CHARACTERIZATION OF INTERFACIAL FORCES USING
ATOMIC FORCE MICROSCOPY: FROM BIOADHESION TO
NANOTRIBOLOGY

AN ABSTRACT

SUBMITTED ON THE SIXTH DAY OF SEPTEMBER 2018
TO THE DEPARTMENT OF CHEMICAL AND BIOMOLECULAR
ENGINEERING
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
OF THE SCHOOL OF SCIENCE AND ENGINEERING
OF TULANE UNIVERSITY
FOR THE DEGREE
OF
DOCTOR OF PHILOSOPHY

BY

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ABSTRACT

The forces in nature can be categorized to four groups, two of which act at the atomic level, the other two forces which are electromagnetic and gravitational interactions, which act between atoms and molecules, have a much larger range of action, and consequently determine properties of every phenomena around us. Electromagnetic forces are known to be the origin of all of the intermolecular interactions. Therefore, electromagnetic forces govern the behavior of solids, liquids, gasses, particles in the solution, and self-assembly processes.

A variety of experimental techniques and instruments are available that provide different insights and information on the intermolecular forces strength and bonding energies. Measuring the equilibrium and dynamic interaction force between two bodies as a function of separation distance is one of the common types of experiments that provide a fundamental insight into different processes. There are many instruments that provide a measurement of forces between bodies, two of which are the surface force apparatus (SFA), and the atomic force microscope (AFM). However, they operate in different ranges of sensitivities and resolutions. AFM is one of the most common and straightforward techniques that allows reliable force measurements at the nano/micro scale and is used extensively in this thesis in two distinct projects as described below.

In the first part of the thesis, I used AFM to investigate adhesion of a mosquito leg to fibrous surfaces. Insects and small animals capable of adhering reversibly to a variety of surfaces employ the unique design of the distal part of their legs. In the case of mosquitoes,
their feet are composed of thousands of micro- and nanoscale protruding structures, which impart superhydrophobic properties. Previous research has shown that the superhydrophobic nature of the feet allows mosquitoes to land on water, which is necessary for their reproduction cycle. In this thesis, we show that van der Waals interactions are the main adhesion mechanism employed by mosquitoes to adhere to various surfaces. We further demonstrate that the judicious creation of surface roughness on an opposing surface can increase the adhesion strength because of the increased number of surface elements interacting with the setae through multiple contact points. Although van der Waals forces are shown to be the predominant mechanism by which mosquitoes adhere to surfaces, capillary forces can also contribute to the total adhesion force when the opposing surface is hydrophilic and under humid conditions. These fundamental properties can potentially be applied in the development of superior Long Lasting Insecticidal Nets (LLINs), which represent one of the most effective methods to mitigate mosquito-transmitted infectious diseases such as Malaria, Filaria, Zika, and Dengue.

In the second part of this thesis, We applied AFM to study the tribological properties between an AFM tip and a Au(111) surface in an aqueous environment and influenced by an applied electrical potential. Using lateral force microscopy, we measure the friction between an AFM tip and a gold surface, while running a cyclic voltammogram simultaneously via a three-electrode setup. Applying a positive potential to the Au surface forms a highly confined ice like water layer at the Au/electrolyte interface which sharply increases friction. However, when a negative potential is applied, water molecules next to Au surface have properties similar to bulk water and results in lower friction. The changes in friction as a function of potential is found to be reversible. Friction experiments are
carried out on ultra-smooth gold surfaces and compared to a gold surface with a larger roughness. Similar trends are observed on both surfaces. An increase in the ionic strength of the electrolyte is found to lower friction. Using an aqueous NaOH solution was found to lower the critical potential at which the friction sharply increases. Normal force curves are also measured as a function of approach velocity and it is found that the normal force linearly increases as the approach velocity increases in agreement with a drainage model. These results provide valuable insight into the effect of applied electrical potentials on the properties of water at charged surfaces and can potentially impact a wide range of fields including tribology, MEMs, energy storage devices, fuel cells and catalysis.
CHARACTERIZATION OF INTERFACIAL FORCES USING ATOMIC FORCE MICROSCOPY: FROM BIOADHESION TO NANOTRIBOLOGY

A DISSERTATION

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# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................................................................................II

TABLE OF CONTENTS ........................................................................................................ IV

LIST OF FIGURES ............................................................................................................... VII

CHAPTER 1- INTRODUCTION AND BACKGROUND..................................................1

1.1. INTERMOLECULAR INTERACTIONS.........................................................1

1.1.1. DLVO forces .........................................................................................1

1.1.1.1. van der Waals between particles and surfaces...............................2

1.1.1.2. Electrostatic forces between surfaces in liquids .........................4

1.1.2. Non-DLVO forces .................................................................................6

1.1.2.1. Solvation forces .............................................................................7

1.1.3. Adhesion and wetting phenomena ....................................................7

1.1.4. Friction ..............................................................................................8

1.2. ATOMIC FORCE MICROSCOPY.........................................................11

1.2.1. Mode of operation ...........................................................................11

1.2.2. Lateral Force Microscopy .................................................................13

1.2.3. Force calibrations .............................................................................15

1.3. CHARACTERIZATION AND INSTRUMENTATION..............................20

1.3.1. Cyclic Voltammetry ..........................................................................20

1.3.2. Thin film deposition: Preparation of the gold coated mica ..............21

1.3.2.1. Thermal evaporation deposition ..................................................21

1.3.2.2. E-Beam evaporation deposition ...............................................23
1.3.3. Scanning electron microscopy (SEM) ..............................................23
1.3.4. Contact angle goniometer ..........................................................24
1.3.4. Profilometer .............................................................................24
1.3.5. Photolithography: preparation of patterned surfaces ...............25

CHAPTER 2: ENHANCED ADHESION OF MOSQUITOES TO ROUGH SURFACES .............................................................................................................26

2.1. INTRODUCTION .............................................................................26

2.2. EXPERIMENTAL SECTION .............................................................29

2.2.1. Attachment of a mosquito leg to AFM cantilever ......................29
2.2.2. Preparation of surfaces with different random roughness ..........29
2.2.3. Fabrication of Patterned surfaces with uniform roughness ........30
2.2.4. HDPE Surface roughness characterization .................................33
2.2.5. Force measurement of a mosquito leg attached to an AFM cantilever .........................................................................................34
2.2.6. Experimental setup to study the effect of surface roughness and humidity ....................................................................................35
2.2.7. SEM Imaging ................................................................................36

2.3. RESULTS AND DISCUSSION .........................................................38

2.3.1. Effect of surface roughness on adhesion force .........................38
2.3.2 Effect of humidity on adhesion force .........................................45
2.3.3. Adhesion force characterization of a mosquito leg on a uniform patterned rough surface .................................................................51
2.3.4.

Discussion ........................................................................................................53

2.4. CONCLUSION ...........................................................................................54

CHAPTER 3: ANOMALOUS POTENTIAL DEPENDENT FRICTION ON AU(111)
MEASURED BY AFM ..........................................................................................56

3.1. INTRODUCTION ..........................................................................................56

3.2. EXPERIMENTAL ........................................................................................58

3.3. RESULT AND DISCUSSION ......................................................................59

3.4. CONCLUSION ..............................................................................................69

CHAPTER 4: REVERSIBLE POTENTIAL-DEPENDENT FRICTION ON
AU(111) ..............................................................................................................71

4.1. INTRODUCTION .........................................................................................71

4.2. EXPERIMENTAL .........................................................................................72

4.2.1. Preparation of gold electrode substrate ..............................................72

4.2.2. Preparation of ultra-smooth gold electrode substrate ......................73

4.2.3. In situ electrochemistry-AFM .................................................................73

4.2.4. Friction measurements using AFM .......................................................75

4.2.5. Normal force measurement using AFM ..............................................76

4.3. RESULT AND DISCUSSION ....................................................................77

4.4. CONCLUSIONS .........................................................................................87

CHAPTER 5: CONCLUSION AND FUTURE WORK ...........................................89

5.1. PART I .........................................................................................................89

5.2. PART II .......................................................................................................91
LIST OF REFERENCES..........................................................................................................................97
APPENDIX A..................................................................................................................................................115
APPENDIX B..................................................................................................................................................129
## LIST OF FIGURES

Figure 1.1. Schematic of DLVO potential as a function of the separation ................................. 2
Figure 1.2. Schematic of van der Waals interaction between atoms ............................................. 3
Figure 1.3. Schematic illustration of the double layer on an electrode .......................................... 5
Figure 1.4. The recorded friction force between two shearing surfaces as a function of time .......................................................................................................................................................................................... 10
Figure 1.5. Schematic illustration of atomic force microscopy (AFM) .............................................. 12
Figure 1.6. (A) a surface structure containing a step in the middle and a relatively rough material in the left side of the step. (B) illustration of the deflection of the tip as it scans the surface. (C) and (D) friction traces in forward and backward scan directions ................................................. 14
Figure 1.7. Plot of photodiode vertical current output versus separation ........................................ 16
Figure 1.8. Plot of photodiode lateral current output versus separation ........................................... 18
Figure 1.9. Illustration of typical cyclic voltammogram ................................................................. 20
Figure 1.10. Schematic of thermal evaporation deposition ............................................................. 22
Figure 2.1. (A) SEM image of a mosquito leg and (B) distal part of a mosquito leg; (C) Schematic illustration of the proposed experiment ................................................................. 27
Figure 2.2. ATR-FTIR spectra of surfaces. (A) flat HDPE surface. (B) fibrous Surface III. (C) Comparison of flat and fibrous surfaces ................................................................. 31
Figure 2.3. Profilometry images of large-scale and local RMS for surfaces I, II, III, and IV. (A)Surface I large-scale RMS, (B) Surface I local RMS, (C) Surface II large-scale RMS, (D) Surface II local RMS, (E)Surface III large-scale RMS, (F)Surface III local RMS, (G)Surface IV large-scale RMS, (H)Surface IV local RMS ................................................................. 32
Figure 2.4. Profilometry images of large-scale RMS for patterned surface. Sq values are equal to RMS values ................................................................................................................. 33
Figure 2.5. (A) SEM images of mosquito legs attached to AFM cantilevers, (B) Typical force-distance curves for the mosquito leg (Specimen I), (C) Bar chart of mean of 100 adhesion point measurements ................................................................................................................. 37
Figure 2.6. SEM images of the distal end of a mosquito leg (A) SEM image of a leg attached to an AFM probe (B) SEM image of the leg without the claw section. (C) SEM image of the same section after performing 100 adhesion measurements..................................................38
Figure 2.7. Adhesion measurements for an Anopheles stephensi mosquito leg ..................39
Figure 2.8. Schematic of van der Waals interaction for legs (A) with no curvature. (B) with higher curvature at the distal ends of the legs.................................................................................40
Figure 2.9. SEM images of specimen I and specimen III ..................................................41
Figure 2.10. (A) SEM images HDPE surfaces with different roughness levels, (B) Bar chart of 100 adhesion measurements.........................................................................................42
Figure 2.11. Typical force vs. separation curves observed for specimen I retracting from surfaces with low (surface I) to high (surface IV) levels of roughness.................................43
Figure 2.12. (A) Plot of the adhesion force of the mosquito leg and smooth HDPE and silicon wafer surfaces as a function of relative humidity. Optical image of a water drop on a (B) hydrophobic surface of smooth HDPE and (C) hydrophilic silicon wafer surface.....44
Figure 2.13. Plot of the normalized adhesion force of the mosquito leg and smooth HDPE and silicon wafer surfaces as a function of relative humidity..................................................46
Figure 2.14. plot the adhesion force as a function of relative humidity calculated for (A) HDPE surface and (B) silicon wafer..................................................................................49
Figure 2.15. Adhesion force between a mosquito leg and a flat silicon surface at different temperatures.................................................................................................................50
Figure 2.16. (A) Bar chart adhesion measurements between a mosquito leg and a patterned surface. (B) Schematic illustration of the different landing positions of a mosquito’s leg on a patterned surface.............................................................................................................52
Figure 3.1. Schematic illustration of the experimental setup.............................................57
Figure 3.2. Plot of the friction force between an AFM tip and a gold-coated mica surface versus applied potential. The inset graph shows CV scans.........................................................60
Figure 3.3. Friction force versus normal force between Au (111) electrode and (A) a sharp AFM tip and (B) a colloidal AFM tip.........................................................................................62
Figure 3.4. Friction force versus shear distance for a sharp AFM tip against a flat Au(111) surface...............................................................................................................................64
Figure 3.5. Friction measurements over multiple repeat cycles........................................66
Figure 3.6. AFM image of a gold surface (A) before, and (B) after shearing cycles........67
Figure 3.7. Approach force curves between a colloidal probe and a gold......................68
Figure 4.1. Schematic illustration of the experimental setup........................................72
Figure 4.2. Schematic illustration of the preparation of ultra-smooth gold substrate.......74
Figure 4.3. Plots of the friction force versus normal load on (A) a gold surface (B) an ultra-smooth Au surface...........................................................................................................76
Figure 4.4. Friction force measurements on ultra-smooth gold in electrolytes of various salt concentrations........................................................................................................79
Figure 4.5. Normal force curves recorded between a colloidal AFM probe and an ultra-smooth gold electrode surface in various electrolyte solution concentration..............81
Figure 4.6. (A) Friction force measurements on ultra-smooth gold surface in an aqueous 0.1 M NaCl solution (black) a aqueous 0.1 M NaOH solution (red). Plot of the friction force as a function of the applied potential in the range of -0.6V to +0.6 V in (B) aqueous NaCl solution and (C) aqueous NaOH solution..............................................................82
Figure 4.7. Plot of the friction force as a function of the applied potential in the range of -0.6V to +0.6 V in aqueous NaOH solution..............................................................................84
Figure 4.8. Normal force curves between a colloidal AFM probe and an ultra-smooth gold electrode surface at the various tip approach velocities........................................86
Figure 5.1. Schematic illustration of proposed mechanism for dry adhesive material....90
Figure 5.2. Bar chart of friction force between an AFM tip and the gold electrode surface in different electrolyte salt............................................................................................92
Figure 5.3. Schematic illustration proposed mechanism for reversible protein binding affinity on the charged gold electrode..................................................................................94
Figure 5.4. Schematic illustration of surface plasmon resonance technique for measuring binding affinity of molecules to the gold thin film.........................................................95
CHAPTER 1: INTRODUCTION AND BACKGROUND

In this chapter, I first provide a review of the fundamentals of intermolecular interactions, which is the underlying theme in my projects (Part I). Then, I will provide an overview of atomic force microscopy (AFM) as a characterization technique of intermolecular forces (Part II). Finally, in Part III of this chapter, I will provide the theoretical background of over instrumentation and methods that are used in projects discussed in next chapters.

Part I

1.1. Intermolecular interactions:

Intermolecular forces are almost always proportional to the product of some molecular properties of two or more particles or surfaces interacting with each other in a medium\(^1\). They can have a short-range (very close to molecular contact) or long-range (acting even beyond 100 nm) effects. Here, we are focusing on DLVO forces including van der Waals between particles and surfaces and electrostatic forces between surfaces in the liquid medium, and also non-DLVO forces e.g. solvation and hydration forces, adhesion phenomena and friction forces.

1.1.1. DLVO forces:

The DLVO theory is a dispersion stabilizing theory that explains the aggregation of particles in an aqueous solution and describes the interactions of charged surfaces in a liquid medium\(^2\)\(^-\)\(^4\). According to DLVO theory, van der Waals attraction and electrostatic repulsion (double layer of counterion) are considered to impact colloidal stability\(^5\). As two particles approach each other and get closer in a aqueous solution, attractive van der Waals forces increase. Meanwhile, the electric double layers of each particles interferes which increases the electrostatic repulsion\(^2\). At each distance, a combination of van der Waals
attraction and electrostatic repulsion determine the net potential energy. As a result, the particles experience a deep attractive well, referred to as the primary minimum, followed by a maximum energy barrier and subsequently a shallow minimum, secondary minimum, at larger distances\(^3\) (Figure 1.1). At the secondary minimum, particles form a weak reversible attraction. Particles stay in the secondary minimum state unless their kinetic energy is sufficient enough to overcome the repulsive maximum energy barrier and fall into primary minimum, in which particle aggregates irreversibly due to attraction potential\(^6\). Next, we will discuss these two forces, attractive van der Waals and repulsive electrostatics, in more details.

1.1.1.1. van der Waals between particles and surfaces:
Van der Waals forces are driven by induced charge fluctuations between two or more adjacent atoms or molecules that come close to each other. The nature of van der Waals force becomes positive when molecules and atoms outer electron clouds just barely touch each other. However, if the atoms get too close, the van der Waals interaction becomes repulsive.

