THE ROLE OF WATER ON THE TRIBOLOGICAL PROPERTIES OF MOLYBDENUM DISULPHIDE FILMS

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2012
To my mom, dad and sister
ACKNOWLEDGMENTS

I would like to thank Professor W. Gregory Sawyer for his help and guidance throughout this process, without which this dissertation would not have been possible. I would also like to thank Dr. Michael T. Dugger for his mentorship, guidance, and support throughout the last year of this process. I would also like to thank the other members of my committee, Prof. David Hahn, Prof. Scott Banks, and Prof. Scott Perry, for their invaluable advice and input during this process. I’m in gratitude for the years of friendship and collaboration with the members of the University of Florida Tribology Laboratory, especially Dr. Nicolas Argibay who has played a crucial role in the development of this dissertation. I am also very appreciative of all the support Andy Korenyi-Both of Tribologix Inc. has been by providing numerous coating batches that have enabled the completion of this work.

I would like to acknowledge the contributions of numerous staff members at Sandia National Laboratories for their input and help developing this work. In particular Robert Sorenson and Samuel Lucero for their advice and the use of the QCM equipment, Robert Grubbs for the use of his tube furnace, Ronald Goeke for his invaluable advice about molybdenum disulphide, Michael Brumbach for his XPS work, and Richard Grant for his SEM work.

I would like to thank my parents, Susan M. Dubinsky and Richard W. Colbert. Without their support and encouragement none of this would have been possible. I would also like to thank my sister, Jessica A. Worthington, for her love and support.
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<td>Atomic Force Microscope</td>
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<tr>
<td>H₂O</td>
<td>Water</td>
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<td>HRSEM</td>
<td>High resolution scanning electron microscopy</td>
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<tr>
<td>LPM</td>
<td>Liter per minute</td>
</tr>
<tr>
<td>Mol/area</td>
<td>Moles per unit area</td>
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<td>MoS₂</td>
<td>Molybdenum disulphide</td>
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<tr>
<td>ppm</td>
<td>Parts per million</td>
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<td>PTFE</td>
<td>Polytetrafluorethylene</td>
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<td>QCM</td>
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<td>RH</td>
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<td>Sb₂O₃</td>
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<td>SEM</td>
<td>Scanning electron microscope</td>
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<td>SWLI</td>
<td>Scanning white light interferometer</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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THE ROLE OF WATER ON THE TRIBOLOGICAL PROPERTIES OF MOLYBDENUM DISULPHIDE FILMS

By

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December 2012

Chair: Wallace Gregory Sawyer
Major: Mechanical Engineering

Molybdenum disulphide (MoS₂) based coating's tribological properties are adversely affected by the addition of water into the environment. The friction coefficient is known to increase with increasing relative humidity and decrease with decreasing relative humidity, which is a repeatable process. There still remains a gap in the literature on the effects water has on the wear of MoS₂ films and the quantities of water uptake that are associated with changes in the relative humidity of the environment. Both of these topics are addressed in this work.

The first studies examined the friction and wear of self-mated composite MoS₂ thin films in a cycled relative humidity environment. The surface topography was evaluated as the environment was cycled through wet and dry conditions and the steady state wear rates in each environment were examined. It was found for all films the wear increased in the higher humidity environment and decreased in the dry nitrogen environment.

The second portion of this work analyzed the quantity of water absorbed in both a pure MoS₂ and composite MoS₂ film at various relative humidities. It was found that
there were two distinct types of water uptake occurring, water that requires additional energy for desorption to occur and water absorbed reversibly at room temperature.

The final portion of this work comments on the diffusion kinetics occurring within the film. Diffusivity values for water into molybdenum disulphide films were calculated and the location of the water during the two observed sorption processes was hypothesized.
CHAPTER 1
INTRODUCTION

Solid lubricant can be defined as a material that provides lubrication to two relatively moving surfaces under dry conditions [1]. This is generally a thin film of a low shear strength solid that lowers the friction coefficient and helps to prevent damage between the mating surfaces. Commonly used solid lubricants include graphite, molybdenum disulphide (MoS$_2$), and polytetrafluoroethylene (PTFE). Although there is documentation on the ‘slippery’ feel of both MoS$_2$ and graphite dating back for centuries, the more modern uses of these solid lubricants dates back only to the 1930s.

There are four main forms of using a solid lubricant: 1) loose powder rubbed onto the mating surface, 2) bonded materials attached to the surface with a binder or the use of sputtering deposition, 3) additives to greases and oils, or 4) self-lubricating materials for devices such as bearings.

Solid lubricants are primarily used when greases and oil lubricants cannot be used. These environments include extreme temperatures (both high and low), high vacuum, and areas of intense radiation [1,2]. The benefit of solid lubricants is that they can perform in these extreme environments as well as more moderate environments.

The main advantage for solid lubricants is their stability at extreme temperatures and in irradiated environments. They are also known to be of lighter weight than oil systems and allow for placement of mechanisms closer to heat sources thus decreasing shaft lengths in assemblies. Solid lubricants also keep surfaces separated during slow sliding under high loads [1].

While the advantages are numerous, there are disadvantages to solid lubricants as well. Generally, the friction coefficients can be higher than with hydrodynamic
lubrication [1]. Additionally, they have a finite wear-life while oils and greases can be replenished into contacts. The wear debris is also a concern as it can contaminate otherwise clean surfaces such as satellite solar arrays.

**Extraterrestrial Environment**

One of the main tasks for solid lubricants lies in moving mechanical assemblies within the aerospace industry. Spacecraft have numerous mission-critical assemblies with tribological components, some of which are depicted in Figure 1-1. These components must operate in the extreme environment of space and survive terrestrial testing as well. The space environment is known for thermal cycling, ultra-high vacuum, solar ultra-violet radiation, atomic oxygen, and debris all of which have the potential to cause issues. The ultra-high vacuum is between $10^{-8}$ torr to $10^{-13}$ torr depending on the orbital height. The temperatures are thought to range between -200 °C up to 100 °C depending on the amount of direct exposure to the sun.

![Figure 1-1. Typical mission critical tribological components in a satellite system that require low friction and low wear to successfully deploy.](image-url)
Atomic oxygen is the most prevalent molecular species in lower Earth orbit and is generated by ultraviolet radiation breaking down molecular oxygen [3]. Banks et al. showed the highly destructive nature which oxidizes and degrades the surfaces of the coatings [4]. The flux of atomic oxygen incident on a forward-facing surface, as a result of spacecraft’s high velocity can be significant [2,3].

These extreme environments imposed on the lubricants in space are only a portion of the conditions they must survive. The difficulty comes from the multiple environments these components must endure. Most mechanisms undergo numerous life cycle testing on ground in a relative humidity (RH) prior to launch, then must survive the launch process, and finally operate as designed in space. Within all these environments low friction and low wearing properties are required for a successful operation to occur.

