, which led to small change in the behaviour of the contact area versus normal force curves. Finally, FEM simulations were also performed for suspended graphene and the results showed that the continuum model would exhibit a higher layer dependent pull-off force compared with the discrete model.

5.2.2 Future Work

The first future work could be focused on the experimental verification. Since the simulation results showed that the adhesion is slightly layer-dependent, the small variation of the pull-off force is difficult to be detected, no mentioned to the fact that it could be masked by the influence from other factors such as surface roughness, humidity, and temperature, etc. Therefore, in order to experimentally verify the simulation results, conducting the adhesion measurements in vacuum, along with more precise experimentation able to eliminate other possible influencing factors is necessary. Additionally, a difference in the adhesion behaviour between the two extreme config-
urations has been observed, suggesting that the adhesion behaviour is affected by the interlayer graphene bond, especially the interlayer lateral friction. Thus, further study on the exact interlayer graphene bond would very helpful for gaining a better insight of the adhesion of graphene.
Bibliography


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