The attractive van der Waals forces originate from three types of interactions: (i) dipole-dipole (ii) dipole-induced dipole (iii) London (dispersion). Movement of electrons within the atoms and molecules causes formation of dipoles, in which a partial positive ($\sigma^+$) as well as a partial negative ($\sigma^-$) charge separated by a small distance occurs inside the same molecules (Figure 1.2). Due to their strong electronegative atoms, polar molecules are able to create such partial charge distribution by themselves and establish a permanent dipole. The interaction between two permanent dipoles results in dipole-dipole interactions. Additionally, dipole molecules can persuade a dipolar nature in an adjacent molecules, which is referred to as induced dipole, creating dipole-induced dipole interaction. The London force (induced dipole-induced dipole interaction) occurs when induced dipoles induce neighboring molecules to have dipole moment by introduction of partial charge distribution and interact with them. The repulsive van der Waals also occurs when the interatomic distance of two atoms in molecules becomes below 0.4 nm, preventing the collapse of molecules.
For macroscopic bodies e.g. particles and surfaces, the van der Waals forces are calculated based on the summation over all interacting pairs and integrating over the total volume of the object\textsuperscript{7,11-12}. Thus, van der Waals interaction energies for pair of bodies depend on shape and geometry of the objects. van der Waal interactions between macroscopic bodies can be approximated in terms of the Hamaker constant and their geometries\textsuperscript{13-16}. The Hamaker constant depends on the material properties and it can have a positive or negative sign depending on the intervening medium\textsuperscript{12}. The Hamaker constant (A) can be estimated by \( A = \pi^2 C_{p1} C_{p2} \), where \( C \) is the coefficient in the atom-atom pair potential and \( p_1 \) and \( p_1 \) are number of atoms per unit volume of two bodies\textsuperscript{1}. Typical values for the Hamaker constant of condensed phase are found to be in the range of \((4 - 0.4) \times 10^{-19} J\). The shape of the bodies interacting with each other is also an important factor influencing the van der Waals interactions. For example, the van der Waals force between two spherical bodies with radii of \( R_1 \) and \( R_2 \), in the case where the spheres diameters are large compared to the distance (D) between them, is estimated to be \( \frac{-A}{6D^2} \left( \frac{R_1 R_2}{R_1 + R_2} \right) \). In the chapter 2 of this thesis, the equation for van der Waals force between a sphere of radius \( R \) and a flat surface, \(-AR/6D\), is used to calculate the van der Waals interaction between a mosquito leg and a polymer surface.

1.1.1.2. Electrostatic forces between surfaces in liquids:

Electrostatic interactions are forces between any two charged molecules and can be attractive or repulsive. At the macroscopic scale, the electrostatic forces between particles suspended in any liquid with high dielectric constant e.g. water have a repulsive nature, that prevent coagulation and precipitation of dissolved particles\textsuperscript{17-18}. 

The surfaces in a liquid can be charged through ionization or dissociation of surface groups, adsorption or binding of ions from solution onto a surface, or charge exchange between two dissimilar surfaces very close together\textsuperscript{19}. The final surface charges (either positive or negative) are electrically screened by oppositely charged counterion within a layer next to the surface\textsuperscript{20-22}. The counterions are either transiently bound to the surface within the Stern or Helmholtz layer or form an atmosphere of ion close to surface, referred as electric double layer\textsuperscript{23} (\textbf{Figure 1.3}). The net charge of these “bound” and “free” counterions in the screening diffuse double layer is equal to the net charge of surface\textsuperscript{24}. The electric potential drops as a function of the distance from the charged surface\textsuperscript{25}. The electric potential at the slipping plane, where mobile fluid is separated from that remains attached to the surface,
is referred as the zeta potential\textsuperscript{26}. Zeta potential can be used as way of estimating the charge of double layer\textsuperscript{27}. Additionally, a characteristic length known as Debye length, $k^{-1}$, is used to describe the characteristic thickness of double layer\textsuperscript{28-29}. In aqueous solution the Debye length is typically on the scale of a few nanometers and the thickness is reciprocally proportional to the square root of the ion concentration $M$\textsuperscript{30}. For example, the Debye length for a monovalent electrolyte can be estimated using the following equation $k^{-1} = 0.304 \times 10^{-9}/\sqrt{M}$. I employed this equation in chapters 3 and 4 of this thesis to estimate the Debye length of a 0.1 M NaCl solution which is calculated to be 0.96 nm\textsuperscript{1}. The interaction energy between two similar surface at constant potential, which usually repels each other in a solution, can be expressed in terms of “interaction constant” $Z$. The interaction constant $Z$, which is analogous to Hamakar constant, depends on the electrolyte valency and properties of the surface. $Z$ can be defined as $64\pi\varepsilon_0\varepsilon (kT/e)^2 \tanh^2 (ze\psi_0/4kT)$, where $\varepsilon_0, \varepsilon, T, \psi_0$ are vacuum permittivity, static permittivity, temperature, and the surface potential, respectively. Similar to van der Waals, the double layer interactions between the bodies also depend on the geometries. For example, the electrostatic double layer interaction energies and forces for two flat surfaces with separation distance of D is defined by $(k/2\pi)Ze^{-kD}$ while that for sphere of radius R and a flat surface is defined by $RZe^{-kD}$\textsuperscript{1}. The latter is applied to measure the electrostatic forces between a colloidal AFM tip and a gold surface in a NaCl solution in chapters 3 and 4 of this thesis.

1.1.2. Non-DLVO forces:

At small separation distances, closer than a few nanometers, the DLVO forces fail to explain the interactions between surfaces and particles approaching each other. At such
separations, non-DLVO forces, which can be repulsive, attractive or oscillatory, come into the play. Solvation and hydration forces between surfaces and particle are examples of non-DLVO forces\textsuperscript{31-32}.

1.1.2.1. Solvation forces:

Solvation forces are short-distance interactions between particles and surfaces and depend on intrinsic properties of solvent molecules\textsuperscript{33}. In addition to the properties of solvent, chemical and physical properties of the surfaces such as roughness, wetting, crystallinity, etc. can influence the magnitude of the solvation forces\textsuperscript{34}. Strong short-range solvation force can be a determinant factor in behavior of two surfaces or particles in “contact” or at their potential energy minimum\textsuperscript{35-36}. For example, when two inter-surfaces in liquids media are approaching towards each other, at a very small separation -near two molecules distance- they resist coming closer due to repulsive solvation forces\textsuperscript{37-38}.

Solvation force are referred to as “hydration force” when water is the medium. When two planer surfaces come very close to each other, the solvent molecules e.g. water form an ordered layer between two surfaces due to short-range solvation interactions \textsuperscript{39-40}. However, the solvation forces-thus ordering- is decaying as a function of separation distance. The magnitude of ordering of solvent molecules is induced if the surfaces are structured by itself\textsuperscript{40}. The ordering level also can be influenced by other properties of the surface such as roughness or external parameter such as applied potential. In Chapters 3 and 4 of this thesis, we will discuss ordering of water molecules between surfaces of an AFM tip and a gold (111) and the effect of applied potential on the magnitude of confinement.

1.1.3. Adhesion and wetting phenomena:
Work of adhesion is defined as the free energy change that is required to separate unit areas of two particles, surfaces, or media in contact and creates new surfaces. If this process involves with separating identical surfaces, it becomes the work of cohesion and the surface energy equals to half of the work of cleaving of the surfaces. However, to determine the work of cleavage between two non-identical surfaces or immiscible medias are in contact, Young-Dupre equation applies: 

$$ W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} $$

where \( \gamma_1 \) and \( \gamma_2 \) are surface energies and \( \gamma_{12} \) is the interfacial energy\(^4^1\).

The underlying mechanisms of adhesion phenomena can generally be described through five scenarios\(^4^2\)-\(^4^3\). The mechanical interlocking at both macro and micro scales is one of the adhesion mechanisms, which can be seen in Velcro. A network of strong chemical bonds such as ionic or covalent bonds as well as weaker bonds such as hydrogen bonding between molecules of surfaces can bring them together. This process is referred as chemical adhesion. The adhesion can also be a result of intermolecular forces such as attractions between molecules through van der Waals, known as dispersive adhesion, or attractive electrostatic forces between charged materials. Diffusion is another type of adhesion mechanism in which molecules of one surface diffuses into other surfaces and causes particles and surfaces join. Diffusive adhesion is a common adhesion mechanism in polymer-on-polymer surfaces\(^4^4\). In chapter 2, I explored the adhesion mechanisms between a mosquito leg and polymer in which van der Waals interaction mostly dominates other mechanisms of adhesion.

**1.1.4. Friction:**

Friction is described as tendency to resist the relative motion of surfaces against each other, resulting in dissipation of energy or transferring of energy from one body to another. For
example, when a body collides with another, it loses its kinetic energy which is distributed among many molecules in the form of internal kinetic energy or heat. Dry friction, relative lateral motion of two surface in contact, is the common form of the friction. Dry friction arises from interaction of surface molecules in adhesive contact. If the surfaces stay in static contact with application of a lateral force, the friction is called as static friction and equals to the applied lateral force. However, if the lateral force can overcome the intermolecular adhesion force holding the top molecules to the bottom molecules, then the surfaces slide against each other and the friction is referred as kinetic friction. The friction for molecularly smooth surface can be estimated by equation $F_\parallel = \mu F_\perp + \sigma A$, where $F_\parallel$ is lateral forces e.g. friction, $\mu$ is coefficient of the friction, $F_\perp$ is the normal forces, external loads and adhesion forces, $\sigma$ and $A$ are the shear stress and contact area, respectively.

One common behavior observed in the study of kinetic friction is stick-slip motion where surfaces move in a sawtooth motion when friction trace is recorded versus time (Figure 1.4). The origin of stick-slip friction can be explain based on the potential energy of the tribological system. The potential energy is at its minimum values when the two surfaces are at “rest” state- not subjected to any lateral forces- at the initial time ($t=0$) (point A). Applying a lateral force increases the potential energy while the surfaces are still at “stuck” state and not moving against each other (point B). The potential energy decreases and dissipates as the surface start to “slip”. At point C, the energy is completely dissipated and the surfaces go back to the “stick “ state again.

Two surfaces separated by a liquid film cannot come into contact due to repulsive solvation, double layer, and hydration forces. The film stays in between the surfaces and
reduces the friction between them and avoids the damages due to shearing\(^49\). The thicker and less viscous film provides better lubrication effect between the bodies. The lubricated friction force for two parallel surfaces can be estimated by equation \(F_{\parallel} = \frac{\eta A V_{\parallel}}{D}\), where \(\eta\), \(A\), \(V_{\parallel}\), and \(D\) are film viscosity, surface area, relative velocity, and separation, respectively\(^1\).

Due to confinement of the liquid molecules between two surfaces, both static and dynamic properties of the thin liquid film, and thereby the lubricated friction, significantly change\(^50\). For example, the shear viscosity of the film confined between two surfaces usually increases, enhancing the viscous force and increasing the \(F_{\parallel}\)\(^51\). The confinement of the molecules between surfaces and formation of an aligned “solid-like” film can be influenced by other stimuli such as applying an external potential to the surfaces. In chapters 3 and 4, I provide an in-depth study of effect of application of potential on the formation of highly viscous “ice-like” water film between an AFM probe and a gold surface. I also investigated the change in the shear viscosity of water next to the charged gold surface and how surface potential will affect the viscosity and resulting friction between these surfaces.

**Figure 1.4.** The recorded friction force at the interface between two shearing surfaces as a function of time.

**Part II**
1.2. Atomic Force Microscopy:

AFM is a scanning probe microscopy (SPM) technique that is capable of visualization of a surface and investigation of the surface and interface phenomena at the atomic scale\textsuperscript{52}. AFM can be employed for topographical application e.g. imaging topography of insulating or conductive surfaces (image mode) and force spectroscopy (force mode)\textsuperscript{53}. The latter is one of the most promising tools for measuring atomic scale forces to estimate intermolecular bonds strength. Because AFM can quantify extremely small forces with a dimensional resolution below 0.1 nm, it has received considerable interest for investigating atomic-scale adhesion and tribological phenomena \textsuperscript{54}. Furthermore, AFM is capable of stimulating relative motion of single asperities against each other. Therefore, it can provide a great insight into mechanism of atomic-scale friction as well as adhesion. Here, we aim to provide a brief overview of the AFM and its application in study of micro/nano scale adhesion and friction.

1.2.1. Mode of operation:

The basic operation of the AFM involves scanning over a sample surface with a sharp tip or a probe (\textbf{Figure 1.5}). The tip is situated at the apex of a flexible cantilever, either a V-shaped or a rectangular shaped, that is used as a transductor of interactions between the tip and a sample. Commercial tip and cantilevers are typically made of silicon or silicon nitride. Depending on specific system, either the cantilever chip or the sample is mounted on a piezoelectric material that can move with precision of sub nanometer. The
Piezoelectric system allows fine movement of the tip in three dimensions with respect to the sample. For imaging, the tip is brought into contact with the sample and it scans over the surface in a raster manner. During scanning, any interaction between the tip and the sample, which causes deflection of the cantilever, can be detected through reflection of a laser beam focused at the back side of the cantilever to a position sensitive photodetector. The photodetector involves a quadrant photodiode divided into four elements, providing different information depending on the operation mode. The differences in signals between summation of two top elements (A+B) and summation of two bottom (C+D) allow detection of the vertical deflection of the cantilever. Similarly, signal differential of two

**Figure 1.5.** Schematic illustration of atomic force microscopy (AFM) instrumentation.
left quadrants (A+C) and two right ones (B+D) provides a measure of lateral deflection of the cantilever.

AFM is able to operate in different modes that provide various types of information about the surface and interface properties of the system being examined. One of the most common modes of operation is contact mode, in which the tip stays in contact with the sample surface during scanning. By switching off the force feedback control, the tip remains in constant z-height and the topographic image is produced by monitoring cantilever deflections. Contact mode is able to be operated in either air or liquid environments. Scanning in fluid environment eliminates the capillary force, which can substantially affect force curves in humid environment, and largely screen the electrostatic forces. There are several drawbacks involve with using contact mode such as image artifacts and data distortion originating from the frictional forces applied to the surface by the tip. Therefore, in the case of softer sample, use of other mode e.g. tapping mode in which the tip is not in constant contact with sample surface during scanning, would be preferred. However, the contact mode is the only mode that provide information about lateral interactions and friction forces between the tip and the surface.

1.2.2. Lateral Force Microscopy:

Lateral force microscopy (LFM) operates very similar to contact mode: however, the torsional deflection of the cantilever is measured in LFM. In this mode, the tip scans the substrate perpendicular to the long axis of cantilever. Forces parallel to plane of substrate surface can cause a torsion of the cantilever around its long axis. For example, friction can decrease and increase the torsional deflection of the cantilever, depending on scanning
This torsional deflection is measured by the quadrant photodiode, allowing tracking of friction trace between the tip and the sample. Figure 1.6 shows friction trace, which indicates torsional deflection of cantilever, as the cantilever scans the surface of the substrate. The surface profile exhibits a step located in the middle (Figure 1.6A). The areas on top and either side of the step is smooth with low friction. The left and right side of the step contains a domain with relatively high and low coefficient of the friction, respectively. Figure 1.6B shows the deflection of the cantilever as the tip scans the surface in the forward direction. Figure 1.6C and D exhibits friction signals for both forward and
backward directions. In the forward scan, as the tip passes the dashed line 1 and scans the region with higher coefficient of the friction, which results in a torsional deflection of the cantilever, an increase in the friction appears in the trace (Figure 1.6C). However, this region causes a torsional deflection of the cantilever in the opposite direction in the backward scan, resulting a drop in the friction signal (Figure 1.6D). The edges of the step (dash line 3 and 4) also generate a change in the friction signal in both forward and backward directions.

1.2.3. Force calibrations

The cantilever deflections, results from the tip and the surface interaction, are converted into voltage-based signal though a position sensitive detector (PSD)\textsuperscript{55}. Essentially, converting the PSD response into meaningful quantitative data requires precise measurement of the tip and the cantilever properties, including normal and lateral force constants, the tip height and structure, and the deflection sensor response.

Overall, the normal $F_N$ and lateral $F_L$ forces acting on the tip can be expressed as a function of cantilever normal $\Delta U_N$ and lateral $\Delta U_L$ deflection through following equations \textsuperscript{56}.

\[
F_N = \alpha \Delta U_N \\
F_L = \beta \Delta U_L
\]

where $\alpha$ and $\beta$ denotes as normal and lateral calibration factor.

The calculation of normal force calibration factor can be quantified using values of normal spring constant and normal photodiode sensitivity \textsuperscript{56}.

\[
F_N = \alpha \Delta U_N = K_N S_N \Delta U_N
\]

Where, $K_N$, $S_N$, and $\Delta U_N$ are the cantilever normal constant, the photodiode normal sensitivity, and the cantilever normal deflection, respectively.
Numerous calibration procedures have been proposed for estimation of normal spring constant including direct measurement, geometrical calculations, finite element analysis, and thermal tune. The cantilever lateral constant can be calculated from continuum elasticity mechanism of isotropy solid.

\[ K_N = \frac{Ewt^3}{4l^3} \]

where, \( E, w, t, \) and \( l \), are Young’s modulus, cantilever width, cantilever thickness, and cantilever length, respectively.