**History of MoS$_2$ as a Solid Lubricant**

Molybdenum disulphide (MoS$_2$) remains one of the most common solid lubricants in use in the aerospace industry because of its low friction behavior and its low wear.

Molybdenum disulphide is a naturally occurring ore which is commonly referred to as molybdenite. It is a dark blue-grey or black solid which feels slippery to the touch [5]. The ease of transfer to most solid surfaces and difficulty to remove it explains its reference by the Greek and Roman civilizations over 2000 years ago as ‘plumbago’ or ‘molybdena’, meaning lead-like. Both of these words referred to graphite, lead, molybdenum disulphide or other various ores up to the 1700s. There was a lack of continuity in the written records differentiating between these solids, in particular between graphite and molybdenum disulphide.
According to Lansdown’s book [5], the earliest written account that identifies molybdenum disulphide as a lubricant was written by Cramer in 1764 [6]. Cramer [6] describes a black-lead substance that is heavier than glimmer-stones, feels much like soap, and lubricates surfaces when rubbed against them. It was also described as a substance that is black and shiny and upon heating loses its color and becomes softer.

Lansdown [5] emphasizes two points that validate this referring to MoS\textsubscript{2} and not graphite. The first is that glimmer-stones refer to micas which have specific gravities similar to graphite, respectively 2.7-3.3 versus 2.0-2.3, while molybdenum is quite heavier with specific gravities on the order of 4.6-4.8. Thus, the mention of heavier glimmer-stones must be MoS\textsubscript{2}. The second point cites the change in color that occurs ‘in the strongest open fire’ which refers to the oxidation to molybdenum trioxide.

Between the late 1700’s and early 1900s there was very little mention of molybdenum in the literature. By 1916, molybdenum disulphide had become readily available commercially. Around the same time its crystal structure was established by Dickinson and Pauling [7], which is shown in Figure 1-2, but it still was not of great interest to the lubrication community. Awareness of molybdenum disulphide increased in the 1930s when technical investigations by industrial organizations began. Numerous patents started to surface containing molybdenum disulphide as either an additive, a film adhered to the surface with a binder, or production of a synthetic version. Finally in 1941, Bell and Findlay published one of the first technical papers which discussed the use of MoS\textsubscript{2} as a lubricant for bearings in high vacuum conditions [8].

Studies by the US National Advisory Committee for Aeronautics (NACA) began in the 1940s and the first technical note on MoS\textsubscript{2} was published in 1948 by Johnson et al.
Solid-surface films of molybdenum disulphide on steel were analyzed for contact pressure and sliding speed effects on the friction. Johnson et al. concluded that MoS\(_2\) was very effective in reducing friction at high sliding velocities. This film was chemically and thermally stable, and should have many practical applications [10]. Experimental studies on MoS\(_2\) performed by NACA and its successor, the National Aeronautics and Space Administration (NASA), greatly increased the public's awareness and the usage of MoS\(_2\).

![Figure 1-2. The atomic arrangement of molybdenum disulphide which was adapted from Fleischauer et al. [7,9].](image)

The military began to use molybdenum disulphide in 1950 and the first military specification for dry powder lubrication was issued in 1952 [5]. The initial applications were for anti-seizure or anti-galling purposes on non-critical components. By 1965, the range of MoS\(_2\) uses had grown and there were nine U.S. and five British military
specifications covering molybdenum disulphide based powders, greases, bonded films, and anti-seizure compounds [5].

Technical studies were continuing and publications of the environmental effects on molybdenum disulphide films began to appear in the late 1950s. Johnson and Vaughn studied the effects of orientation of the crystallites in the sliding surface and adsorption of vapor by the MoS₂ surface. Johnson et al. developed a theory, the ‘buildup effect’, which explained the increase in friction coefficient after sliding was halted for a period of time [10]. After every test stoppage the friction would increase, but eventually run back into a similar steady state value as before. This was the first discussion on how water vapor affects MoS₂ films. In 1966, Haltner and Oliver studied the effect of water vapor on the friction coefficient of a MoS₂ film [11]. They confirmed that as water vapor concentrations were increased, the friction of MoS₂ increased, yet for graphite the friction coefficient decreased under the same conditions [11,12]. An explanation for the effect of humidity on MoS₂ friction could not be thoroughly explained at this point in time.

During the 1950s and 1960s the effect of temperature on MoS₂ coatings was investigated as well. Both oxidation and sublimation temperatures were examined. Cannon discussed the lack of agreement in the research community on the melting point of MoS₂ with reported values ranging from 1300-1700 °C [13]. After additional testing was done, the melting point was not confirmed, but sublimation was noted to have occurred at 1250 °C. Godfrey et al. and Bisson et al. showed that oxidation becomes appreciable above 360 °C but rapidly increases above 560 °C when tested in ambient environments [14,15]. When coatings were heated in nitrogen or hydrogen
environments they could withstand temperatures up to 650 °C and still provide satisfactory lubrication [16,17].

By 1967, a new technique for applying a thin MoS₂ film was established and discussed by Spalvins et al.[18]. Prior to this time, MoS₂ was adhered through the use of binders and burnishing methods, with both techniques having some major downfalls. Binders had the potential to be undesirable due to potential chemical interactions that affect the film’s adherence to the substrate. Burnished films, those in which the surface is rubbed in a particular orientation in order to align the surface layers, lacked uniformity, tended to have a higher friction coefficient, and had adherence issues to the substrate. Spalvins et al. established a vacuum-deposition method, also known as physical direct-current sputtering [18,19]. The films produced by this method showed an increase in wear life as well as a more stable friction response for the life of the films on varying substrates. The cleanliness of the substrate prior to deposition was emphasized as an important factor on performance of the film.

Over the next decade the analysis of MoS₂ focused on film development, explanations of run-in periods, and additional temperature affects. Hopkins and Campbell analyzed twenty-two MoS₂ based films at temperatures ranging from -70 °C up to 200 °C [20]. Not one film performed well at all temperatures and the conclusion was made that further developments must occur but until then films must be matched to the specific conditions of interest. While the crystal structure of MoS₂ was investigated in the 1930s, its lubricating mechanisms explaining the run-in period of the friction coefficient was under investigation during the 1970s. During the early portion of this decade the characteristic behavior of molybdenum disulphide’s grains to orient under
mechanical stress and to form homogeneous smooth films on both sliding surfaces was discovered [21,22].

Developments in MoS$_2$ films were important during this time. Three types of sputtering were used to produce satisfactory films in the early 1980s: radio frequency sputtering, direct current diode sputtering, and direct current-triode-assisted sputtering. Three essential features for a satisfactory performance of a sputtered MoS$_2$ film include 1) a good substrate to achieve interfacial adhesion, 2) proper chemical composition with stoichiometry as near as possible to natural MoS$_2$, and 3) production of a stable structure of the films [23]. Metal dopants were used to strengthen the sputtered films, as well as aid in its crystal growth and stabilize the film structure [23].