However, this equation is only applicable for calculating spring constant of single beam cantilever and other methods such as finite element analysis (FEA) can be utilized for V-shaped cantilevers. Additionally, the accurate measurement of the spring constant using above mentioned equation demands precise determination of the cantilever dimensions.

**Figure 1.7.** Plot of photodiode current output versus separation. The red line/blue line corresponds to the tip approaching/retracting to/from the surface.
cantilever material properties, and the tip height. Additionally, reflective coatings of
cantilevers further influence the cantilever lateral stiffness and increases the inaccuracy of
the calculations. To overcome these challenges, other methods such as thermal fluctuation,
have been proposed to precisely measure the cantilever spring constant\(^57\).
The thermal fluctuation, also known as thermal tune method, most commonly calculation
of spring constant through change in cantilever’s resonance frequency induced by thermal
fluctuations\(^57\)\(^-\)\(^58\). Thermal tune is a fast and direct method that has been increasingly
adopted by researchers to determine cantilever normal spring constant. In our work, we
used thermal tune method as a reliable method of cantilever normal spring constant
calibration.

The normal sensitivity of the photodiode \((S_N)\) relates the normal displacement of the
cantilever and the resulting photocurrent in the photodiode. The normal sensitivity can be
determined by the slope of vertical voltage signal verses distance curve \(S_N = X_N / I_N\) \(^54\).

**Figure 1.7** is recorded by engaging the tip on a hard surface and ramping while measuring
the resulting photodiode current. During a ramping experiment, the tip approaches to,
engage on, and retract from the surface once and the interaction between the tip and
surfaces is recorded based on change in photodiode currents, due to the cantilever
deflection, versus separation.

Interpretation of cantilever response to the lateral forces is not as straightforward as
calibration of normal forces and obtaining reproducible quantitative measurements
necessitates further calibration steps. Although, number of calibration methods have been
proposed for measurement of lateral calibration factor\(^59\)\(^-\)\(^61\), there is still no single
standardized calibration method that offers an easy, fast and accurate way for quantifying
the lateral force. Most of the proposed calibration approaches can be categorized into two groups: two-step calibration method and the wedge (direct) methods. In this thesis, I chose two-step calibration procedure for calibration of lateral spring constant of the cantilever. The two-step calibration method relies on measurements of (i) the spring lateral constant \( (K_L) \) of the cantilever based on geometries and material properties and (ii) the photodiode lateral sensitivity \( (S_L) \). Analogous to the calculation of the normal force, the lateral force can be expressed as

\[
F_L = K_L S_L \Delta U_L = \beta \Delta U_L
\]

Similar to cantilever normal calibration, the cantilever lateral constant can also be calculated from continuum elasticity mechanism of isotropy solid

\[
K_L = \frac{G wt^3}{3lh^2}
\]

\[
G = \frac{E}{2(1 + v)}
\]

---

**Figure 1.8.** Plot of photodiode lateral current output versus separation. The red line/blue line corresponds to the forward/backward scan direction.
where, $G$, $v$, and $h$ are shear modulus, Poisson’s ratio, and the tip height, respectively.

The photodiode lateral sensitivity $S_L$ can be determined via different procedures. One of the common methods to obtain $S_L$ is measurement of initial slope of friction loop, in which the photodiode response to lateral deflection in the cantilever is plotted against the piezo displacement in both forward and backward directions\(^6^5\) (Figure 1.8). At the beginning of scan in forward or backward direction, the tip sticks to the surface due to static friction. If one assumes the contact between the tip and the surface is infinitely stiff, then the deflection occurs only in the cantilever and the slope can be interpreted as photodiode output. However, in real system, finite contacts, lateral contact stiffness, and lateral cantilever stiffness affects the initial slope of the friction loop\(^6^5\).

The two-step calibration approach can also be utilized to calibrate frictional forces using colloidal probes\(^6^6\). Due to their smaller stress region and a broader choice of probe material, the colloidal probes have been found to have extensive application in the study of tribological phenomena. However, the quantitative measurement of lateral forces by a colloidal probe deals with higher level of complications because total lateral stiffness of a cantilever will consist of both cantilever lateral stiffness and colloidal tip lateral stiffness whereas the tip lateral stiffness is considered negligible for integrated tip probes.

The lateral sensitivity of the colloidal probe can be estimated by the slope of linear part of the friction loop similar to the integrated tip probes. However, larger area of the colloidal probe causes finite contact area between the tip and the surface which can be subject to significant deformation, affecting the overall lateral stiffness\(^6^7\). To resolve this issue, the lateral sensitivity should be estimated from the slope of linear part of the friction loop at a comparatively large normal applied loads, in which the lateral probe surface stiffness will
approach zero. Lateral sensitivity values of the colloidal probe are calculated for different loading forces. Plotting lateral sensitivity verses load, the lateral sensitivity will reach a plateau which is the point that the sensitivity is calculated as the overall lateral sensitivity of the probe.

Part III

1.3. Characterization and instrumentation:

1.3.1. Cyclic Voltammetry

The cyclic voltammetry is a potentiodynamic electrochemical experiment, in which the current is measured as the potential of working electrode is ramped linearly versus time in cyclical phases. Because the potential of working electrode is kept constant against a reference electrode, applying a potential produce a current signal, which is measured between the working electrode and the counter electrode. The resulting current versus applied potential signal produce a plot that is similar to the figure 1.9. During the forward
scan, the potential is swept to the right - an increasingly reducing potential is applied- a cathodic current begins to flow, resulting in reduction of analytes in the system which appears as a peak. As the concentration reducible analyte decreases, the current decreases.

During the reverse scan, the analyte oxidizes -if the redox couple is reversible, and a similar oxidation peak appears.

In my experiments, I assembled a homebuilt AFM friendly 3-electrodes electrochemical cell setup to run cyclic voltammetry experiments and simultaneously track changes in friction between an AFM tip and a gold surface as a function of applied potential. To perform 3-electrode cyclic voltammetry electrochemistry, I used a gold substrate, Pt mesh, and Ag wire as the working, counter, and reference electrodes, respectively. I performed similar cyclic voltammetry (CV) tests on the gold electrode using a conventional PTFE cell and I observed similar CV data as our homebuilt set-up, which conformed the reliability of our set-up.

1.3.2. Thin film deposition: Preparation of the gold coated mica

1.3.2.1. Thermal evaporation deposition:

Thermal evaporation is a physical evaporation technique that allows uniform thin film deposition of materials on varieties of substrates. In a vacuum chamber, a deposition material- commonly metals such as gold- is heated up to its evaporation point. The evaporated molecules travel through the chamber and when they colloid to the substrate surface, they lose their kinetic energy, deposit on the substrate, and form a thin film of the evaporation material (Figure 1.10). A quartz crystal is used throughout of film depositions to calibrate and control the deposition rate and the film thickness. A film proportional to the one deposited on the substrate, coats the surface of the crystal cause a change of
frequency which can be related to the mass change per crystal area and then the thickness of the deposited film on the substrate.

In our experiments, we utilized thermal evaporation technique to prepare the gold substrate as a working electrode. A 15-mm mica disk (Highest Grade V1 AFM Mica Discs, Ted Pella, Inc.) was cleaved using a sharp blade and immediately inserted to the sputtering
vacuum chamber (ATC Orion Sputtering System, AJA International, Inc.). A 100 nm gold film was deposited on the mica substrate via thermal evaporation using a deposition rate of 1Å/sec and the vacuum was maintained at approximately $10^{-6}$ Torr. The gold-coated mica substrate was allowed to slowly cool down to room temperature over 20 minutes. The substrate was then washed and cleaned with deionized water, dried in air, and used as a working electrode.

1.3.2.2. E-Beam evaporation deposition:

E-beam evaporation is another type of physical vapor deposition, that utilizes high energy electron beam to heat up a evaporation material in a high vacuum environment. An electron beam, which is given off by a charged tungsten filament, bombards a target anode (evaporation material), heating up the target, causing atoms from the target evaporate in the chamber. The evaporated atoms travel in the chamber and participate on the substrate in form a solid film. One of the e-beam evaporation advantages over thermal evaporation is being able to precisely control the thickness and uniformity of the film.

3.3. Scanning electron microscopy (SEM):

Scanning electron microscopy operates based on interaction between a beam of electrons and a sample surface. The electron beam scans over the sample in as a raster pattern and interacts with the surface. Thus, some of the electrons knock out from the surface as secondary electrons while some of them are backscattered. Additionally, radiations such as x-ray can also be generated during the process. A detector positioned above the sample in the chamber collects secondary electrons and accelerates them. The highly energetic accelerated electrons emit flashes of lights that are guided to a photomultiplier, in where the electrical signal is amplified. Finally, the photomultiplier output is displayed as a gray
scale image. It should be consider that the sample used for SEM imaging must be electrically conductive. Otherwise, charging of non-conductive sample happens, that can cause scanning faults and image artifacts. To avoid charging issues, non-conductive materials are coated with a thin film of electrically conductive material including graphite and gold. In this work, the SEM is used to collect high resolution images of specimens and characterize the morphology of surfaces.

1.3.4. Contact angle goniometer:
Utilizing an optical system, the contact angle goniometer allows capturing of the profile of a pure liquid droplet on a solid substrate. The contact angle is defined as the angle between the liquid-solid interface and the liquid-vapor interface. The contact angle quantifies the wettability properties of solid surfaces. In this work, a contact angle goniometer is used to measure contact angles of water on the surfaces e.g. silicon wafer and characterize the hydrophilicity/ hydrophobicity.

1.3.4. Profilometer:
A profilometer allows measurement of the profile, topography, and roughness of surfaces. In this work, we only used an optical profilometer that able to measure the surface topography with a single camera acquisition. Using optical profilometer can be a challenging task when we attempt to capture profile of a dark non-reflective sample such as high density poly ethylene (HDPE), which is used in the first project of this work. To overcome such challenges, a layer of ultrathin coating with a reflective material e.g. gold is needed.
1.3.5. Photolithography: preparation of patterned surfaces

Photolithography is a microfabrication technique that utilizes light to transfer a pattern from a photo-mask to a light-sensitive material—known as photoresist—coated on a substrate. The photolithography process starts with spin coating of a cleaned substrate with photoresist material, followed by pre-baking via heating the substrate to remove the solvent. After aligning the photomask, the photoresist-coated substrate is exposed to an intense light e.g. UV light that causes a chemical reaction with the photoresist, allowing unexposed or exposed area—depending on the photoresist—to be removed by a solvent. Then, the substrate goes under a post-exposure bake by heat. In this work, I utilized photolithography to make a uniform pillar pattern on a silicon wafer. SU-8 3024 was chosen as the photoresist and spun coated at the speed of 2000 rpm to obtain a 40 micrometers film thickness on a silicon wafer.
CHAPTER 2: ENHANCED ADHESION OF MOSQUITOES TO ROUGH SURFACES

2.1. Introduction

Numerous studies have been conducted to understand the mechanism of biological adhesion of animals including geckos, spiders, and beetles\textsuperscript{68-73}. Particularly, in hairy attachment systems, the setae (micro and nanoscale structures) have been found to greatly enhance adhesion on a variety of surface topographies\textsuperscript{74-80}. For example, the integument and microfeatures in the feet of geckos and flies have drawn immense attention in the scientific world and have inspired the design of synthetic dry adhesives\textsuperscript{81-84}. It has been shown that van der Waals interactions in gecko foot pads are responsible for the strong adhesion to a variety of surfaces\textsuperscript{82, 85}. However, for flies, strong adhesion is caused by a sticky secretion in addition to van der Waals and electrostatic forces\textsuperscript{83}. Mosquitoes utilize a foot pad similar to flies in adhering to smooth surfaces but they are also capable of walking on water like a water strider\textsuperscript{86-87}. Mosquito legs consist of a large number of oriented micro/nanostructure scales (Figure 2.1A and 2.1B) which result in superhydrophobic legs (contact angle of water $\sim 153^\circ$)\textsuperscript{88-89}. Previous studies of mosquito legs have focused on the interactions with water which play a crucial role in their reproductive cycle\textsuperscript{88-90}. However, less attention has been given to understanding the underlying mechanism by which mosquitoes adhere to solid surfaces of various wetting properties, roughness and different humidity conditions. Here we show the effect of rough surfaces (by imparting fibrous elements) on mosquito adhesion and provide
Figure 2.1. (A) SEM image of a mosquito leg showing the micro-/nanoscale setae structures (false color was added to the SEM images using ImageJ software to highlight the nano/microscale features of the mosquito leg); (B) SEM image of distal part of a mosquito leg; (C) Schematic illustration of the micro/nano-scale structures on the leg making intimate contact with fibers on the rough surface (right image) compared to smooth surface (left image).
greater insight into the adhesion mechanism, i.e., the relative contribution of van der Waals forces to the overall adhesion force under various temperature ranges and humidity levels. The micro/nano-scale structures on the mosquito leg result in multiple points of contact with the fibrous elements on rough surfaces resulting in an enhancement of van der Waals interactions (Figure 2.1C). By introducing more asperities, the tarsus part of the leg contributes more to the adhesion with the rough surface compared to the smooth surface. Previous studies on natural and synthetic dry adhesives have shown that increasing roughness typically reduces adhesion between surfaces due to an overall decrease in the true contact area between the adhering surfaces\textsuperscript{91-93}. For example, Jin et al. showed that gecko adhesion can be mimicked as smooth dry adhesive pads; however, the adhesion was only effective when used on highly flat surfaces\textsuperscript{94}. However, in this study, we hypothesize that increasing surface roughness by adding fibrous structures can further increase adhesion forces by creating multiple contact points. To my knowledge, this is the first study that investigates the interaction between a mosquito leg and surfaces (smooth, rough, and patterned) by using atomic force microscopy, presumably because of the difficulty associated with the length scale and fragile nature of the mosquito legs, and the lack of sensitivity of other force measurement techniques. Our results bring new insights to the adhesion mechanism of mosquitoes and can potentially be applied directly to improve the efficiency of Long Lasting Insecticidal Nets (LLINs). LLINs have played an important role in the control of mosquitoes which are vectors for a number of parasites and viral pathogens affecting hundreds of millions of people worldwide\textsuperscript{95-96}. By introducing fibrous elements in LLINs, the adhesion of mosquitoes to the nets are expected to increase thereby increasing the duration of insecticide exposure leading to greater mosquito deaths.
2.2. Experimental Section

2.2.1. Attachment of a mosquito leg to AFM cantilever. Colonies of *Anopheles gambiae* and *Anopheles stephensi* mosquitoes were maintained in an environmentally controlled room maintained at 70-80% relative humidity and 27°C. The distal portion of a leg was sheared off an *A. gambiae* mosquito with the aid of ultra-fine tip tweezers. Using an optical microscope, the specimen was then glued to the end of a contact mode cantilever of an AFM probe (MPP-31200-10 probe, No Coatings, Bruker). Super glue (Loctite ultra gel, Loctite) was used to adhere the mosquito leg perpendicularly to the cantilever. SEM images were then used to verify that the glue did not spread along the terminal end of the leg or the cantilever. Three specimens with different limb curvatures (resulting in different tilt angles upon contact) were attached to an AFM cantilever following the same procedure and were installed in the AFM (Dimension Icon, Bruker).

2.2.2. Preparation of surfaces with different random roughness. High density polyethylene (HDPE, McMaster-Carr) sheets and silicon wafers (Test grade, University Wafers) were used as the opposing surfaces to measure adhesion forces. The rough surface was created by shearing a smooth HDPE surface using mechanical drilling (Dremel8100) with stainless steel and aluminum cleaning and deburring brush attachment. Brush attachments with different diameters were supplied by McMaster-Carr. First, a pre-force of 294 mN was applied on the HDPE surface with the Dremel brush tip. The brush was spun at a setting of 2 (corresponding to approximately 5000 RPM) and moved laterally over the surface at a speed of 3 mm s⁻¹. Low roughness, intermediate roughness and high roughness surfaces were prepared by using 1.5-in, 1-in and 0.75-in diameter brush attachments, respectively. An unmodified HDPE sheet was utilized as a smooth surface.
ATR-FTIR\textsuperscript{97} was used to confirm that there was not any change in the surface chemistry of the HDPE due to mechanical drilling (Figure\textsuperscript{2.2}). A silicon wafer was cut into 1x1 cm\textsuperscript{2} pieces, cleaned with sulfuric acid and rinsed with water to create a hydrophilic surface. The static contact angle of water on both silicon wafer and HDPE sheet were determined by means of the contact angle goniometer (Rame-Hart Instrument co.). The HDPE sheets were inherently hydrophobic and the acid-cleaned silicon wafer was hydrophilic.