New film development continued to thrive in the 1990s. Modifications to the films to increase performance were done by layering or co-depositing metals which promotes the formation of MoS$_2$ with basal plane orientation and low porosity [23-27]. The tribological performance is dependent on the sputtering conditions which control the microstructure and thus controls the crystallinity, morphology, and composition [28]. Spalvins and Roberts summarized various sputtering conditions that were shown to affect the film’s characteristics including the cleanliness of the substrate, deposition rate, partial pressure of water, structure of the film, and final film thickness [29,2]. It was noted that the adherence of the film depends strongly on the preparation and cleanliness of the substrate surface prior to deposition [29]. The deposition rate and amount of water vapor have an impact on the stoichiometry of the film; a high deposition rate and low partial pressures of water vapor allow for stoichiometric films to be deposited. If a lower rate of deposition and a higher partial pressure of water exist then
the films become sulfur deficient and contaminated with oxygen [2,29]. The structure of sputtered MoS$_2$ can be varied from crystalline to amorphous with substrate temperature changes. Ambient and elevated temperatures are preferred to allow columnar structure of crystalline growth in which low shear basal planes are aligned perpendicular to the substrate surface. This structure has the tendency to not be fully dense but can be densified by low-pressure deposition, ion beam bombardment during film growth, co-sputtering with alloy dopants, or multilayer deposition. For a low friction and acceptable wear life coating an ideal film thickness between 0.2 – 0.6 µm was suggested by Spalvins in 1992 [29].

By the late 1990s, molybdenum disulphide films had been successfully used in space for many years [30-35]. The friction behavior and wear performance of MoS$_2$ were still greatly dependent on the testing environment. Thus, modifications to these films to increase performance were done by layering or co-depositing metals in attempts to develop ‘chameleon’ coatings that can adapt to various environments [23-27]. These adaptations and additions to the coatings were made to decrease the sensitivity to atmospheric conditions.

Research in the field of coating development is still an ongoing process. While there have been numerous studies of various environmental effects on molybdenum disulphide coatings, the role water plays on the lubricity and wear is still not fully understood. The focus of this research is to analyze the effect water has on MoS$_2$ films to gain a better understanding of the wear, associated sorption isotherms, and diffusion mechanisms into the film.
CHAPTER 2
THEORETICAL BACKGROUND

Before understanding the origin of low friction and wear exhibited by this material, the fundamental theories associated with friction and wear must be understood. This chapter discusses a survey of topics devoted to understanding interactions between contacting bodies and the general theories applied for this research. The theories associated with contact area, friction, and wear are discussed in the first section. The second section goes over the theory of a quartz crystal microbalance. The final section discusses these theories as applied to molybdenum disulphide.

Contact Area, Friction, and Wear

Contact Area

Comprehending the difference between the real area of contact and apparent area of contact is crucial within tribological systems. While the ideal case of topographically smooth contacting bodies does exist on rare occasions, there is in fact a significant difference between the apparent and real area of contact between two mated surfaces. This difference in contact areas stems from the fact that surfaces, whether polished or not, are all relatively rough and on a microscopic scale exhibit roughness or asperities. The apparent area of contact is the amount of area where contact would exist if ideally smooth surfaces were mated. The real area of contact is the area of the asperities of the two surfaces that are in contact with one another which is only a fraction of the apparent area of contact. The distinction between these two areas of contact is shown in Figure 2-1.

Hertz was the first to describe the elastic deformation of two contacting solid surfaces as a function of the applied load [36]. Hertzian contact stress refers to a
localized stress that develops as two curved surfaces of varying radii come into contact and deform slightly under the load imposed. The amount of deformation that occurs is dependent upon the modulus of elasticity of the mated materials, the geometry of the contacting bodies, and the applied normal load. The roughness of the material’s surface is neglected in Hertz’s theory. The expression for the real area of contact is shown in Equation 2-1 which is dependent on the normal force \( F_n \), combined radius \( R' \), and the combined modulus of elasticity \( E' \).

\[
A_{r-Hertz} = \pi \left( \frac{3F_nR'}{4E'} \right)^{\frac{2}{3}}
\]  

(2-1)

As can be seen from the equation above, there exists a power law relationship between the real area of contact and the applied force, \( A_r \propto F_n^\frac{2}{3} \) (Hertz).

Holm proposed another contact modeling approach that assumed the material’s elastic limit was always exceeded by local stresses on the asperity level and thus plastic deformation occurs [37]. Even though the pressure over the apparent area of contact may be considered elastic, the force is distributed over the minimal contacting asperities of the real area of contact which plastically deform due to these applied pressures. The
real contact area is related to the applied load \((F_n)\) and the material’s indentation hardness \((H)\) but is independent of geometry for this approach. Holm found the expression for contact area assuming only plastic deformation of the surfaces which is shown in Equation 2-2.

\[ A_{r-Holm} = \frac{F_n}{H} \quad (2-2) \]

In the 1950s Archard published an article [38,39] negating the validity of Holm’s theory that contact between surfaces results in solely plastic deformation of asperities. Archard made the point that it is reasonable to assume plastic flow for the first cycles of the bodies contacting, but it is illogical to assume plastic flow for the entirety of a life cycle test [39,38]. The point was made that the asperities may be rubbed many times without being damaged, but when plastic deformation does occur, the asperities must reach a steady-state in which the load is supported elastically [38,39].

On a microscopic scale, the combination of Holm and Archard’s models of contact are better equipped to describe the deformation that is occurring to form the contact area between the surfaces. Macroscopically, for a pin-on-disk experiment, the two surfaces can be modeled as an ideally smooth ball mated with a smooth flat surface, allowing for Hertz’s single asperity contact model to be used. Hertzian contact pressures are used due to their simplicity and popularity by providing researchers with a nominal pressure value associated with the system of interest [40]. While, these Hertzian pressures are not necessarily the most accurate predictors of the actual pressures associated with the system, they are a good estimate to understand the magnitude of pressures being imposed.
Revolute Joints: Misalignment and Clearances

There are additional contact mechanics to consider in conjunction with the contact area considerations for tribological applications. Appropriate constraints and degrees of freedom are provided with the tribological interface for most systems and especially in bushings [41,42]. The design of a shaft revolving in a slightly larger journal or bushing is subject to evolutions of geometry, contact area, and pressure distribution which in turn affect the evolution in friction coefficient and torque. While this is of particular importance for bushing systems it also affects other contacting areas as well.

Colbert et al. showed the importance of edge geometry on bushing systems [43]. Edge geometry was studied by examining unmodified, chamfered, and radiused edges of bushings. All bushings for this study were coated with MoS$_2$/Au/Sb$_2$O$_3$ coatings approximately 2 µm thick and were tested in high vacuum environments. The friction coefficient versus sliding distance is shown for all bushing types in Figure 2-2 and a value greater than $\mu=0.27$ was established as coating failure. It was found that between two different standard bushings there was a three order of magnitude difference in wear life, but the variations in wear life were negligible in comparison to the chamfered and radiused bushings.

Interrogation of the standard bushings wear scars revealed a large contrast in the behaviors of nominally identical samples. This was most likely due to concentrated loading that occurred from slight sample differences in the bushings and shaft misalignments. The sample that had almost immediate failure showed a thin wear scar at the edge of the bushing which implies a concentrated load at one edge of the bushing which caused the quickened failure of the film and thus steel on steel contact. The wear scar of the second bushing was biased towards one edge as well, but to a lesser extent.
This difference in behavior between the precision machined shafts and bushings implies a severe sensitivity to system misalignment.

Figure 2-2. The difference in the number of cycles to failure for coated standard, radiused, and chamfered bushing. A) Friction coefficient ($\mu'$) is plotted versus sliding distance for nominally identical standard bushings coated with commercially available solid lubricant coatings. B) The cycles to failure are plotted versus friction coefficient ($\mu'$) for standard and edge modified bushings. The contrasting frictional behavior result from a strong sensitivity to angular misalignment between the bushing and shaft. This figure is reproduced from Colbert et al. [43].

The chamfered and radiused bushings were tested under identical conditions and showed a substantial improvement in wear life. As can be seen from Figure 2-2b the chamfered bushing failed after 35,000 sliding cycles and the radiused bushing ran for over 60,000 cycles without failure. Over-constraints are inevitable in application, but this data shows the importance of edge modifications to mitigate adverse effects of potential misalignments in systems.

Contact mechanics play an important role in all tribological systems. The contact area of the system affects the contact pressures applied to the system which in turn can affect the elastic/plastic regime being imposed on the tribological system. While the roughness of the associated system is important, sample design plays a vital role as
well. Simple adjustments of the design, like applying a radius to an edge can improve the life of a system by orders of magnitude.

**Friction**

Reduction of friction has been a topic of concern for centuries whenever mobile parts have been involved in the design of transportation, machines, or mechanical tools [46]. When sliding surfaces come into contact the friction between them arises from two main areas. The first factor is adhesion which occurs at the real area of contact [44,45]. The second factor arises from ploughing, grooving, or cracking of asperities on the mated surface.

The first studies on friction coefficients were done by Leonardo da Vinci in the late 1400s in which he distinguished between sliding and rolling friction. Since his findings were only recorded in his journals and never published, the credit for the basic laws of dry friction went to Guillaume Amontons over 200 years later in 1699 [5]. These basic laws of dry friction were stated as:

1. The friction force is independent of the apparent area of contact
2. The friction force is proportional to the applied load

Friction coefficient, $\mu$, is defined by Amontons’s second law in Equation 2-3 as a dimensionless ratio of friction force ($F_f$) between the mated bodies and the applied normal force ($F_n$).

$$\mu = \frac{F_f}{F_n} \quad (2-3)$$

In the early 1900s the frictional force was shown to be proportional to the real area of contact [46-48]. The real area of contact is affected by the material’s deformation...
regime whether it is plastic, elastic, or a combination of the two. This is discussed previously in the contact area section.

The validity of Amontons’s laws of friction was discussed by Archard [38,44,49]. If a single asperity is assumed to be in contact and the deformation is elastic, the area of contact, from Equation 2-1, is proportional to the normal force to the two-thirds power,

\[ A_r \propto F_n^{2/3}. \]

From the definition of the friction force in Equation 2-4 which is shown to be a function of \( A_r \) and the effective shear strength, \( s \), the proportionality between the normal force and friction force is found and shown in Equation 2-5.

\[
F_f = A_r s
\]

\[
F_f \propto F_n^{2/3}
\] (2-5)

This proportionality leads to the following.

\[
\mu \propto F_n^{-1/3}
\] (2-6)

This result does not portray the friction coefficient as constant and thus is inconsistent with Amontons’s law. If the deformation is now assumed to be plastic instead of elastic the load can be defined as a function of \( A_r \) and the flow pressure, \( p_m \).

\[
F_n = A_r p_m
\] (2-7)

From this definition the friction coefficient is defined as

\[
\mu = \frac{F_f}{F_n} = \frac{s}{p_m}
\] (2-8)

This validates Amontons’s law for single asperity plastic deformation as the friction coefficient will remain constant.
When multiple asperities are in contact on a surface under an assumption of solely elastic deformation, the load is now distributed amongst them and there is an associated area of contact for each asperity as well. Archard modeled a multiple asperity contact as spherical protuberances evenly distributed over a spherical surface which can be seen in Figure 2-3a [44]. The assumption was made that all spherical asperities were identical and thus the area of each contact was alike. The real area of contact was found to have the following proportionality.

\[ A_r \propto F_n^{8/9} \]  \hspace{1cm} (2-9)

Figure 2-3. Models of surfaces in contact showing the real area of contact under elastic conditions which was adapted from Archard [49]. The relationship between the normal force, \( F_n \), and the real area of contact, \( A_r \), are as follows: A) \( A_r \propto F_n^{2/3} \), (B) \( A_r \propto F_n^{4/3} \), (C) \( A_r \propto F_n^{8/9} \), (D) \( A_r \propto F_n^{14/15} \), (E) \( A_r \propto F_n^{26/27} \), (F) \( A_r \propto F_n^{44/45} \).

Archard continued this study by examining additional surfaces of varying asperity types. Figure 2-3b takes the initial surface and superimposes smaller asperities. This trend of increasing superposition of even smaller protuberances across the surface is
shown in Figure 2-3c-f. The proportionalities between the real area of contact and the normal force, listed in Figure 2-3 caption, become increasingly closer to unity. Archard thus concluded that in any real situation where elastic deformation is occurring the area of contact will be proportional to \( F_n^x \), where \( x \) lies between 2/3 and 1 [44,45]. This indicates that for multiple contact cases, even when the deformation is elastic, the real area of contact tends to be almost linearly proportional to the normal force which validates Amontons’s law.

**Wear Regimes**

A general definition of wear is the loss of material as loose particles from solid surfaces as a result of mechanical action [50]. Severe wear is generally thought to be the cause of failure for thin films. Abrasive and adhesive wear are the two main types associated with coatings. Abrasive wear occurs when a hard rough surface comes into contact with a softer asperity or surface and it results in deformation of the softer material. It is also known to remove material through ploughing, cutting, or scratching of the surface. There are two main types of abrasive wear, two-body and three-body. When hard debris particles are generated and they adhere to the surface that is known as two-body abrasive wear. Third-body abrasive wear occurs when these hard particulates are not constrained and are free to roll and slide in the contact. Fatigue induced cracking is at times considered abrasive wear, but is limited to brittle materials which are not addressed by this research.