### 2.2.3. Fabrication of Patterned surfaces with uniform roughness:

Using photolithography, a uniform pillar patterned was created on a silicon wafer (test grade, University Wafers) using SU-8 photoresist (MicroChem). According the protocol provided by MicroChem, SU-8 3025 was selected and spun coated at a speed of 2000 RPM to obtain a 40 μm film thickness on a silicon wafer. The wafer then was thoroughly washed by DI water and dried by air. The pillars diameters, heights, and spacing were characterized using an optical profilometer and SEM.

### Table 2.1. Roughness of HDPE and Patterned surfaces.

Scan sizes were 834x834 μm\textsuperscript{2} and 167x167 μm\textsuperscript{2} for the large-scale RMS and local RMS values, respectively.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Large-scale RMS [μm]</th>
<th>Local RMS [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I : (smooth)</td>
<td>4.51±0.75</td>
<td>2.31±0.20</td>
</tr>
<tr>
<td>II : (low roughness)</td>
<td>14.3±2.29</td>
<td>7.32±0.87</td>
</tr>
<tr>
<td>III : (intermediate roughness)</td>
<td>62.7±7.47</td>
<td>8.27±2.25</td>
</tr>
<tr>
<td>IV : (high roughness)</td>
<td>148±13.4</td>
<td>20.7±6.17</td>
</tr>
<tr>
<td>Patterned</td>
<td>5.88±0.59</td>
<td>---</td>
</tr>
</tbody>
</table>
Figure 2.2. ATR-FTIR spectra of surfaces. (A) ATR-FTIR spectra for flat HDPE surface. (B) ATR-FTIR spectra for fibrous Surface III. (C) Comparison of ATR-FTIR spectra of flat and fibrous surfaces.
Figure 2.3. Profilometry images of large-scale and local RMS for surfaces I, II, III, and IV. Sq values are equal to RMS values. (A) Surface I large-scale RMS, (B) Surface I local RMS, (C) Surface II large-scale RMS, (D) Surface II local RMS, (E) Surface III large-scale RMS, (F) Surface III local RMS, (G) Surface IV large-scale RMS, (H) Surface IV local RMS.
2.2.4. HDPE Surface roughness characterization. An optical profilometer (Zegage, Zygo) was used for measuring the roughness of the HDPE surfaces and the patterned surface. To increase reflectivity and clarity of the HDPE profilometer images, the HDPE surfaces were coated with a gold film (thickness $\approx 400\text{nm}$) via sputtering (ATC Orion Sputtering System, AJA International Inc). Local roughness and large-scale roughness values are reported in Table 2.1 were averaged over 5 randomly picked regions (167 $\mu\text{m} \times 167 \mu\text{m}$) and (834 $\mu\text{m} \times 834 \mu\text{m}$), measured by using a 50X and a 10X magnification, respectively. Representative profilometery images of all HDPE surfaces are available in Figure 2.3. The average roughness values of the patterned surface are reported in the Table 2.1. Because of uniformity of the features on
the patterned surface, only large-scale roughness values were measured. A representative profilometer images of the patterned surfaces is shown Figure 2.4. Table 2.2 and Table 2.3 exhibit all the roughness parameters for large-scale and local scale roughness for the patterned surface and HDPE surfaces.

2.2.5. Force measurement of a mosquito leg attached to an AFM cantilever. Using the well-established thermal noise method, uncoated contact silicon cantilevers were

Table 2.2. Large-scale roughness characterization of the patterned and HDPE surfaces. Sa, Sq, Spv, Sk, Spk, Svk are arithmetical mean roughness, root mean square roughness, Maximum height of profile (differences between highest and lowest point of height profile), core roughness depth, reduced peak height, and reduced valley depth, respectively.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Sa</th>
<th>Sq</th>
<th>Spv</th>
<th>Sk</th>
<th>Spk</th>
<th>Svk</th>
</tr>
</thead>
<tbody>
<tr>
<td>I : (smooth)</td>
<td>3.6±0.60</td>
<td>4.51±0.75</td>
<td>31.1±9.59</td>
<td>9.76±1.24</td>
<td>3.41±0.68</td>
<td>2.27±0.08</td>
</tr>
<tr>
<td>II : (low roughness)</td>
<td>10.9±2.18</td>
<td>14.3±2.29</td>
<td>175±34.8</td>
<td>38.6±9.05</td>
<td>45.5±7.09</td>
<td>6.9±0.31</td>
</tr>
<tr>
<td>III : (intermediate roughness)</td>
<td>48.8±7.14</td>
<td>62.7±7.47</td>
<td>419±79.8</td>
<td>134±14.8</td>
<td>31.3±11.1</td>
<td>36.9±5.01</td>
</tr>
<tr>
<td>IV : (high roughness)</td>
<td>78.5±29.5</td>
<td>148±13.4</td>
<td>580±92.6</td>
<td>207±50.5</td>
<td>208±66.3</td>
<td>255±39.2</td>
</tr>
<tr>
<td>Patterned</td>
<td>2.9±0.44</td>
<td>5.88±0.59</td>
<td>59.4±0.42</td>
<td>5.05±0.65</td>
<td>17.5±1.07</td>
<td>8.49±0.70</td>
</tr>
</tbody>
</table>

Table 2.3. Local-scale roughness characterization of HDPE surfaces. Sa, Sq, Spv, Sk, Spk, Svk are arithmetical mean roughness, root mean square roughness, Maximum height of profile (differences between highest and lowest point of height profile), core roughness depth, reduced peak height, and reduced valley depth, respectively.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Sa</th>
<th>Sq</th>
<th>Spv</th>
<th>Sk</th>
<th>Spk</th>
<th>Svk</th>
</tr>
</thead>
<tbody>
<tr>
<td>I : (smooth)</td>
<td>1.76±0.26</td>
<td>2.31±0.20</td>
<td>13.4±1.52</td>
<td>4.8±0.71</td>
<td>1.45±0.08</td>
<td>1.91±0.13</td>
</tr>
<tr>
<td>II : (low roughness)</td>
<td>4.80±0.78</td>
<td>7.32±0.87</td>
<td>46.7±18.7</td>
<td>11.7±0.80</td>
<td>9.9±0.82</td>
<td>2.69±0.05</td>
</tr>
<tr>
<td>III : (intermediate roughness)</td>
<td>5.82±2.03</td>
<td>8.27±2.25</td>
<td>62.2±24.6</td>
<td>32.8±9.35</td>
<td>64.9±15.1</td>
<td>27.3±3.62</td>
</tr>
<tr>
<td>IV : (high roughness)</td>
<td>19.5±9.03</td>
<td>20.7±6.17</td>
<td>164±57.3</td>
<td>85.1±18.0</td>
<td>30.2±12.1</td>
<td>51.3±11.4</td>
</tr>
<tr>
<td>Patterned</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
calibrated to measure the spring constant. The spring constants and sensitivities ranged from 0.34 N m\(^{-1}\) to 0.44 N m\(^{-1}\) and from 213 nmV\(^{-1}\) to 273 nmV\(^{-1}\), respectively. Since the mosquito legs were not perfectly positioned at the tips of cantilever, the spring constants were corrected using \(K = K_0 (L - ΔL)^3\) where \(K_0\) is the initial spring constant, \(L\) is the length of cantilever and \(ΔL\) is distance that the mosquito leg is offset from the end of the cantilever\(^9\). Each leg (attached to the tip of the AFM cantilever) was brought into contact with the surface by applying a vertical preload of 50 nN to ensure contact between the leg and the surface of interest. Experiments were performed using ramp mode in Peak Force Quantitative Nanomechanical Mapping (PFQNM) in air at 20 °C and a relative humidity (RH) of 75% to quantify the adhesion force between the specimen and the surface. During ramping, a tip is moved towards (i.e., approached) the surface until contact is achieved, followed by separation (i.e., retraction). The force is simultaneously recorded over the entire process. In this study, the preload was limited to <50 nN so as to avoid damaging either the leg specimen or AFM probe.

2.2.6. Experimental setup to study the effect of surface roughness and humidity.

Three types of experiment were performed to study the influence of surface roughness and humidity. The first set of experiments consisted of collecting adhesion data between a mosquito leg (3 different mosquito leg specimens were used) against a smooth surface (i.e., smooth HDPE), and against a rough HDPE surface (intermediate roughness). The second set of experiments involved collecting adhesion force data between specimen I against smooth, low roughness, intermediate roughness, and high roughness surfaces to investigate the effect of roughness on the adhesion forces. For these experiments, adhesion measurements were performed between the specimen and 100 test points on the
surface chosen at random. The average of the 100 adhesion force measurements was reported as the adhesion force. The third set of experiments was performed to investigate the effect of humidity on the adhesion force between a mosquito leg and surfaces with different surface energies (or wetting properties). The experimental set up consisted of a chamber placed around the AFM head, which allowed relative humidity control. The humidity level was adjusted by varying the ratio of flow rate of dry nitrogen to the flow rate of a saturated water vapor air stream. This ratio varied from 1, 0.67, 0.53, 0.41, 0.36, 0.32, 0.26, 0.17, and 0 resulting in relative humidity values ranging from 10 % to 90 % in 10 % increments, respectively. The substrate types used were a silicon wafer and smooth HDPE sheet. 100 test point measurements were performed repeatedly on two random points for both surfaces. It was found that the mosquito claw broke off during force measurements on randomly rough surfaces presumably due to mechanical interlocking and loosely bound setae were also lost. By not including the first 10 force data points, only adhesion force contributions from intact setae and the opposing surface are measured. Another set of experiments was performed to characterize the interaction between a mosquito leg and a patterned rough surface comprising of cylindrical pillars in a square lattice. In this experiment, 20 test points were chosen for four different mosquito leg landing locations (fewer test points were needed due to the low variability of the data). The average force and the standard deviation (i.e., error bars) were reported. The AFM optical camera attachment was used to precisely record the location of contact for each experiment.

2.2.7. SEM Imaging. Scanning electron microscopy (Hitachi High –Technologies Corporation, Tokyo, Japan) was used to verify the leg attachment to the AFM cantilever,
Figure 2.5. (A) SEM images of mosquito legs attached to AFM cantilevers. (B) Typical force-distance curves for the mosquito leg (Specimen I) during its retraction from a smooth surface (red line) compared to rough surface (blue line); (C) Bar chart of mean of 100 adhesion point measurements. Error bars are standard deviations of data.
characterize HDPE surfaces and the patterned surface, and also monitor any damage to the mosquito leg after adhesion tests. The samples were mounted on the sample holder and a thin layer of carbon was deposited on the samples by a sputter-coating device (Cressington Scientific Instruments Ltd.).

2.3. Results and Discussion

2.3.1. Effect of surface roughness on adhesion force. Experiments were conducted using an atomic force microscopy (AFM) to study adhesion properties of a mosquito leg (Anopheles gambiae) on high density polyethylene (HDPE) surfaces. Distal parts of three mosquito legs were attached to AFM cantilevers as shown in Figure 2.5A. The claws on the mosquito feet typically broke off after the initial 10 pull-off adhesion experiments (these data points were not included in the reported force data) thereby allowing for the interaction force measurement solely between the setae and the opposing surfaces. Figure 2.5B shows typical retraction force curves obtained for the interaction of a mosquito foot with a smooth compared to a rough surface. The large negative peak in the force curve

![Figure 2.6](image_url)

Figure 2.6. SEM images of the distal end of a mosquito leg after repeated adhesion force measurements. (A) SEM image of a leg attached to an AFM probe showing the distal part of the leg. Inset shows a zoomed in image. The red line shows the position where the foot claw breaks off. (B) SEM image of the leg without the claw section. Inset image shows a higher magnification view of the terminal end after performing 100 adhesion measurement on a flat HDPE surface. (C) SEM image of the same section after performing 100 adhesion measurements on the intermediate rough surface.
obtained with rough surface (blue line) corresponds to a higher adhesion force on the rough surface. Experiments were repeated with 3 separate mosquito leg specimen samples. For all three specimens, higher adhesion forces between the leg and a rough surface were recorded compared to a smooth surface (Figure 2.5C). A control experiment was performed to confirm that no damage of the setae takes place during adhesion force measurements (Figure 2.6).

Similar results were observed for the leg of another species of mosquito, i.e., Anopheles stephensi (Figure 2.7). We hypothesize that roughness increases the real contact area between the mosquito leg and the HDPE surface by creating multiple points of contact between the rough surface elements and micro/nano-scales setae on the mosquito leg. On a smooth surface, only the terminal end of the mosquito foot comes into contact with the surface, whereas on a rough surface, the distal part of the mosquito leg (which also contains setae) also contributes to the adhesion force. Specimen I produced an average adhesion

![Figure 2.7. Average adhesion force results for 100 adhesion measurements between an Anopheles stephensi mosquito leg and a smooth surface (red column) and a rough surface (blue column).](image-url)
force of 12.04±6.95 nN on a smooth surface and 76.22±67.41 nN on a rough surface, an increase of adhesion by a factor of six. The adhesion forces were slightly higher for specimen II (smooth surface ≈22.97±10.93 nN, rough surface 75.18±48.17 nN) and specimen III (smooth surface ≈125.23±71.63 nN, rough surface 370.96±239.92 nN). We attribute the difference in the adhesion forces between the three specimens to the relative orientation differences of the distal portions of the legs. Higher curvatures of the distal ends of leg III resulted in greater van der Waals interactions between the leg and fibrous elements on the rough surface. This suggests that the adhesion forces are sensitive to the curvature of the distal portion of the specimens (Figure 2.8). Based on an analysis of the increase in contact area of the distal part of the mosquito foot as a function of the curvature, the adhesion force can be partially explained by the increased van der Waals interactions. However, mechanical interlocking and/or setae density variations can also contribute to the increased forces.

To estimate the effect of curvature on the adhesion force, we can estimate the ratio of area that specimen I exposes to fibers compared to specimen III. Since the leg is covered by

![Figure 2.8](image_url)

**Figure 2.8.** Schematic of van der Waals interaction for legs with different curvatures at the distal ends of the legs. (a) The distal end of leg does not have any curvature. (b) The distal portion of the leg has higher curvature, resulting in more setae interacting with surface leading to higher adhesion forces.
setae, the density of the setae has an additional effect on the contact area between fibers and the specimens.

\[
\frac{A_{III}}{A_i} = \frac{\pi D_{III} X + \pi D_{III}^2}{\pi D_i Y + \pi D_i^2} \cdot \frac{\rho_{III}}{\rho_i},
\]

where \(A_{III}\) and \(A_i\) are area of specimen III and specimen I surrounded by fibers. \(D_{III}\) and \(D_i\) are diameters of specimen I (c.a. 40.5 µm) and specimen III (c.a. 48.7 µm), respectively. \(X\) is the height from the , thus \(X\) µm of specimen I and \(Y\) µm of specimen III are surrounded by fibers on the surface (Figure 2.9). \(\rho_{III}\) and \(\rho_i\) are density of fibers on the specimen III and specimen I.

Average length of fibers on the intermediate rough surface is approximately around 150 µm. Since the angle between specimen III and surface is approximately 34° (figure), then \(Y\) equals to 268.2µm. Thus,

\[
\frac{A_{III}}{A_i} = 2.02 \cdot \frac{\rho_{III}}{\rho_i}
\]

The ratio of adhesion force of specimen III to specimen I is around 4.7 while the area ratio specimen III to specimen I is 2.01. Thus, the net contact area does not only depend on the
curvature of the specimen III and the setae density of specimen III is probably higher than specimen I which result in further increase in adhesion of specimen III.

Figure 2.10. (A) SEM images of (I) smooth, (II) low roughness, (III) intermediate roughness and (IV) high roughness HDPE surfaces; (B) Bar chart of mean of 100 adhesion point measurements between specimen I and HDPE surfaces I, II, III and IV. Error bars are standard deviations of
Figure 2.10A displays SEM images of smooth, low roughness, intermediate roughness and high roughness HDPE surfaces with their corresponding roughness reported in Table 2.1. Because of the inhomogeneity in the roughness, two levels of roughness, i.e., overall RMS and local RMS are provided for better characterization. The adhesion force of specimen I was found to be 12.04±6.95 nN for the interaction with the smooth surface, 37.15±17.52 nN for low roughness, 76.22±67.41 nN for intermediate roughness and 111.62±75.5 nN for high roughness surfaces (Figure 2.10B). Typical retraction force curves observed for specimen I for different level of surface roughness are displayed in Figure 2.11. By increasing the surface roughness, the adhesion forces were found to increase. It is essential to note that the large deviation in data arises from the dependence of adhesion force on the landing site of the leg on the rough polymer surface. In the event that the leg lands on an

![Image](image_url)

**Figure 2.11.** Typical force vs. separation curves observed for specimen I retracting from surfaces with low (surface I) to high (surface IV) levels of roughness.
Figure 2.12. (A) Plot of the adhesion force of the mosquito leg and smooth HDPE and silicon wafer surfaces as a function of relative humidity. Error bars are standard deviations of data. Optical image of a water drop on a (B) hydrophobic surface of smooth HDPE (CA=95.3˚), and (C) hydrophilic silicon wafer surface (CA= 25.4˚).
area between the fibers (for e.g., a valley), the adhesion force is much larger than when it lands on a tip of a fiber due to the difference in true contact area. Because of the inhomogeneity in the roughness of the HDPE surfaces created for this study, we provide semi-quantitative results for the influence of surface roughness on the adhesion force.