Adhesive wear occurs when two surfaces come into contact and material transfer from one surface to another occurs due to localized bonding between the contacting asperities. This bonding can be due to cold welding or galling of the surfaces. When metallic bonding between atoms on opposing surfaces occurs, this is known as cold
welding. Galling on the other hand occurs from excessive friction between asperities results in localized welding which subsequently causes metal tear out or metal transfer to occur between the mated surfaces [51]. While in both cases seizure of the surfaces occurs, a distinction between the two is important. The main difference is that contaminant free surfaces are required for cold welding to occur, while galling is caused by high friction between the mated surfaces.

In space conditions both of these seizures must be accounted for during the design process. While surfaces are not likely to become sufficiently clean for cold welding to occur during a practical mission lifetime, galling caused by loss of the lubricant is more likely. It is for this reason that design engineers are faced with the task of over designing for multiple lifetimes to limit the possibility for failure caused by galling. Adhesion is one of the largest contributors to friction and wear of coatings. As discussed previously, surfaces of most materials are rough on the microscopic scale thus causing load between the two surfaces to be supported only at the points where the asperities touch. The real area of contact is thus minimal and the resulting pressures generated at these contacts are high, often surpassing the yield stress of the material. These high pressures cause adhesion of the contacting asperities which in turn requires a greater lateral force, or frictional force, to allow sliding to occur [5].

Wear Rates

The measurement of wear is typically presented as a wear rate and may involve a single measurement at the end of an experiment or multiple measurements throughout the experiment. Wear data is influenced by inherent material properties, testing conditions, surface preparation, and measurement methods [52]. There are four
established methods to obtain wear rate values: i) analysis of the spherical cap, ii) linear displacement, iii) mass loss measurements, or iv) area loss measurements.

Mass loss measurements are considered impractical for solid lubricant thin films due to material transfer that occurs from the coating to the mated surface. Similarly, linear displacement measurements of the amount of material worn from the pin do not apply either. The concept of analyzing the wear on a spherical cap of the pin is possible, but requires an estimate of an average radius which increases the uncertainty in the measurement. The final method is an area loss measurement which is the primary methodology for these studies.

Area loss measurements are done with either a scanning white light interferometer or profilometer. In order to estimate the wear volume with this method, the technique discussed by Williamson and Hunt [53] and Sayles [54] was employed. The technique evaluates a surface before and after deformation has occurred. Thus, an initial surface scan of the virgin material can be compared to a surface scan of the wear scar after wear has occurred and an area loss measurement can be obtained. Multiple measurements can be made throughout the wear track to compute a best estimate of the average area loss. Thus the average area can be extrapolated over the entire length of the wear scar and a volume loss can be estimated.

Archard proposed that the total wear volume is proportional to the real area of contact times the sliding distance [49]. From this postulation, a wear coefficient, $K$, was introduced that has dimensionless proportionality between the real area of contact, $A_r$, sliding distance, $d$, and the volume of material lost, $V$, which is shown in Equation 2-10.

$$K = \frac{V}{A_r d} = \frac{VH}{F_n d}$$

(2-10)
This wear coefficient is often used as an index of the severity of wear occurring in systems [55]. The lower the value of $k$ the smaller the amount of wear produced. The specific wear rate, $k$, is a similar term to the wear coefficient, but not dimensionless which is shown in Equation 2-11.

\[
k = \frac{V}{F_n d}
\]  

(2-11)

Both of these wear descriptors are used frequently in literature and thus attention must be paid as to the units being addressed. The specific wear rate, with units of $(\text{mm}^3/\text{Nm})$ will be the focus of the research discussed in this paper.

The uncertainty associated with the wear rate is dependent upon the volume loss, normal force, and sliding distance uncertainties. The normal force uncertainty depends on the method of measurement. If the force is measured then the uncertainty associated will be dependent upon the force transducer used. If a dead weight loading system is in place, then the uncertainty will be associated with the calibration of the load used. For sliding distance, the main computational methods for linear stages are either the use of an LVDT or encoder. With rotary stages either an encoder is used or the speed is measured and multiplied by the duration of the experiment. For LVDT’s and encoders, their associated uncertainty is dependent upon the uncertainty of the equipment. The uncertainty with rotary stages measuring distance from speed and time measurements depends upon the uncertainty in the duration of the test, angular speed, and wear track radius [52]. The uncertainty in volume loss according to Burris and Sawyer [52] dominate all other values. The volume loss values depend greatly on the variations in the wear track. Colbert et al. describe the variability in volume loss measurements as far more significant than the uncertainties of the instruments.
themselves [56]. It is for this reason that the recommendation is to measure multiple scans throughout the wear track to account for potential variations. A useful measurement of uncertainty should consider the number of scans taken, the variation between those scans, and the geometry of the experimental system [56]. This method of calculating uncertainty is derived by Colbert et al. and the final definition is shown below in Equation 2-12.

\[ u_v \approx \frac{2\pi R}{\sqrt{N}} \sqrt{\sigma_A^2 + \frac{u_R^2}{R^2} \left( \sigma_A^2 + \bar{A}^2 \right)} \]  

(2-12)

According to Colbert et al., the uncertainty in the volume is dependent upon the radius of the wear track, \( R \), variation of the scanned areas, \( \sigma_A \) and \( \bar{A} \), and the number of scans, \( N \), utilized. In many instances the uncertainty of the radius, \( u_R \), is significantly smaller than the actual radius value and thus second term of Equation 2-12 can be neglected. From this knowledge, the equation can be simplified and is defined in Equation 2-13 below.

\[ u_v \approx \frac{2\pi R}{\sqrt{N}} \sigma_A \]  

(2-13)

Equation 2-13 demonstrates that the uncertainties in the volume loss depend on the variation in the wear track and the number of scans utilized to measure the volume loss. A general trend of the uncertainty diminishing as more scans are performed was found.

In some instances multiple scans throughout the wear track cannot be taken and the uncertainty in the instrumentation used must be applied. While this is not an ideal case, it provides a bound to the uncertainty expected for such measurements. For this case the uncertainty in volume loss is shown in Equation 2-14 and is dependent upon
the total number of pixels, \( I \), dimensions of pixels, \( \Delta x \) and \( \Delta y \), and the surface height after cycle \( n \) at pixel \( i \), \( h_{i,n} \).

\[
 u_c \cong \sqrt{I(\Delta x \Delta y)^2 u(h_{i,n})^2 + I(\Delta x \Delta y)^2 u(h_{i,n+m})^2}
\]

(2-14)

As the uncertainty in \( h_{i,n} \) and \( h_{i,n+m} \) is identical, the uncertainty in the volume loss equation can be simplified to that shown in Equation 2-15.

\[
 u_c \cong \sqrt{2I(\Delta x \Delta y)^2 u(h)^2}
\]

(2-15)

**Quartz Crystal Microbalance Theory**

In order to study quantities of water uptake, a quartz crystal microbalance (QCM) was necessary. Quartz crystal microbalances are used to measure the change in resonant frequency which can be directly related to the change in mass per unit area. Techniques can be applied in both liquid and gaseous environments, but for the purposes of these tests, a gaseous environment is the only one of interest.