Furthermore, a control experiment was performed to monitor possible damage that may occur on the mosquito leg specimens during each experiment. A mosquito leg was attached to AFM cantilever and imaged by SEM before the experiment (Figure 2.6A). The mosquito foot claw was purposely removed by applying a high preload. 100 force measurements were performed between the mosquito leg and a flat HDPE surface. SEM was again used to obtain an image of the leg (Figure 2.6B). An additional 100 force measurements were performed on the intermediate rough HDPE surface and a final SEM image of the leg was obtained (Figure 2.6C). No significant damage (in terms of setae loss) was noticed.

2.3.2 Effect of humidity on adhesion force. To understand the relative contribution of van der Waals forces compared to capillary forces in the adhesion of mosquito legs to surfaces, adhesion force measurements were repeated for a wide range of relative humidity. Figure 2.12A shows the adhesion force of specimen I on two samples of smooth HDPE and flat silicon wafer surfaces as a function of humidity. With increasing humidity, the adhesion force was found to be relatively constant for an HDPE surface. However, the same experiment conducted on the silicon wafer substrate resulted in an increase of the adhesion force. We repeated the humidity experiments on silicon wafers for two different points on the surface. Although there are differences between values of adhesion, both points exhibit similar behavior and the maximum adhesion increases by a factor of approximately 4
compared to their corresponding 10% relatively humidity adhesion force (Figure 2.13). We attribute this difference to the effect of humidity on the wetting properties of a silicon wafer compared to HDPE. As shown in Figure 2.12B and 2.12C, the water contact angle on a flat HDPE surfaces is approximately 95±3° (i.e., hydrophobic) compared to the water contact angle of a flat acid-cleaned silicon wafer which is approximately 25±3°. Increasing relative humidity causes the formation of a thin film of water\(^9\) (~1.2 nm at 60% humidity\(^1\)) on the hydrophilic surface of the silicon wafer which is accompanied by the formation of a capillary bridge between the mosquito leg and the hydrophilic surface leading to larger adhesion forces. The decreased adhesion force between the mosquito leg and the silicon wafer.

![Plot of normalized adhesion force of mosquito leg and smooth HDPE and silicon wafer surfaces as a function of relative humidity.](image)

**Figure 2.13.** Plot of the normalized adhesion force of the mosquito leg and smooth HDPE and silicon wafer surfaces as a function of relative humidity.
wafer at higher humidity is a result of the decrease in the capillary pressure as noted by several researchers.\textsuperscript{101-102} Therefore it can be inferred that increased adhesion force between a mosquito leg and a hydrophobic rough surface is through by van der Waals forces. However, capillary forces can contribute to an increase in the adhesion force if the opposing surface is relatively hydrophilic. Xiao et al.\textsuperscript{101} measured the adhesion force between a hydrophilic AFM tip and a silicon oxide surface, and furthermore were able to account for the relative contributions of capillary forces to van der Waals forces. A similar analysis was performed on our system to confirm that capillary interactions play a significant role in the overall adhesion between a mosquito leg and a hydrophilic silicon oxide surface. However, on a hydrophobic HDPE surface, capillary forces are negligible. To calculate contribution of the capillary force to the measured adhesion force in the Figure 2.12, we use similar method suggested by Xiao et al.

\[ F_{ad} = F_c + F_{vdw} \]

\( F_{ad}, F_c, \text{ and } F_{vdw} \) are adhesion, capillary, and van der Waals forces, respectively.

The capillary force applied on the mosquito leg by the meniscus comes from the capillary pressure (\( F_p \)) and the surface tension (\( F_s \)).

\[ F_c = F_p + F_s \]

\[ F_p = \pi \gamma R \left( -\sin x + \frac{\cos(\theta + \phi) + \cos \varphi}{d^0 R} + 1 - \cos \phi \right) \sin \phi^2 \]

\[ F_s = 2\pi \gamma R \sin \phi \sin(\phi + \theta) \]

\( \phi \) is the filling angle. \( \theta \) and \( \varphi \) are the contact angle of two surfaces. \( \gamma, R, \text{ and } d^0 \) are the surface tension, radius of the sphere, and cut off distance, respectively.
At thermal equilibrium, the filling angle $\theta$ at different level of relative humidity can be determined by the Kelvin equation

$$\frac{K T \ln \frac{p}{p_0}}{\gamma V_0} = \frac{1}{R \sin \theta} \left( \cos(\theta + \varphi) + \cos \varphi \right) - \frac{\cos \varphi}{d_0 + R(1 - \cos \theta)}$$

Where $V_0$ and $\frac{p}{p_0}$ are the molar volume and relative pressure (relative humidity for water).

The capillary pressure and the surface tension is determined by inserting $\theta$ value in above equations. Therefore, dependence of the capillary force on relative humidity can be determined theoretically.

We plan to investigate the capillary contribution of the mosquito leg on a point on hydrophilic silicon wafer in Figure 2.12 and compare the result with the one on hydrophobic HDPE. Here we give an example our calculation of relative contribution of the capillary force in the adhesion force for silicon wafer 2 (Figure 2.12)

At the relative humidity less than 10%, capillary force is very small compare to van der Waals because the water meniscus has just started to form. Thus, the adhesion force comes from van der Waals between the leg and the silicon wafer surface ($F_{ad} = F_{vdw}$).

$$F_{vdw} = \frac{HR}{6d_0^2}$$

$H = 6.5 \times 10^{-20}\text{J}$ is the Hamaker constant for silicon wafer in air. At 10% relative humidity;

$$F_{ad} = F_{vdw} = 19.38 \text{ nN}$$

Using equations these equations, $R$ is measured to be 73.84 nN.

To simulate the result on silicon wafer surface, we take $d_0 = 2\text{Å}$, $\gamma = 73 \text{ mJ/m}^2$, $V_0 = 30\text{ ml}$, $\theta = 75^\circ$, and $\varphi = 25^\circ$. Using these values, we can calculate the filling angle $\theta$ for
different relative humidity values, and thereby the capillary force. We assume that the van der Waals force is constant for different humidity level and equals to the adhesion force at the 10% relative humidity. Therefore, by using first equation, we can plot the adhesion force as a function of relative humidity (Figure 2.14). A decrease in the capillary pressure

![Figure 2.14](image)

Figure 2.14. plot the adhesion force as a function of relative humidity calculated for (A) HDPE surface and (B) silicon wafer.
contribution to the overall adhesion force was found at above 60% relative humidity consistent with observations from the Xiao et al. study\textsuperscript{101}.

Additionally, it was confirmed that the adhesion force on silicon is roughly constant at different temperatures consistent with the prediction from a van der Waals adhesion dominated mechanism in which temperature has a negligible effect over a 20 °C range. (Figure 2.15). The experiment was performed on the heating-cooling stage in the AFM. The temperature of the stage was adjusted by the temperature controller integrated with the Bruker Dimension Icon AFM instrument and was reported by the Nanoscope software. This

![Figure 2.15. Adhesion force between a mosquito leg and a flat silicon surface at different temperatures.](image)

temperature range was chosen to mimic realistic temperatures, which mosquitoes would experience in their natural environment.

2.3.3. Adhesion force characterization of a mosquito leg on a uniform patterned rough surface. Because of the technique used to fabricate the rough HDPE surfaces, the resulting surface roughness is random, which limits a quantitative understanding of the adhesion mechanism. Therefore, the adhesion of a mosquito foot to a patterned rough surface was also measured so as to obtain greater insight into the interfacial contacts and the origin of the variability in our data. An SEM image of the patterned surface shows cylindrical pillars arranged in a square lattice with the following dimension; 25 µm diameters, 40 µm heights, and 60 µm spacing (inset image in Figure 2.16A). The large-scale roughness values of the patterned surface are reported in Table 2.1. Adhesion forces were recorded throughout and could be classified into four distinct types of contacts or landing positions: (i) partial contact with the top of the pillars, (ii) full contact with the top of the pillars, (iii) contact in between the pillars, and (iv) full side contact with the pillars (Figure 2.16B). The latter could be identified using the camera attachment of the AFM. Figure 2.16A shows the average of 20 adhesion measurements for each of four different landing positions. When the leg lands partially on top of pillars, adhesion is at its minimum value of 7.28± 2.80 nN (red column). However, the adhesion force is increased to 16.24±0.73nN (orange column) when the leg lands completely on top of the pillar. Since the mosquito leg has a larger diameter (around 40 µm) compared to the pillar diameter (25 µm), a larger contact area and adhesion force is expected for this landing position compared to partial contact with the top of the pillars. The next landing position occurs in between the pillars. For this landing position, an
Figure 2.16. (A) Bar chart of mean of 20 adhesion points measurements between a mosquito leg and a patterned surface when a mosquito leg lands partially on top of a pillar (black bar), completely on top of a pillar (green bar), space between pillars (blue bar), and contacts walls of pillars (red bar). Error bars are standard deviations of data. The inset box is SEM image of the patterned surface. (B) Schematic illustration of the different landing positions of a mosquito’s leg on a patterned surface; (i) partial contact with the top of the pillars, (ii) full contact with the top of the pillars, (iii) contact in between the pillars, and (iv) full side contact with the pillars.
intermediate adhesion force is measured (25.84±3.70 nN, green column) where full contact of the mosquito is achieved with the flat area in between the pillars. The largest contact, leading to the highest adhesion (49.26±6.32 nN) forces, is achieved when the mosquito leg additionally makes side contact with the pillars. At this position, not only does the bottom of the mosquito foot make full contact with the surface but additionally, side contact of the setae with the pillar walls occurs. The overall low error bars associated with these experiments compared to the randomly rough surface points to the variation in contacts associated with a randomly rough HDPE surface.

2.3.4. Discussion. The essential findings of this study show that the adhesion force of a mosquito leg on surfaces increases significantly by increasing surface roughness (Figure 2.5C and 2.10 B) which can be attributed purely to van der Waals forces (Figure 2.12A). This notable behavior suggests that the presence of fibers on the surface, which results in multiple contact points between the micro-/nanostructure setae on the mosquito leg and the surface fibers, can greatly influence the adhesion force. A theoretical analysis of the adhesion force between a mosquito leg and a smooth HDPE surface is in agreement with our hypothesis that van der Waals forces are sufficient and the main contributor to the adhesion force. The magnitude of adhesion force for specimen I on the smooth HDPE can be analyzed by the van der Waals body-body equation: $F_{\text{vdw}} = \frac{HR(6d_0^2)}{1}$, where $d_0 \approx 1.9\text{Å}$ is the cutoff distance, $H \approx 8.43 \times 10^{-20}\text{ J}$ is the Hamaker constant for polyethylene at room temperature\(^\text{\textsuperscript{103}}\) and $R$ is the sphere body radius\(^\text{\textsuperscript{1}}\). We estimate $R$ to be on the order of several nanometers, based on the nanoscale stripped structures found on the individual setae where contact is expected with opposing surfaces. With these assumptions, $F_{\text{vdw}}$ is expected to be on the order of nano-Newton for a single seta and because only a few number of setae (10’s
to 100’s) contribute to the adhesion in an actual mosquito foot, the measured adhesion force ought to be on a similar range. In our AFM force measurements under zero relative humidity, we obtain adhesion forces ranging from 10’s to 100’s of nanoNewtons, which is consistent with theory. We note that depending on the mosquito leg landing position, the number of setae interacting with the surface can vary resulting in a variation in the measured force. Another factor to consider is that increasing the preload can engage the attachment of more setae to the surface thereby increasing the adhesion force. Mosquitoes, weighing approximately 2.5 mg typically apply a preload around 4 mN per foot; therefore, the number of setae engaging the surface and adhesion force is expected to be higher in live mosquitoes compared to the forces measured in our study (in which a significantly smaller preload of 50 nN was used). Future work aims at performing live mosquito experiments in which the residence time (i.e., average time that a mosquito remains on a surface) will be monitored as a function of the surface roughness of the LLIN.

2.4. Conclusion

In this study, we investigated the effect of surface roughness (i.e., using rough surfaces) on the adhesion of mosquitoes legs to HDPE surfaces. Using AFM force measurements on a single mosquito leg, it was found that surface roughness increased the adhesion force. We attribute this increase in adhesion force to increased number of surface elements interacting with the setae of the mosquito leg through multiple contact points. We also found that although the adhesion force could be attributed predominantly to van der Waals interactions on hydrophobic surfaces, capillary forces also played a role to increase the adhesion on hydrophilic surfaces. These results provide a better understanding of how a mosquito leg interacts with solid surfaces of varying wetting properties and roughness,
which can potentially be applied in the development of superior Long Lasting Insecticidal Nets (LLINs), which have embedded surface roughness and composed of hydrophilic materials.
CHAPTER 3: ANOMALOUS POTENTIAL DEPENDENT FRICTION ON AU(111) MEASURED BY AFM

3.1. Introduction

Understanding interfacial and tribological behavior at the molecular scale has been an area of continued scientific interest\textsuperscript{1, 104-105}. Atomic force microscopy (AFM) allows for the study of nano-scale interfacial interactions between atoms and molecules of opposite surfaces\textsuperscript{106-108}. A significant number of studies have been conducted aiming to measure and control the nanoscale frictional properties of a system\textsuperscript{109-112}. The ability to control and manipulate friction during sliding is important for variety of technologies such as microelectromechanical systems (MEMS)\textsuperscript{113-114}. An explored strategy to control frictional forces involves reversible responses to active external stimuli such as electrical potential\textsuperscript{115-117}. An electrochemical environment not only allows quick and reversible changes of interfaces and thus friction\textsuperscript{118-120}, but also enables preparation of a clean surface, which is essential to get quantitatively reliable and interpretable results\textsuperscript{121}. Water molecules have been shown to rearrange into an ordered and confined structure within a few molecular diameters from a solid surface\textsuperscript{122-124}. The confined water layer exhibits properties different from those found in bulk water\textsuperscript{125-128}. Several studies have confirmed drastic increases in the effective viscosity of water layer extended up to 5 nm away from a solid surface\textsuperscript{129-131}. The presence of an applied electric field on the solid surface can further increase the effective viscosity of confined water by order of $10^6-10^7$\textsuperscript{132-134}. Danielewicz-Ferchmin and Ferchmin\textsuperscript{135} provided theoretical evidence of a phase transition in water at ambient conditions in a local electric field within the range of $0.77 \times 10^9$ V/m to $1.36 \times 10^9$ V/m. Although there is a growing understanding of the “ice-like” water structure and its
properties next to charged surfaces, there is limited information about the frictional properties as a result of the confined water layer especially in the presence of an applied electric field. Previous studies suggest that the friction between a gold surface and an opposing surface can be tuned under an applied potential, which can be explained by the higher confinement of water layers near the charged gold surfaces\textsuperscript{136-137}.

Dhopatkar et al. showed that an ice-like water layer eases friction at the interface of two surfactant monolayer coated surfaces but the friction could only be tuned through changing the surfactant concentrations\textsuperscript{137}. Labuda et al. investigated the friction force between a gold electrode and an AFM tip in a 0.1 M HClO\textsubscript{4} solution\textsuperscript{121}. They observed that the friction on the gold surface increases from a low value at a +0.8 V applied potential to a high value at a +1.15 V (versus Ag/AgCl) applied potential. They attributed the increase in the friction to the electrochemical oxidation of the gold electrode. Valtiner et al. investigated the effect of an electrochemical potential on the friction between a mica surface and a gold electrode\textsuperscript{136}. They found that a positively charged gold surface showed higher friction compared to a neutral gold surface, which was attributed to the formation of a viscous water layer at the positively charged electrode. Because the range of the applied potentials

\textbf{Figure 3.1.} Schematic illustration of the experimental setup used to measure friction forces with AFM.
in their study was limited to 0 to +0.4 V (versus Ag/AgCl), the changes in the friction forces were relatively small. Although several studies have shown that the interfacial and physical properties of water next to a charged surface are different from the bulk, there is still a debate over the origin and magnitudes of the physical properties reported. Here we present a systematic study of the friction forces over a wider range of applied potentials, i.e., from -0.6 V to +0.6 V (versus Ag), which we attribute to the formation of the ice-like water layer (Figure 3.1). We believe that these types of friction and normal force experiments provide a sensitive technique to obtain greater insight into the physical properties of the ice-like water layer, which has implications in MEMs devices, fuel cells, and photocatalytic oxidation.