The QCM technology relies on the piezoelectric properties of quartz. The piezoelectric effect was first discovered by Jacques and Pierre Curie [57]. The Curie brothers discovered when a mechanical stress is applied to the surfaces of certain crystals, this resulted in an electrical potential across the crystal. This allows for the acoustic resonance to be probed by electrical means, which has led to the development of QCM systems as well as other standing acoustic wave devices.

The QCM is comprised of a thin quartz crystal, or other piezoelectric material, which is sandwiched between two electrodes. An alternating current is applied between these two electrodes which produces vibrational motion at the crystal’s resonant frequency. As mass is added to the crystal, a frequency shift occurs. Typical
QCM systems are sensitive to the addition of less than 1 ng/cm² of mass and have a measurement range of resonant frequencies between 5 and 30 MHz.

Sauerbrey was the first to recognize the sensitivity of these piezoelectric devices towards mass changes. He developed a method to correlate the mass change per unit area at the QCM surface to the measured change in oscillation frequency of the crystal. From these studies the change in mass per unit area, \( \frac{\Delta m}{A} \), is related to the change in frequency, \( \Delta f \), initial resonant frequency, \( f_o \), the density of the quartz crystal, \( \rho_q \), and the shear modulus of the quartz crystal, \( \mu_q \). This relation is known as the Sauerbrey equation which is defined in Equation 2-16.

\[
\frac{\Delta m}{A} = -\frac{\Delta f}{2f_o^2} \sqrt{\mu_q \rho_q}
\]  

(2-16)

In order for the Sauerbrey equation to remain valid the additional mass must be treated as an extension of the thickness of the crystal and the following three criteria must be met: the additional mass must be rigid, the additional mass must be distributed uniformly, and the change in frequency divided by the characteristic frequency, \( \frac{\Delta f}{f_o} \), must be less than 0.02.

If these conditions cannot be met, the Sauerbrey equation does not hold and other methods must be applied to account for acoustic impedance due to either environmental effects or viscoelastic mass being added to the crystal. For the research described in the next sections the mass changes are assumed to be ideal masses that follow the three criteria and thus the Sauerbrey equation is valid.
Temperature has a strong influence on the resonating frequency of the crystals. The frequency versus temperature characteristics of the crystal are affected by the cut of the crystal. The characteristic curves for AT, DT, SL, and XY cut crystals are shown in Figure 2-4. The plot shows the change in frequency with respect to the resonant frequency versus the temperature difference from 25°C. AT cut crystals are known to have less of a temperature dependence around room temperature, as can be seen from the graph.
the curve, and is the primary reason for their popularity. In order to account for the a
temperature change a third order polynomial fit to heating/cooling frequency can be
used to correct for the changes due to thermal gradients.

**Molybdenum Disulphide Theoretical Background**

Molybdenum disulphide is the main focus of this research. An understanding of its
lubrication mechanisms and how various environments have been shown to influence
the tribological properties will be discussed.

**Lubricious Properties of MoS₂**

The lubricious nature of molybdenum disulphide has long been known, but the
reason for this behavior has been under debate for years. In 1967 Winer summarized
the three main areas of thought on the mechanism for this low friction behavior as: 1)
the easy cleavage which provides low friction coefficient, 2) the low friction is dependent
on adsorbed molecules between crystallites, and 3) the frictional behavior is dominated
by the forces acting between individual crystallites with cleavage taking place along
grain boundaries as opposed to between the layers in an individual crystal [59]. The
mechanism which is most supported in the literature is the first which bases the
frictional properties off of the nature of the crystal structure. This mechanism will be the
main discussion on the lubricity of molybdenum disulphide.

The suggestion of easy cleavage of MoS₂ occurring due to its crystal structure was
first made by Dickinson and Pauling [7]. They noted that the intrinsic crystal structure
was made up of lamina. Further studies have since been performed and molybdenum
disulphide has been shown to be hexagonal in nature with a layer-lattice structure.

Each sulfur atom is equidistant from three molybdenum atoms and each
molybdenum atom is equidistant from six sulfur atoms which form a triangular prism
structure [5,21,22]. Strong covalent bonding occurs between the metal molybdenum with a high polarizing influence and the non-metal sulfur which is easily polarized [22]. These tri-layer planes are stacked, with larger distances between the adjacent sulfur layers than the thickness of the layers themselves, with weak attractive van der Waals forces between them [21,22]. These van der Waals forces allow for relatively weak shear forces to be required to displace lamella with respect to one another, thus allowing for the low friction properties.

There are three main conditions which must be satisfied for molybdenum disulphide films to exhibit low friction coefficients. First is the formation of a well adhered, uniform transfer film on the mated material. The second requirement is the reorientation of the (0001) basal planes of the MoS$_2$ grains within the interface to be parallel to the sliding direction. This reorientation must occur on the surface of the film, the transfer film, and the third bodies formed as well [60]. The last requirement is the lack of contaminants such as oxygen, carbon, and water. MoS$_2$ films are known to be contaminated by oxygen as molybdenum oxide or by substitution of oxygen atoms in the lamellar structure [61]. Carbon contamination largely comes from the sputtering deposition process and is usually a surface contaminant of the films [60]. Finally, the contaminant of the biggest concern is water.

**Water Vapor Affects**

The role of water vapor has been a prominent topic of research in the molybdenum disulphide community since the 1950s. As coatings were tested in varying relative humidity, the trend of increasing friction coefficient with increasing relative humidity was found [5,62,12,63,64]. There reaches a point where the friction no longer
increases (about 40% - 65% RH Figure 2-5a and 2-5b), and after that point the there is a potential for the friction to decrease which is shown in Figure 2-5a.

![Graph showing the effect of relative humidity on the friction coefficient of MoS$_2$.](image)

Figure 2-5. The effect relative humidity has on the friction coefficient of MoS$_2$ A) adapted from Peterson and Johnson [64] and B) Pritchard and Midgley [63].

One theory for the rise in friction coefficient was presented by Pardee [65] in which oxidation of the surface of molybdenum disulphide films to molybdenum oxides is the cause of this rise in friction. The slight reduction in friction at the highest humidity was proposed to occur from the formation of hydrogen sulphide as a by-product of the oxidation process which reacts with the substrate to form a sulphide film thus providing the reduction in friction [65].

Another explanation for increased friction with humidity was proposed by Gao et al. [66]. It was suggested that in humid environments the ease of interlamellar slip is decreased for molybdenum disulphide. The absorption of water vapor was theorized to soften the films thus allowing for deformation with plowing to occur, which in turn disorients the film and increases the friction.
A distinction between adsorption and absorption must be discussed. Adsorption is the adhesion of atoms or molecules to a surface. Absorption refers to a process in which the atoms or molecules permeate the surface into the bulk. For this discussion of molybdenum disulphide, the results leave questions as to which is occurring.