3.2. Experimental

A 15-mm mica disk (Highest Grade V1 AFM Mica Discs, Ted Pella, Inc.) was cleaved using a sharp blade and immediately inserted to the sputtering vacuum chamber (ATC Orion Sputtering System, AJA International, Inc.). A 100 nm gold film was deposited on the mica substrate via thermal evaporation using a deposition rate of 1 Å/sec and the vacuum was maintained at approximately 10^-6 Torr. The gold-coated mica substrate was allowed to slowly cool down to room temperature over 20 minutes. The substrate was then washed and cleaned with deionized water, dried in air, and used as a working electrode. The 3-electrode cyclic voltammetry experiments were performed in a 0.1 M aqueous NaCl (ReagentPlus, Sigma-Aldrich) solution. A gold-coated mica substrate, Pt mesh, and Ag wire were used as working, counter, and reference electrodes, respectively. Thermally evaporated gold on mica was chosen as a substrate due to its inert nature which allowed for a wide potential range without inducing surface oxidation or other chemical
reactions\textsuperscript{138}. Cyclic voltammetry (CV) tests on the gold-coated mica surface were performed using a custom-made PTFE cell\textsuperscript{139} and controlled using a potentiostat (SP-150, BioLogic Science Instruments). All potentials are reported relative to a Ag wire. Friction experiments were performed using an atomic force microscopy (AFM) (Dimension Icon, Bruker). Friction force measurements were acquired in the lateral force microscopy (LFM) mode by using two types of AFM probes; an AFM probe (Antinomy n-doped Si, RTESP, Bruker) with a sharp tip (estimated radius 10 nm, height 15 µm, spring constant Kc = 34 N/m) and an AFM probe (CP-NCH-SiO-D, sQube) with a spherical colloidal tip (estimated radius 10 µm, spring constant Kc = 37 N/m). The cantilever lateral constant was calibrated based on the equation $G wt^3 (3h^2 l)^{-1}$ where h is tip height and $G, w, t, l$ are shear module, width, thickness, and length of the cantilever, respectively. Friction was measured by scanning the tip perpendicular to the cantilever long axis. The scan size (or shear distance) and shear speed were 500 nm and 1 µm/s, respectively. In a typical measurement, the potential on the gold-coated surface was changed and maintained at a predetermined value while the lateral deflection of the tip was monitored by AFM. The lateral deflection signal typically required approximately 15 seconds to equilibrate to a steady value. The recorded lateral deflection signal was then converted to the friction force using a similar technique proposed by Cannara et al.\textsuperscript{67}. Force-distance curves were collected using Ramp mode in which the tip is approached to the gold surface at a constant velocity until contact is achieved followed by separation (or retraction) from the surface. The force-distance curves are recorded with a ramp size (i.e., normal displacement) of 200 nm and tip velocity of 100 nm/s.

\textbf{3.3. Result and Discussion}
Figure 3.2 shows a plot of the friction force as a function of the applied potential on a gold-coated mica surface. The friction is approximately constant and at its lowest value for applied potential from -0.9 V to -0.6 V. A gradual increase in friction is observed as the applied potential increases to +0.3 V. As the potential is further increased, a sharp increase in friction is observed over the potential range from +0.3 V to +0.6 V. The friction then levels off at potentials greater than +0.6 V. A cyclic voltammogram (the inset graph) on the system exhibits all characteristic peaks for an aqueous NaCl solution and a Au (111)
surface in the potential range of -0.6 V to +0.6 V (solid line) and -0.9 V to +0.9 V (dash line). The positive peak around +0.6 V occurs due to adsorption of ion to electrode (i.e., chemisorption of chloride ions from the solution to the surface). The positive peak at +0.9 V corresponds to the oxidation of gold, which results in occurrence of a reduction peak at +0.14 V during the sweep in the reverse direction. We limited our study to potentials in the range of -0.6 V to +0.6 V because this region is where the significant changes in friction force values were observed and more importantly because it is free of any faradaic processes including gold oxidation. Although potential dependent friction changes have been reported by Valtiner et al.\textsuperscript{136}, to our knowledge, we are the first to report such large anomalous changes in friction from a value of approximately 0.2 µN (at negative potentials) to approximately 7 µN (at positive potentials) corresponding to a difference by a factor of 35.

A possible explanation for the observed drastic changes in the friction can be attributed to dependency of shear viscosity of water at the gold interface on the surface potential. Previous studies showed an increase in the shear viscosity of interface water (\sim10^7 higher than bulk water) when the surface of the gold is positively charged\textsuperscript{132, 134}, which is likely due to reconstruction of water at the interface into highly confined ice-like layers. Other studies\textsuperscript{140} suggest that the higher confinement of interfacial water comes from a larger number of saturated hydrogen bonds, which resembles bulk ice on a positively charged surface. On the other hand, when the surface is negatively charged, the number of broken hydrogen bonds increases and interfacial water behaves similar to bulk water i.e., same physical properties. Thus, the shear viscosity of water at the negatively charged interface is much lower than the positively charged interface. At a surface potential lower than –
Figure 3.3. Friction force versus normal force for dry, open circuit, applied -0.6V and +0.6V potential conditions between Au (111) electrode and (A) a sharp AFM tip and (B) a colloidal AFM tip (scan size 500nm, scan speed 1 µm. S⁻¹). Coefficient of friction (CoF) is calculated by measuring slope of a fitting line (dashed line) on each data set. (C)Schematic illustration of the confined interfacial water region. The shear planes of the AFM probe are shown by the dashed line.
0.6V, the shear viscosity of water is at its lowest value and water acts as a boundary lubricant, which decreases friction between the AFM tip and the gold-coated mica surface. As the surface potential becomes more positive, water molecules gradually orient at the interface exposing a higher number of dangling hydrogen molecules capable of hydrogen bonding to the AFM tip. Further increase in the potential (i.e., greater than +0.3 V) leads to the formation of an even more highly confined viscous layer of water leading to a sharp change in friction. Higher applied positive potentials beyond +0.6 V do not have a significant effect on friction up to +0.9 V, which was the upper potential limit used in this study.

**Figure 3.3** shows a plot of the friction force dependence as a function of the applied load. Four conditions were explored including the friction force (i) on dry gold, (ii) on gold under aqueous condition with no applied potential (i.e., open circuit potential), (iii) on gold under aqueous condition with a -0.6 V potential, and (iv) on gold under aqueous condition with a +0.6 V potential. When using a sharp AFM tip (**Figure 3.3A**), the friction force increases linearly with applied load following Amontons’ law. A linear fit of the data provides the coefficient of friction (CoF). Under dry conditions, the friction force is relatively high with a CoF of 0.78. Running the same experiment in an aqueous NaCl solution without applying a potential lowers the friction force and reduces the CoF to 0.51. Although no potential is applied on the gold surface, the latter will inherently gain a slight negative charge (-0.12 V relative to the electrolyte solution). Under these conditions, water molecules next to the Au surface have broken hydrogen bonds\textsuperscript{138}, which affects and also determines the interaction between the hydrophilic AFM tip (also capable of hydrogen bonding to water molecules) and the Au surface. At a negative potential (i.e., -0.6 V), the number of broken hydrogen
bonds in water increases (lowering its viscosity) and the attractive interaction between the Au surface and the AFM tip is reduced significantly resulting in a CoF of 0.12. Under these conditions, water behaves as an effective boundary lubricant. Thus, a higher viscosity is expected for interfacial water at an open circuit potential compared to that of a negative charged surface consistent with prior work. However, upon increasing the potential to +0.6 V, water molecules next to the Au surface are highly oriented with few broken hydrogen bonds thereby increasing the viscosity of water next to the Au surface. These highly oriented water molecules can also hydrogen bond with the AFM tip thereby increasing the interaction. As a result, the friction force is significantly higher than all the

**Figure 3.4.** Representative plot of friction force as a function of shear distance for a sharp AFM tip against a flat Au(111) surface under aqueous 0.1 M NaCl under an applied potential of (i) -0.6 V, (ii) +0.6 V, and (iii) open circuit potential.
other cases with a CoF of 3.1. Under these conditions, water no longer acts as an effective boundary lubricant. Representative friction traces under different applied potentials can be found in Figure 3.4.

To ensure that the anomalous friction behavior was not unique to this specific system (i.e., sharp AFM tip resulting in high pressures), the experiments were repeated using an AFM colloidal probe (Figure 3.3B), which would reduce the contact pressure under the same applied normal load range. Under dry conditions, the CoF was identical (i.e., CoF = 0.78) to the case when using a sharp AFM tip again consistent with Amontons’ Law in which the friction forces is only dependent on the applied load and the CoF (being unique for a pair of shearing materials). We note that the applied load range in this study is significantly higher than internal loads (van der Waals or electrostatics contributions) and therefore can assume that the friction force is not dependent on contact area. Under aqueous conditions and an open circuit potential, the CoF was lower (CoF = 0.27) compared to the sharp AFM tip case. If we assume that the number of broken hydrogen bonds is lowest (i.e., highly viscous water) next to a positively charged Au surface and increases moving away from the Au surface until bulk properties are reached (as shown schematically in Figure 3.3 C), then one would expect that the interaction of a probe within a shearing plane of water would diminish as the probe/Au surface distance is increased. This is consistent with our observation since a colloidal probe shearing on the Au surface is expected to have a lower contact pressure leading to a larger separation distance compared to a sharp AFM tip (Figure 3.3 C). At a potential of -0.6 V, the CoF is again observed to be low (CoF = 0.16). At a potential of +0.6 V, the coefficient of friction increases to 2.1. Again, since the colloidal probe shears over the Au surface with a larger separation distance, the number of
broken hydrogen bonds on the corresponding shearing plane (dashed line in Figure 3.3 C) is larger leading to a reduced interaction.

Although the Debye length in our system is <1 nm, it is worth considering the magnitude of interaction forces. The magnitude of double-layer interaction force between a sharp tip and a flat surface can be estimated by the double layer body-body interaction equation $F = k R Z e^{-k D}$, where $k^{-1} \approx 1 \text{ nm}$ is the Debye length, $R \approx 10 \text{ nm}$ is the tip radius, $Z$ is the interaction constant and $D$ is distance between the tip and the electrode surface. $Z$ at 25°C is given by $9.22 \times 10^{-11} \tanh^2(\psi_0/103) \text{ J/m}$, where the surface potential $\psi_0$ can be estimated to be on the order of 100 mV. With these assumptions, the double layer interaction force is approximately 0.2 nN at a separation distance of 1 nm. Using a colloidal
probe of radius 10 \( \mu m \) increases the interaction force to 0.2 \( \mu N \). These interactions forces are smaller than the range of applied loads in this study. In addition, considering the modified version of Amontons’ equation\(^{142} \) 
\[ F = \mu (L_0 + L) \]
where \( \mu \) is coefficient of friction, \( L \) is the external load and \( L_0 \) is internal load, the latter contribution can be neglected when calculating the friction force, i.e., the applied load \( L \) contribution dominates.

**Figure 3.5** shows a plot of the friction force over 15 shearing cycles, which consist of switching the potential between -0.6 V to +0.6 V. The friction forces (at both extremes) do not appear to change over multiple shear cycles. We note that relatively high normal loads were applied in our experiments, which has the potential to damage the thin layer of Au coated over the mica substrate. However, the fact that our friction data remained consistent throughout the several shearing cycles would infer that surface damage was not present. To further support our claim, AFM was used in contact mode to image the surface.

**Figure 3.6.** AFM image of a gold-coated mica surface (A) before, and (B) after 15 shearing cycles, which consist of switching the potential between -0.6 V to +0.6 V. A 2 \( \mu m \) x 2 \( \mu m \) image of the Au surface was obtained before the experiment.
before and after the shearing experiments. The shearing experiments were then carried out with an applied load of 2.5 µN over a 500 nm shearing distance at a scan speed of 1 µm/s. After the shearing experiments, the same area 2 µm x 2 µm was imaged again to check for surface damage. No noticeable damage was found. (Figure 3.6).

Since our explanation of the origin of the observed anomalous friction behavior relies on the ice-like viscous layer than forms at positively charged surfaces, force curves were obtain for our system at relatively high approach velocities. Electrostatic forces were not considered since the ionic strength of our electrolyte was relatively high (i.e., 0.1 M NaCl which corresponds to a Debye length of ~ 1 nm). Figure 3.7 displays typical force curves.
measured during the approach of a colloidal tip probe to the gold substrate under different applied potentials. Separation is defined as the distance between the colloidal probe and gold electrode. A noticeable difference in the force curves was observed with repulsive forces extending further out as the potential is increased. The sharp change in the friction forces that was observed in Figure 3.2 (between +0.4 V and +0.6 V) is also reflected in the force curve with the same potential range with significant increase the repulsive forces. We can estimate the viscosity of the interfacial water layer based on the classical hydrodynamic theory of drainage $F = 6\pi \eta R^2 V/D$ where $\eta$ is effective viscosity, $R$ is the tip radius, $V$ is the approach velocity and $D$ is separation distance between tip and surface\textsuperscript{129}. By fitting the experimental data for a surface potential of +0.6 V, the effective viscosity of water is estimated as 150 Pa.s, which is 5 orders of magnitude higher than bulk water and consistent with prior findings\textsuperscript{39, 132, 136}. This high viscosity ice-like water layer has the potential to affect the adsorption/desorption of molecules at charged surfaces, which to our knowledge, is not considered in developing kinetic models.

3.4. Conclusion

The findings of this study demonstrate the reversible control of friction by tuning the surface potential. The anomalous reversible friction dependence on potential originates from the ice-like formation of interfacial water. At negative potentials, the viscosity of interfacial water is lower compared to bulk and at positive potentials, the viscosity can increase by a factor of $10^5$. These viscosity changes affect the interaction of a hydrophilic AFM tip as it shears along a shear plane through the interfacial water layer thereby affecting friction forces. A reversible change in friction by a factor of 35 was measured at
the two extremes of applied potentials. The results can significantly impact a variety of areas including MEMs, fuel cells and photocatalytic oxidation.
CHAPTER 4: REVERSIBLE POTENTIAL-DEPENDENT FRICTION ON AU(111)

4.1. Introduction

In our previous chapter, we presented an exploratory study on the effect of an applied potential on friction force between an AFM tip and a gold electrode surface over a wide range of applied potentials (-0.6V to +0.6 V vs. Ag)\textsuperscript{144}. We observed a reversible potential-dependent friction behavior on a gold electrode surface as the surface potential was increased from negative to positive values. At approximately +0.4V, a sharp increase in the friction forces were observed. The coefficient of friction (CoF) of gold surface at the applied potential of +0.6 V was reported to be 26 times higher than that at the applied potential of -0.6V. The drastic change in the CoF can be attributed to the formation of an ice-like water layer on the positively charged electrode surface. However, there are several parameters in such electrochemical systems including the electrolyte concentration that can possibly impact the properties and the formation of the ice-like water layer.

This chapter shows an extension of previous chapter and provides a better understanding of how several experimental parameters (i.e., surface roughness and salt composition and concentration) affect the tribological properties of a gold surfaces exposed to an applied electrical potential in a aqueous electrolyte solution (Figure 4.1). In addition, normal force measurements conducted at various approach velocities further support our hypothesis of the formation of a highly viscous water layer and is in consistent with hydrodynamic drainage theory. These results provide a better understanding of the interaction between surfaces in the presence of an applied potential and can have a
transformative impact in several areas of science including tribology, MEMs, energy storage devices, fuel cells and catalysis.

4.2. Experimental

4.2.1. Preparation of gold electrode substrate

15-mm mica disks (Highest Grade V1 AFM Mica Disc) were purchased from Ted Pella, Inc. and utilized upon cleaving by a fresh sharp blade. Using thermal evaporation deposition (ATC Orion Sputtering System, AJA International, Inc.), the freshly cleaved mica was coated with a 5 nm Cr film, acting as an adhesion layer, topped with a 100 nm

Figure 4.1. Schematic illustration of the experimental setup used to measure the friction force between an AFM tip and a Au surface subject to applied potentials.
gold film. A uniform smooth gold film was obtained by maintaining a slow deposition rate (1Å/sec) and a high vacuum (~ 10^-6).

The substrate was allowed to cool down in the chamber before rinsing with distilled water and drying in air. AFM was used to characterize the surface roughness of the gold substrate (rms ~3.5 nm) based on AFM images (Figure 4.3).

4.2.2. Preparation of ultra-smooth gold electrode substrate

Atomically smooth gold surfaces were prepared using the mica templating method145 (Figure 4.2). First, a 42 nm gold film on mica was deposited in an electron-beam evaporation system. A muscovite mica sheet of 10 cm in diameter and a few hundred micrometers thick were freshly cleaved before the deposition to avoid any contamination.

Second, pieces of 1.5×1.5 cm² step-free regions of the gold-coated mica sheet were cut and silicon wafer pieces were cut in squares of 1×1 cm². A few hundred micrometer thick layer of UV-curing glue (Norland 81) was applied on top of each clean silicon wafers piece in a laminar flood hood environment before carefully place the gold-coated mica pieces with the gold side facing down on the glue. The UV glue was cured for at least two hours. Lastly, right before using the gold surface, the mica was peeled off the gold.

In both thermal evaporation and E-beam evaporation devices, a quartz crystal was used to calibrate and control the deposition rate and the film thickness.