Holinski and Gansheimer [22] theorized that the increase in friction coefficient with water present in the environment is due to the polarity of the sulfur surface which allows the water molecules to be easily adsorbed onto a run-in MoS$_2$ film. The water molecules bond with hydrogen bonding and thus connect molybdenum disulphide layers which causes the increase in friction coefficient. The amount of hydrogen bonding is proportional to the amount of sorbed water which is related to the humidity of the environment.

Johnston and Moore studied the sorption properties of MoS$_2$ powder samples[67]. The authors found that there was a reversible process of water uptake with the MoS$_2$ powder sample which they describe as an adsorption process. The data can be seen in Figure 2-6. It was suggested that this reversible process, which increased rapidly at higher relative humidities, could suggest capillary condensation of water molecules either between or within particles. This aligns with Holinski and Gansheimer’s theory as well.

Johnston and Moore [67] further studied the properties of MoS$_2$ sorption after degassing the sample at either 350 °C or 950 °C which can be seen in Figure 2-7. It was noted that after the first adsorption/desorption run, there was an irreversible amount of water that was sorbed onto the powder samples. When the second adsorption/desorption run was performed the data followed the curve of the first
desorption run. This again showed the reversibility of water sorption onto the powder samples after a quantity of water was irreversibly sorbed.

![Graph showing adsorption and desorption of water vapor at 30°C on MoS_2 powder](image)

Figure 2-6. Sorption and desorption of water vapor at 30°C on MoS_2 powder adapted from Johnston and Moore [67].

A transient effect in moist conditions was discovered by Haltner in which the coefficient of friction was shown to increase when the sample was exposed for a period of time [68]. The test was started and a run-in of the friction coefficient was observed, but when sliding was stopped for a period of time and then motion was resumed, the friction coefficient was shown to have increased but upon sliding dropped back down to the steady state value shown previously. After the stoppage time there was an increase in the friction coefficient. A similar experiment was performed in a dry nitrogen environment and for this test the friction was shown to remain at the run-in value after a period of no motion. This data is shown in Figure 2-8. This indicates that having moisture in the environment potentially contaminates the surface of the MoS_2 films causing the increase in friction coefficient after a period of exposure time.
Research on the effects of moisture on MoS$_2$ coatings expanded to include speed, temperature, and load affects. Friction was found to decrease with increased sliding speed [10,62,68]. Pritchard et al. found a decrease in friction with increasing temperature and attributed it to decreasing moisture content in the film from the temperature increase [63]. This theory was applied to both the sliding speed affects and the effects of load shown by Barrwell as well as Milne and Gansheimer that friction decreased with increasing load [69,70]. Figure 2-9 provides an example of the loading effects on MoS$_2$ films with varying relative humidity environments. For both speed and load affects, frictional heating is increased with increasing speed or increasing load which affects the moisture content of the film. Barry and Binkelman [71] made similar conclusions with respect to load and speed; friction was found to decrease with both increasing load and speed only when moisture was present in the environment. When
the same tests were performed in a dry environment, the variation in friction with respect to speed and load was almost nonexistent. These results substantiated Pritchard and Midgley’s theory of lowering the moisture content in the film lowers the friction resistance.

![Figure 2-8](image)

Figure 2-8. The effect of exposure time on the coefficient of friction in both A) 50% relative humidity and B) dry nitrogen environments adapted from Haltner 1964 [68].

Overall, water effects and oxidation are still a large topic of research in the molybdenum disulphide community. A complete understanding of the role water plays on the film is still to be determined. What is known from the literature is that by introducing moisture into the environment the friction coefficient of both pure and composite MoS$_2$ films will increase and when moisture is removed the friction coefficient decreases again. Studies of the sorption isotherms on MoS$_2$ powder demonstrated that after a residual quantity of water was sorbed onto the powder, the adsorption/desorption process was reversible as well.

**Solid Lubricant Dopant Additions to MoS$_2$**

Once the effects of moisture on MoS$_2$ were beginning to be understood, the research community began to examine ways to limit the oxidation of the films. The
main area of focus became the formation of composite coatings to attempt to improve the structure of the coating, increase the density, and provide greater environmental stability. While numerous dopants have been attempted with MoS$_2$, the main ones of interest in this study are graphite (Gr), diamond-like carbon (DLC), antimony trioxide (Sb$_2$O$_3$), and gold (Au).

Figure 2-9. The effect of load and relative humidity on the friction coefficient adapted from Winer [59].
Graphite

Graphite has been in use as a solid lubricant for over 2000 years and until the mid-1900s was the most extensively used solid lubricant [5]. The appearance and tribological characteristics of graphite are quite similar to molybdenum disulphide which explains the lack of differentiation between the two in early written records. Both materials are dark, grey-black in color and have hexagonal lamellar, layer-lattice structures [5,41,72,73]. The crystal structure of graphite is shown in Figure 2-10. Within the layer, strong covalent bonds between the atoms form planes of high strength which provides the structural strength of the material, which is similar to the molybdenum disulphide structure. In directions normal to these planes weak bonding occurs due to the distance between atoms. This weak bonding allows for the materials to shear with greater ease in that direction. While this is similar to molybdenum disulphide, the main difference is due to each layer consisting of a repeated hexagonal arrangement of carbon atoms, not differing atoms as in MoS$_2$.

![Figure 2-10. Crystal structure of graphite adapted from Lansdown [5].](image)

Graphite and molybdenum disulphide are quite similar in structure; but there are distinct differences between the two materials. Molybdenum disulphide is made up of two elemental species while graphite is made of only carbon atoms. This distinct difference accounts for the discrepancy between the van der Waals forces among the
molybdenum disulphide molecules and the coulombic attraction between the carbon atoms [5]. For graphite, a tendency for interlayer bonding is increased as basal plane deformation from sliding exposes high energy edge sites. With an increase in the adhesion between layers, the friction and wear increase unless the edge sites can be neutralized [74]. Another difference comes from the environment in which each of these substances exhibits a low friction coefficient. Graphite exhibits a low friction characteristic in air, yet in vacuum it exhibits high friction and wear behavior. The high erratic friction characteristic in inert environments is known as ‘dusting’ from the disintegration of the material into a cloud of fine dust-like debris [73]. The low friction behavior requires the presence of water vapor or other condensable vapors which act to neutralize the energetic edge sites [73,75,76].