4.2.3. In situ electrochemistry-AFM

A 3-electrode electrochemical cell was used to track changes in friction as a function of applied potential between the AFM tip and the gold surface. The potential range was limited so as to prevent the oxidation of gold. A gold substrate, Pt mesh, and Ag wire
served as the working, counter, and reference electrode, respectively. Electrochemical experiments performed in different concentrations of aqueous NaCl (i.e., 1 mM, 10 mM, 0.1 M, and 1 M) to investigate the effect of salt concentration on friction forces. To explore the influence of ions on the potential-dependent friction, 0.1 M aqueous NaOH was used.
as an alternative electrolyte. In order to confirm that the electrochemical setup in the AFM experiments was reliable, similar electrochemical reactions were performed using a conventional PTFE electrochemical cell.

4.2.4. Friction measurements using AFM

Friction forces were measured using atomic force microscopy (AFM) (Dimension Icon, Bruker) in lateral force friction (LFM) mode. An AFM probe (NTESP, Bruker) with a sharp tip (estimated radius 10 nm, height 15 µm spring constant $K_c = 34$ N/m) was used for the friction measurements on the gold substrates. Additionally, an AFM colloidal probe (CP-NCH-SiO-D, sQube, estimated radius 10 µm, spring constant $K_c = 37$ N/m) was used to measure force curves (i.e., normal forces as a function of separation distance between the colloidal probe and the gold surface).

The normal spring constant of the cantilever was calibrated by using the thermal tune technique in air and liquid. The lateral spring constant of the cantilever was obtained by using the following equation: $Gwt^3(3h^2l)^{-1}$ where $G, w, t, l$ are the shear module, width, thickness, length of the cantilever, respectively, and $h$ is tip height. The normal sensitivity of the cantilever was obtained via measuring the slope of the vertical voltage signal versus distance curve. The lateral sensitivity of the cantilever was calculated by averaging the initial slope of the friction loop, in which lateral voltage signal is plotted versus lateral distance, in both forward and backward scan directions.

Friction was measured by recording the lateral deflection of the cantilever as the tip scanned the surface perpendicular to long axis of the cantilever (scan size of 500 nm and speed of 1 μm. s$^{-1}$) while the electrical potential of the gold surface was varied. A method
previously proposed in the literature\textsuperscript{62} was used to convert the lateral voltage signal into quantitative friction forces.

\textbf{Figure 4.3.} Plots of the friction force versus normal load for dry, open circuit, and applied potentials of -0.6V and +0.6V between a sharp AFM tip and (A) a gold surface formed by sputtering (B) an ultra-smooth Au surface formed by e-beam deposition. The images to the right are AFM height images of the corresponding gold surfaces. A scan size of 500 nm and scan speed of 1 µm. s\textsuperscript{-1} was used for friction measurements.

\textbf{4.2.5. Normal force measurement using AFM}

AFM Ramp mode was used to record normal forces versus separation distance as a tip approaches the gold substrate followed by jumping into contact with the surface and then
separates and retracts from the surface. To study the effect of the approach velocity on the normal force interactions, force-distance curves were obtained for approaching velocities of 50 nm/s, 100 nm/s, 200 nm/s, 500 nm/s, and 900 nm/s. A 200 nm normal scan size was used in the ramp experiments.

4.3. Result and discussion

Figure 4.3A shows the friction force between a sharp AFM tip and a gold surface as a function of the applied normal load under four different conditions: (i) on dry gold, (ii) on gold under aqueous conditions with no applied potential (i.e., open circuit potential), (iii) on gold under aqueous conditions with a $-0.6 \text{ V}$ vs Ag potential, and (iv) on gold under aqueous conditions with a $+0.6 \text{ V}$ vs Ag potential. The friction force increases linearly with load in an agreement with Amontons’ law. The coefficient of friction (CoF) between the AFM tip and the gold surface under dry condition is found to be approximately 0.51 which is in a similar range to previously reported values in the literatures. Under aqueous NaCl solution conditions and without applying a potential, the gold surface inherently gains a slight negative charge of $-0.12 \text{ V}$ and the CoF is lowered to 0.17. Under these conditions, the aqueous salt solution serves as a boundary lubricant thereby reducing the interaction between the AFM tip and the Au surface. Hydrogen bonding between the AFM tip and the interfacial water layer is still present. By applying a negative potential on the Au surface, the number of broken hydrogen bonds increase, which in turn decreasing the attractive interaction between the tip and the surface. Thus, under aqueous conditions with a $-0.6 \text{ V}$ applied potential, water behaves as a more effective boundary lubricant and lowers the friction further, resulting in a CoF of 0.11. Upon applying a positive potential, e.g., $+0.6 \text{ V}$, hydrogen bonding becomes more effective, resulting in water molecules next to Au
surface reorganize into a nanostructured fluid. Formation of highly oriented water molecules increase the viscosity of water next to Au surface. Under these conditions, the highly confined viscous water layer, which no longer acts as an effective boundary lubricant, increases the attractive interaction through hydrogen bonding to the AFM tip and results in a high CoF of 2.62.

The same experiment was conducted on an ultra-smooth gold surface to verify if the roughness of the gold surface affected the formation of the viscous water layer. The ultra-smooth gold surface had an rms value of 0.2 nm (See Figure 4.3B) compared to the gold surface previously used with an rms of 3.3 nm. Figure 4.3B shows a plot of friction force on the ultra-smooth gold surface versus applied normal load under the same aforementioned conditions. Under dry conditions, the CoF on the ultra-smooth gold surface was 0.26. Ultra-smooth gold contains smaller and fewer asperities thereby resulting in lower friction forces. Under aqueous conditions and an open circuit potential, the CoF is measured as 0.15. At the potential of -0.6 V, the coefficient the friction decreases to 0.09. At the potential of +0.6 V, the CoF is again observed to be high (CoF = 1.9). Although the value of coefficient of the friction on the ultra-smooth gold surface is smaller than that observed on the regular gold surface, the trend of the change in friction depending on the applied load and potential is similar to that on rougher gold surfaces. Both gold substrates exhibit very high CoF values when a positive potential is applied but very low CoF values when a negative potential is applied. Based on these results, and to avoid any potential
influence of surface roughness, all future experiments described below were conducted on ultra smooth Au surfaces.

Figure 4.4 displays the effect of electrolyte concentration on friction forces of ultra-smooth gold under aqueous condition and (i) open circuit, (ii) applied potential of -0.6 V, and (iii) applied potential of +0.6 V. The friction experiments were performed in electrolytes with concentrations of 1 mM, 10 mM, 0.1 M and 1 M. At a potential of -0.6 V, low friction values were obtained for all concentrations. Similarly, under aqueous conditions and no applied potential, the friction forces were similar for all concentrations. However, decrease
in friction was observed with an increase in electrolyte ionic strength. At the potential of +0.6 V, the friction force is approximately 7.56 ± 0.3 µN in 0.001M electrolyte compared to 4.38±0.1 µN in 1M electrolyte. We attribute this decrease in friction to a similar mechanism that is involved in the freezing point depression of water in the presence of salt. In the latter case, salt ions disrupt the equilibrium of water molecules entering and leaving the solid state\textsuperscript{149}. A similar explanation is proposed to explain the decrease in friction forces with increasing salt concentration. The presence of salt disrupts the hydrogen bonding between the AFM tip and the oriented water layer thereby reducing friction.

To study the effect of electrolyte anion on the friction forces of the ultra-smooth gold surface, friction experiments were performed using 0.1 M NaOH as a electrolyte instead of 0.1 M NaCl. Figure 4.5A exhibits the friction forces on the positively and negatively charged surface using NaOH compared to NaCl. At the potential of -0.6 V, the friction force is similar for both NaOH (red column) and NaCl (black column) electrolytes. At the potential of +0.6 V, the friction is observed to be higher in an NaCl electrolyte solution compared to an NaOH electrolyte solution. Figure 4.5B exhibits a plot of friction forces as a function of applied potential on an ultra-smooth gold surface and using NaCl as the electrolyte. At the applied potential of -0.6 V, the friction is at its lowest value. As the applied potential increases to +0.2 V, the friction gradually increases. Further increase in the applied potential (i.e, > +0.2 V) leads to a sharp increase in the friction force. In the previous chapter, we demonstrated that the potential range of -0.6 V to +0.6 V, where main changes in friction forces occur, is free of any Faradaic process including gold oxidation\textsuperscript{144}. The friction of the ultra-smooth gold drastically increases from a value of 0.2 µN (at -0.6 V) to 5.2 µN (at +0.6 V) corresponding to an increase in friction by a factor of
26. The sharp changes in the friction can be explained by dependency of the shear viscosity of interfacial water (which is dependent on the number of hydrogen bonds) at the gold interfaces on the surface potential.

**Figure 4.5** exhibits the effect of the electrolyte concentration on the normal force between a colloidal AFM tip probe and an ultra-smooth gold substrate under +0.6 V applied potential condition. A difference in the forces curves is observed with the repulsion force region extending outwards as the electrolyte concentration decreases.

**Figure 4.5.** Normal force curves recorded between a colloidal AFM probe and an ultra-smooth gold electrode surface in 1M, 0.1M, 0.001M, and 0.0001M NaCl as the electrolyte.
Figure 4.6. (A) Bar chart of the mean of five friction force measurements on ultra-smooth gold surface in an aqueous 0.1 M NaCl solution (black) a aqueous 0.1 M NaOH solution (red). Plot of the friction force as a function of the applied potential in the range of -0.6 V to +0.6 V in (B) aqueous NaCl solution and (C) aqueous NaOH solution. Error bars indicate standard deviations.
Reorientation of water molecule at the interface to a highly confined ice-like layer at the positively charged gold surface increases the shear viscosity, thereby increasing the friction. However, at the negatively charged surface, the shear viscosity of water next to the gold surface becomes smaller due to lower number of hydrogens bonds, resulting in a decrease in friction.

Figure 4.6C shows data for the same experiment as above with the exception of substituting NaCl with NaOH to form the electrolyte. The friction is again observed to be at the lowest at the potential of -0.6V, follows with a gradual increase in friction as the potential increases. Similarly, a sharp rise in friction is seen over the range of 0V to +0.2V. The friction then levels off as the applied potential is increased to +0.6 V. The potential, where the drastic change in friction is observed, shifts to the lower values when NaOH is used as the electrolyte. The observed shift in voltage where the drastic change in friction takes place can be attributed to differences between inhibition of the hydrogen bonds by Cl⁻ ions compared to OH⁻ ions. Due to the self-ionization of water (i.e., H₂O + H₂O ↔ H₃O⁺ + OH⁻), the addition of OH⁻ (i.e., the increase in pH as a result of using NaOH) is not expected to significantly disrupt hydrogen bonding or the ice-like interfacial water formation. However, Cl⁻ ions disrupt hydrogen bond formation which manifests as requiring a higher positive potential (or driving force) to form the ice-like interfacial water layer. The difference in equilibrium potential of a Ag wire in 0.1 M NaOH compared to 0.1 M NaCl was measured and found to be negligible. Therefore the difference in potential cannot be attributed to the reference electrode. Another feature that is apparent when comparing Figures 4.6B and C is the fact the friction force levels at a value of 4.3 µN in the case of using NaOH compared to a still increasing value beyond 5 µN in the case of
using NaCl, at high positive potentials. The latter would imply that the AFM tip experiences stronger interactions with the ice-like water layer in the presence of NaCl compared to NaOH. We attribute this difference to the fact that at a high pH (i.e., in the presence of 0.1 M NaOH), the hydroxyl group present on the AFM tip are de-protonated, thereby yielding a larger negative charge on the AFM tip. As a result, hydrogen bonding is disrupted (similar to when a negative potential is applied to a gold surface) at the ice-like water/AFM tip interface, which results in a decrease in the magnitude of the friction force.

**Figure 4.7.** Plot of the friction force as a function of the applied potential in the range of -0.6V to +0.6 V in aqueous NaOH solution
Finally, it is necessary to mention that, we ran an experiment tracking friction when the applied potential ranges from -0.9 V to +0.9 V Vs. Ag using 0.1M NaOH electrolyte solution (Figure 4.7). Similar experiment was perform in NaCl solution in the previous chapter. Although there is a shift in voltage where the drastic change in friction occurs, the friction levels off in before -0.6 V and after +0.6 V.

Figure 4.8 shows the effect of the approach velocity on the normal force between a colloidal AFM tip probe and an ultra-smooth gold substrate. Experiments were performed under open circuit, an applied potential of -0.6 V, and an applied potential of +0.6 V, using approach velocities of 50 nm/s, 100 nm/s, 200 nm/s, 500 nm/s, and 900 nm/s. A repulsive force regime is observed in the force curves under both open circuit and the applied potential of +0.6 V conditions (Figures 4.8A and C, respectively), that can be attributed to the presence of a high viscosity interfacial ice-like water layer. Under these conditions, a noticeable difference in the forces curves is observed with the repulsion force region extending outwards as the approach velocity is increased. Under the applied potential of -0.6 V, the repulsive force is negligible at the small velocities, which is consistent with the data from the previous chapter. However, upon increasing the velocity to 900 nm/s, a small repulsive force regime appears in the force curves (Figure 4.8B). The classical hydrodynamic drainage model $F = 6\pi\eta R^2V/D$, where $\eta$ is the effective viscosity, $R$ is the tip radius, $V$ is the approach velocity, and $D$ is the separation distance between the tip and surface predicts a linear dependence of the force $F$ with increasing velocity. The insets in figure 4.8 show plots of the normal force as a function of the approach velocity. The forces are reported at separation distances of 2 nm, 4 nm, and 5.5 nm (dotted lines) from the force curves in figure 4.8. The latter separation distances were chosen for our analysis.
Figure 4.8. Normal force curves recorded between a colloidal AFM probe and an ultra-smooth gold electrode surface at the various tip approach velocities and in 0.1M NaCl as the electrolyte. The inset plots correspond to force versus velocity data at a specific separation distance (denoted by the dashed lines).
based on when a repulsive force become noticeable in the force curves. In all three cases, a linear dependence between the normal force and the approach velocity was obtained which further confirms the formation of an ice-like water layer of high viscosity. Electrical double layer forces are negligible in our system due to the high ionic strength of the electrolyte (i.e., 0.1 M NaCl resulting in a Debye length of ~ 1 nm). A linear regression of the normal force versus approach velocity data yields a slope that correlates with the viscosity at a constant separation distance. The linear plotted graph under applied potential of +0.6 V condition exhibits the highest slope, thereby the highest viscosity. Previously, it has been shown that the effective viscosity of water next to the gold with the surface potential of +0.6 V is approximately 5 orders of magnitude higher than for bulk water. At a surface potential of -0.6 V, the viscosity of water layer next to the gold surface deceases to lower values, even lower compared to the OCP case. The latter is again consistent with the fact that in the OCP case, water still orients to a certain extent.

4.4. Conclusions

In this study the effect of several system parameters (surface roughness, salt concentration and composition) on the friction force between an AFM tip and a gold surface was investigated. Applying a positive potential on a gold surface, irrespective of surface roughness, results in the formation of a highly oriented viscous water layer. The effective hydrogen bonding between the viscous water layer and the AFM tip results in high friction. However, interfacial water next to a gold surface with a negative applied potential has properties closer to bulk water which results in lower friction. Higher friction forces were observed when using electrolyte solutions of lower ionic strength when a potential of +0.6
V was applied on the Au surface. Additionally, it was found the sharp rise in friction was still present when using NaOH instead of NaCl as the aqueous electrolyte albeit the sharp rise occurred at different applied potentials. Force curve measurements performed at different approach velocities yielded a linear dependence which is consistent with a hydrodynamic drainage model.
CHAPTER 5: CONCLUSION AND FUTURE WORK

In this work, we successfully utilized atomic force microscopy to study interfaces and characterize intermolecular forces between a variety of surfaces in both air and liquid media. In the final chapter of this thesis, we briefly summarize the work that have been discussed in previous chapters and propose new directions for future research. Part I addresses the future directions of the project involving the adhesion of mosquitoes to fibrous surfaces. Part II addresses the second and third chapters involving the formation of an ice-like water layer at the interface between a charged gold (111) surface and an aqueous electrolyte solution.

5.1. Part I.

As we discussed in chapter 2, we successfully demonstrated that van der Waals interactions are the main adhesion mechanism employed by mosquitoes to adhere to various surfaces. We showed that creation of surface roughness on an opposing surface can create multiple contact points between surface elements and the setae on a mosquito leg, thereby increasing the adhesion strength. Although van der Waals forces are shown to be the predominant mechanism by which mosquitoes adhere to surfaces, capillary forces can also contribute to the total adhesion force when the opposing surface is hydrophilic and under humid conditions. These fundamental properties can potentially be applied in the development of superior Long Lasting Insecticidal Nets (LLINs), which represent one of the most effective methods to mitigate mosquito-transmitted infectious diseases such as Malaria, Filaria, Zika, and Dengue.
The data and analysis in chapter 2 are based on the nano-scale interactions of mosquito leg e.g. interaction of nanoscales structures on the leg with the opposing surfaces. In this study, the applied load on the mosquito leg upon contact with the surface was on the order of sub-hundred nano-newtons. However, based on the weight of a mosquito, we know that higher loads are exerted when they land on a surface. Thus, in our study, the mosquito leg would not be expected to be fully engaged with the surface and only a few setae are able to interact with asperities on the surface. Using our current set-up, applying a higher load results in damaging the AFM cantilever. Thus, performing a similar study using a setup that allows the study of the interaction between a mosquito leg and an opposing surface in micro-scale force range via applying higher loads, is desired.

As our data suggests, higher surface roughness increases the adhesion between mosquito legs and HDPE surfaces, which can be utilized to increase the residence time of mosquito on an insecticide-infused surface and thereby potentially enhancing the delivery of an insecticide to mosquitoes. Thus, future work aims at performing live mosquito experiments in which the residence time (i.e., average time that a mosquito remains on a surface) will be monitored as a function of the LLIN surface roughness. The residence time on rough

**Figure 5.1.** Schematic illustration of proposed mechanism for dry adhesive material inspired by mosquito legs.
LLIN surfaces will be compared to that of the commercially available LLIN. Furthermore, our results suggests that hydrophilic surfaces allows higher adhesion between a mosquito leg and the surface. It would be interesting to investigate the effect of hydrophilicity of material on the residence time of live mosquito.

Additionally, the result of this study can bring useful insight in the biomimicry area of study. For example, there are several attempts to mimic gecko toes in order to synthesize dry adhesive materials. However, such synthesized materials are very sensitive to surfaces roughness and mostly applicable only on smooth surfaces. The adhesion of mosquitoes, on other hand, introduces a new mechanism of adhesion because the latter utilize structures alongside their leg as opposed to setae only present at the end of the leg. Introducing hierarchical structures (e.g. as shown in Figure 5.1) on a biomimetic dry adhesive surface can potentially allow adhesion to rough surfaces as well as smooth surfaces.

5.2. Part II.

In Chapters 3 and 4, we presented an exploratory study of the tribological properties between an AFM probe and a Au(111) surface under an aqueous environment while subjected to applied surface potentials. Using a 3-electrode setup, the electrical potential and interfacial electric field on a Au(111) working electrode was controlled. Lateral force microscopy was used to measure the friction forces between the AFM probe and the Au surface. Normal forces were also measured as the AFM probe approached the surface to gain insight into the interfacial forces. When a positive potential was applied on the Au surface, the friction was found to rise sharply at a critical potential and level off at a relatively high value. However, when a negative potential was applied, the friction forces
was low, even lower compared to the open circuit potential case. These changes in friction, by a factor of approximately 35, as a function of the applied potential were found to be reversible over multiple cycles. We attributed the origin of the high friction at positive potentials to the formation of a highly confined ordered ice-like water layer at the Au/electrolyte interface which resulted in effective hydrogen bonding with the AFM probe. At negative potentials, the ice-like water layer was disrupted resulting in the water molecules acting as boundary lubricants and providing low friction. Using an ultra-smooth gold surface compared to a regular gold surface, we were able to confirm that the changes in friction as a function of the applied potential was independent of surface roughness. Increasing NaCl salt concentration, thereby Cl⁻ ions, in aqueous electrolyte disturbed the number of hydrogen bonds in the ice-like water layer next to Au surface and decreased the friction. Substituting the salt with NaOH in the aqueous electrolyte caused a shift in critical potential that caused a sharp increase in the friction value. Moreover, the interaction forces

![Friction Chart](image)

**Figure 5.2.** Bar chart of friction force between an AFM tip and the gold electrode surface in different electrolyte salt.
was influenced by the velocity of the tip approaching the gold surface. The normal force linearly increased as the approach velocity was increased.

We also performed several experiment substituting the salt with KCl, KOH, and MgCl$_2$ (Figure 5.2). In all cases, the friction value was similar and a high friction value at the positively charged gold surface and a low friction value at the negatively charged gold surface were observed. However, this experiment requires more analysis which can be addressed in future work.

We note that the hydrodynamic theory of drainage assumes a constant effective viscosity of the orientated water layer. However, based on our results, we propose that the viscous water layer consists of a gradient with most highly oriented water molecules next to the electrode. Future research can focus on modifying the hydrodynamic theory of drainage model to include the varying viscosity of the layer from the electrode surface to the bulk.

Future work also aims to investigate the effect of surface wettability on friction properties of electrodes. Previous studies have shown that the water confinement occurs near hydrophilic electrodes. Thus, similar trend/dependency of the friction on the applied potential, for other hydrophilic surfaces is expected. Similar experiment can be conducted using a similar set up with different working electrodes such as Ag, Pt, and Cu. Confinement and orientation of water molecules at the interface of hydrophobic electrodes is still a controversial subject. Therefore, a deeper understanding of the “ice-like water” layer on the surface of electrode is needed. One of the interesting future study directions is performing a similar experiment to study the interface properties of a hydrophobic charged electrode (for e.g., highly oriented pyrolytic graphite (HOPG)) and investigate the
effect of positive and negative applied potentials on friction of the surface. Another way of studying the effect of wettability of the surface is comparing hydrophobic and hydrophilic AFM colloidal probe tips. These type of studies can provide a better understanding of the interaction of a variety of surfaces with the ice-like water layer. Quasi-static Neutron Scattering can also be used to study mobility of water at the surface.

Also, the results of this study can potentially have applications in the field of biology and biomedicine. Because changing the interfacial interaction between gold and surfaces using electric fields is a reversible process, it can possibly affect the binding affinity of molecules e.g. proteins to the gold electrode (Figure 5.3). We hypothesize a lower protein binding affinity for the positive surface potential because the ice-like interfacial layer next to the positively charged electrode can disrupt the binding of molecules and organisms. Also, a

![Diagram](image)

**Figure 5.3.** Schematic illustration proposed mechanism for reversible protein binding affinity on the charged gold electrode.
higher binding of molecules to a negatively charged surface, even compared to the open circuit potential condition, is expected due to disturbed structure of water at the interface of the negatively charged surface. Thus, application of an external electric field can be utilized to control the surface properties of gold that allow the reversible control of protein adsorption and the regulation of the adhesion of biological cells and drug molecules. Controlling the affinity of biological molecules can open opportunities for many applications, for example, capturing and releasing special cells, detecting pathogen, targeted delivery of drugs, and etc.

Figure 5.4. Schematic illustration of surface plasmon resonance technique for measuring binding affinity of molecules to the gold thin film.

The affinity of biological molecules to surfaces can be studied via surface plasmon resonance (SPR). SPR allows measurement of the adsorption of molecules onto planer metals e.g. gold surfaces. In SPR system, the surface must be coated with a thin film of metal with conduction band electrons e.g. gold on the reflection site. Upon a light beam hitting the surface, the light photons are absorbed and converted into surface...
plasmons$^{156}$ (Figure 5.4). If the momentum of incoming light equals to the momentum of plasmons, resonance occurs. The binding of molecules on the surface results in the change of the reflective index, which also affect the SPR reflected light angle$^{157}$. Thus, a change in the SPR angle and the reflective index can be correlated to the number of molecules bound to the surface. Integration of an electrochemical cell into the SPR technique, known as EC-SPR, allows us to perform in-situ SPR electrochemistry experiments$^{158}$. Using EC-SPR, the affinity of biomolecules to the surface can be measured as the cyclic voltammetry experiment simultaneously is run. Thus, the regulation of biomolecules to the gold surface can be studied as a function of applied potential.

Additionally, the result of this study can also be used to study crystallization of the proteins or peg oligomers which can order at charged surfaces.
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APPENDIX A

Calibration of Normal Spring Constant:

Following is an step-by-step process of calibration of the cantilever’s normal constant.

1. In order to calibrate the spring constant, a hard substrate is needed. In our experiment, we are using fused silica substrate provided by Bruker.
2. Opening Nanoscope software, we choose mechanical properties quantitative nanomechanical mapping (QNM) in Air (for experiments in air) from the experiments category.
3. Choose desired scan size and setpoint and make sure the ScanAsyst auto control is on. Then choose engage.
4. After engaging the tip on the surface, we can see the tip is scanning the surface and collecting the height image.
5. Choose Ramp from the menu, use Deflection error vs \( Z \) for the data type. Then, collect at least three deflection versus \( Z \) curves through single ramps.
6. Open each file in the Nanoscope Analysis software.
7. Correct the baseline by choosing the baseline correction from the toolbar.
8. Set cursors on contact curves, choose the area with the slope
9. From the menu, under Commands tab, choose update sensitivity.
10. Average at least three sensitivity values using the collected Ramp curves. This averaged sensitivity value equals to the value we used for the deflection sensitivity discussed in the Chapter 1.
11. Return to NanoScope software, under the Calibrate tab, choose Detector and enter the averaged sensitivity value in deflection Sensitivity.
12. Withdraw from the surface and choose thermal tune from the tool bar.

13. After choosing the appropriate range under the thermal tune range, acquire data, fit the data.
14. Set cursors on the peak area of the data. Then choose calculate spring K. The spring constant value shows up in the window.
APPENDIX B

The defense presentation

CHARACTERIZATION OF INTERFACIAL FORCES USING ATOMIC FORCE MICROSCOPY: FROM BIOADHESION TO NANOTRIBOLOGY

A Dissertation Defense
By
Leila Pashazanusi
Chemical & Biomolecular Engineering Department
09/06/2018
Introduction And Backgrounds

Project 1: Bio-adhesion

Project 2: Nanotribology

Summary and Acknowledgment

Outline

Atomic Force Microscopy (AFM)

- The AFM, a high resolution microscope, has three major abilities: force measurement, imaging, and manipulation.
- AFM is working based on interaction of a sharp tip with a substrate surface.
- Any interaction can be detected through reflection of a laser beam focused at the back side of the cantilever to a position sensitive photodetector.

Operation Modes:
- AFM operates in different modes mainly: contact mode, tapping mode, and force spectroscopy.
- AFM operates in both air and liquid media.
AFM: Normal Force Measurement

- Vertical deflection of AFM cantilever can be detected by laser and converted to force data.

AFM: Lateral Force Measurement

- Torsional deflection of AFM cantilever can be detected by laser and converted to friction force data.
OUTLINE

- Introduction And Backgrounds
- Project 1: Bio-adhesion
- Project 2: Nanotribology
- Summary and Acknowledgment

BIO-ADHESION

ENHANCED ADHESION OF MOSQUITOES TO ROUGH SURFACES
Long Lasting Insecticidal Net

- Mosquito borne disease: Malaria, Zika, Dengue, …
- 700 million cases and around 1 million death
- No 100 percent effective vaccine or cure
- Prevention
- LLIN: Physical barrier + coated with insecticide

Modification

- Improving the net performance by introducing roughness, in form of fibers.
- The micro/nano-scale structures on the mosquito leg result in multiple points of contact with the fibrous elements.

Original net surface
- Low contact area
- Low adhesion

Modified net surface
- High contact area
- High adhesion
- Higher exposure time to insecticide

SEM image of a mosquito leg
- Mosquito legs consist of a large number of oriented micro/nanostructure scales.
Preparation and Characterization of Rough Surfaces

SEM images of HDPE surfaces with different roughness levels.

Profilometry images of large-scale and local RMS for surfaces I.

Roughness values of smooth and rough HDPE surfaces.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Large-scale RMS [μm]</th>
<th>Local RMS [μm]</th>
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<tbody>
<tr>
<td>I (smooth)</td>
<td>4.5±2.75</td>
<td>2.3±1.20</td>
</tr>
<tr>
<td>II (low-rough)</td>
<td>14.3±2.20</td>
<td>7.3±2.57</td>
</tr>
<tr>
<td>III (intermediate rough)</td>
<td>63.7±1.47</td>
<td>8.2±2.25</td>
</tr>
<tr>
<td>IV (high rough)</td>
<td>148±13.4</td>
<td>20.7±8.17</td>
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Attaching a Mosquito Leg to a AFM Cantilever

- The distal portion of a leg was sheared off a mosquito with the aid of ultra-fine tip tweezers.
- Using an optical microscope, the specimen was then glued to the end of a cantilever of an AFM probe.
- Super glue was used to adhere the mosquito leg perpendicularly to the cantilever.
A higher adhesion is observed between a mosquito leg and a rough surface compared to a smooth surface.


By increasing the surface roughness, the adhesion forces were found to increase.

A large deviation in adhesion data is observed.

Uniform Roughness

- The large deviation in data arises from the dependence of adhesion force on the landing site of the leg on the rough polymer surface.

- Four types of landing positions:
  (i) partial contact with the top of the pillars
  (ii) full contact with the top of the pillars
  (iii) contact in between the pillars
  (iv) full side contact with the pillars

Effect of Humidity and Temperature

- Water contact angle on HDPE = 95.27˚
- Water contact angle on a silicon wafer = 25.43˚

Conclusion and Future Work

• Effect of surface roughness on the adhesion of mosquitoes legs to HDPE surfaces was investigated and it was found that surface roughness increased the adhesion force.

• It was found that although the adhesion force could be attributed predominantly to van der Waals interactions on hydrophobic surfaces.

• These results can potentially be applied in the development of superior Long Lasting Insecticidal Nets.

Future Work:

• Monitoring residence time of live mosquitoes as a function of LLIN roughness.

• Investigating the effect of hydrophilicity of material on the residence time of live mosquito.

• Other applications that can be inspired by study of mosquito adhesion to fibrous surface such as dry adhesive material.

Outline

Introduction And Backgrounds

Project 1: Bio-adhesion

Project 2: Nanotribology

Summary and Acknowledgment
NANOTRIBOLOGY

REVERSIBLE POTENTIAL DEPENDENT FRICTION ON Au(111) MEASURED BY AFM

Previous Works on Nanoscale Friction


Effect of an Applied Potential on the Electrode/Electrolyte Interface

- Formation of a highly structured “ice-like” layer at the interface of positively charged electrode.
- Water layer at negatively charged electrode interface behaves like bulk water.


Modification

Water Oriented water

Solid Substrate

Nanometer layer

Density (g/mL)

Distance from Au surface (nm)

Low COF

High COF
Surprisingly higher viscosity of the “ice-like layer at the positively charged electrode (Electro-viscosity).


Tunable Friction
Experimental Set up

Working electrode: Gold substrate
Counter electrode: Pt
Reference electrode: Ag wire

How Is Friction Affected by the Applied Potential?

A sharp increase in friction is observed when the surface potential changes from negative to positive.

Is the Change in Friction Reversible?

Reversible over 15 cycles with minimal change in the minimum and maximum friction forces with no apparent surface damage.

How Does an Applied Potential Affect the Electrode/Electrolyte Interface?

Higher number of hydrogen bonding between water molecules at the positively charged surface.
How Is Friction Affected by the Applied Load?

- Coefficient of friction changes by a factor of 24
- Coefficient of friction changes by a factor of 22

- Coefficient of friction changes by a factor of 17

How Is Friction Affected by Salt Concentration?

- Salt ions disrupt the equilibrium of water molecules entering and leaving the solid state.
- The presence of salt disrupts the hydrogen bonding between the AFM tip and the oriented water layer thereby reducing friction.

Decrease in friction was observed with an increase in electrolyte ionic strength.

How Is Friction Affected by Anion/pH?

- Due to the self-ionization of water (i.e., $\text{H}_2\text{O} \rightarrow \text{H}^+ \text{OH}^-$), the addition of OH$^-$ is not expected to significantly disrupt hydrogen bonding or the ice-like interfacial water formation.
- Cl$^-$ ions disrupt hydrogen bond formation which manifests as requiring a higher positive potential (or driving force) to form the ice-like interfacial water layer.
How Is the Normal Force Affected by Applied Potential?

\[ F = 6\pi R^2 \eta v / D \]

A longer range repulsive force is measured at positive potentials with a viscous layer about $10^5$ times larger than bulk water.

How Is the Normal Force Affected by Approach Velocity?

- A linear dependence between the normal force and the approach velocity confirms the formation of an ice-like water layer of high viscosity.
- +0.6 V condition exhibits the highest slope, thereby the highest viscosity.

\[ \text{Viscosity} \approx 150 \text{ Pa.s} \]

(about $10^5$ times larger than bulk water!)

Future Work:

- Modifying the hydrodynamic theory of drainage model to include the varying viscosity of the layer from the electrode surface to the bulk.
- Application of an external electric field can be utilized to control the surface properties of gold that allow controlling the affinity of biological molecules e.g. the reversible control of protein adsorption and the regulation of the adhesion of biological cells and drug molecules.

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<tr>
<th>Outline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction And Backgrounds</td>
</tr>
<tr>
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List of Publications


• **Pashazanusi, Leila**, Kai Kristiansen, and Noshir S. Pesika. "Formation of Highly Viscous Water at Charged Solid/Liquid Interfaces." Submitted to *Langmuir*


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