Yen [73] found that both oxygen and water can act as neutralizers for graphitic films reducing the friction and wear rate. When a film was transitioned between dry nitrogen and dry air, with water vapor content in the chamber being held constant at 100 ppm, the friction immediately dropped from 0.4 to 0.2 and this process was shown to be reversible as can be seen in Figure 2-11A. This implies that the oxygen in air can inhibit the increase in friction between the graphite layers. The next experiment was a transition from wet nitrogen to wet air environments which is shown in Figure 2-11b. For this experiment the chamber was maintained at a constant 50% RH. In this instance, the coating was initially at a lower friction value around 0.15 and immediately increased to 0.2 with the addition of wet air. For this case, the introduction of oxygen into the environment increased the friction of graphite back to the value shown for the transition between dry nitrogen and air and was shown to be reversible in nature. This
reversible process suggests that oxygen can modify the surface chemistry of graphite through either a chemisorption or physisorption process [73]. While it was reversible, there was a gradual irreversible increase in friction as well. This increase is suggested to be from the gradual flattening of asperities by wear as sliding is progressed; a greater real area of contact is formed and thus higher friction is obtained [77].

Figure 2-11. The environmental dependence on the friction coefficient of graphitic films reproduced from Yen [73]. A) friction coefficient changes as the environment is varied from dry nitrogen to dry air with constant water vapor content of 100 ppm. B) Friction coefficient changes as the environment is varied from wet nitrogen to wet air with moisture levels maintained at 50% RH.

Due to the beneficial performance of graphite in ambient conditions, composites have been attempted with molybdenum disulphide to combine the beneficial vacuum/inert properties of MoS₂ with the beneficial ambient properties of graphite. This has shown to improve the environmental stability in the presence of water vapor [78]. An understanding of which component expresses itself at the surface during the varying environments has been under scrutiny. Zabinski et al. [78] and Voevodin et al. [34] showed with Raman spectroscopy on a MoS₂/Sb₂O₃/graphite film that graphite becomes the primary component to express itself at the interface in ambient conditions and MoS₂ for dry sliding conditions. Voevodin et al.'s data is depicted in Figure 2-12.
Figure 2-12. The effect cycling the relative humidity from dry (0% RH) to 40% RH has on the friction coefficient which is reproduced from Voevodin et al. [35].

Diamond-like Carbon

Diamond-like carbon (DLC) describes a hard carbon film that is composed of amorphous materials but can include microcrystalline phases [79]. Within the DLC family, there are two main types of films, hydrogenated or hydrogen-free. Both types have numerous varieties that include amorphous structures and a mixture of sp\(^2\) (diamond bonding) and sp\(^3\) (graphite bonding) [80-85]. DLC films are gaining in popularity by showing promising tribological characteristics including high hardness, chemical resistance, wear resistance, and electrical resistivity [79,86].

Mechanical and tribological properties are dependent on the deposition process and thus the microstructures, chemistry, hydrogen content, and the sp\(^2\)/sp\(^3\) bonded carbon ratio [82,87-91]. DLC films are generally hydrogenated when ion beam or plasma-assisted chemical vapor deposition processes are used with hydrocarbon
precursor gases. Physical vapor deposition process use graphite as a precursor and offer the capability for hydrogen-free DLC growth [82].

While deposition plays a large factor in the properties, the testing conditions and environment greatly influence the tribological properties as well. Friction coefficient values reported in literature vary substantially ranging from 0.01 to > 0.5 [80]. The greatest effect on the friction of DLC films seems to be the moisture content in the environment, but the films do not necessarily have the same dependence on water vapor that graphite does [80,82]. Hydrogen-free DLC coatings tend to have improvements in the tribological properties in the presence of water vapor [82]. These characteristics are proposed to be from similar mechanisms as graphite with intercalation, or passivation of the dangling bonds, which allows for reduced shear strength. Hydrogenated DLC coatings have reduced friction and wear in inert and vacuum environments. Its degradation in moisture-rich environments is due to increased frictional forces from oxygen contamination on the surface [82].

Figure 2-13. The effect cycling the relative humidity from dry (0% RH) to 40% RH has on the friction coefficient for a Al₂O₃/DLC/Au/MoS₂ film which is adapted from Baker [92].
Similar to graphite, the addition of DLC has been suggested to improve environmental stability of the MoS\textsubscript{2} films. Baker et al. showed this improvement of frictional properties when the environment was cycled between air (40% RH) to dry nitrogen (<1% RH) and is shown in Figure 2-13 [92]. Chromik et al. showed that for a composite YSZ/Au/MoS\textsubscript{2}/C film the MoS\textsubscript{2} remains in the contact for both humid and dry environments and is the primary reason for the low friction coefficient [78,93,35]. Like that of graphite, there is still debate on the role these constituents play on the improvement of molybdenum disulphide’s environmental stability.

**Antimony Trioxide**

Antimony trioxide (Sb\textsubscript{2}O\textsubscript{3}) is an inorganic compound and probably one of the most important additives to molybdenum disulphide films for wear life improvement [94-96]. The first successful applications of Sb\textsubscript{2}O\textsubscript{3} and MoS\textsubscript{2} were reported by both Calhoun et al. [94][95] and Murphy [96] in 1965. While there has been a great deal of research into wear and friction mechanisms of MoS\textsubscript{2}/Sb\textsubscript{2}O\textsubscript{3} composites, a complete understanding of the mechanism has not been made. The improvement of performance is attributed to the formation of a Sb\textsubscript{2}O\textsubscript{3}-MoO\textsubscript{3} eutectic [95], limiting of MoS\textsubscript{2} oxidation to MoO\textsubscript{3} in which the mechanism is still undetermined [94], or the protection of MoS\textsubscript{2} by sacrificial oxidation of Sb\textsubscript{2}O\textsubscript{3} [97].

The mechanistic explanations of the early work can be split into two categories, chemical phenomena and mechanical phenomena. Lavik et al. [95] first suggested an explanation of chemical interactions. The friction and wear of MoS\textsubscript{2} films both with and without Sb\textsubscript{2}O\textsubscript{3} additives were examined and the addition was shown to decrease the friction. From these results, a theory was introduced that the performance was improved by the formation of eutectics with molybdenum oxides or through the
presence of low-melting oxides which combine easily. Further studies by Nosov [98] and Yamamoto et al. [99] suggested that Sb$_2$O$_3$ is preferentially oxidized over MoS$_2$. These first two theories were rejected by Centers [100] who took the mechanistic approach that Sb$_2$O$_3$ and other additives plastically deform at flash temperatures on asperities which in turn help to retain MoS$_2$’s preferred crystallographic orientation.

This idea of Sb$_2$O$_3$ forming a structural component in the films agrees with the previous studies. Harmer and Pantano [101] discussed an increase in density with the addition of Sb$_2$O$_3$ when sintered with MoS$_2$. This densification of the composite helps in the structural support suggested by Centers. Porosity that develops in films affects tribological properties by providing additional mechanisms for water to diffuse into the film or potentially collapsing during contact and thus causing debris/wear of the coating [31]. It has been noted that basal planes of MoS$_2$ which orient themselves in the sliding direction are formed on the sliding surfaces [102,103]. The structural support provided by Sb$_2$O$_3$ allows for the formation of these basal planes.
A limited number of tribological materials are qualified for use in space vehicles. Soft metals such as gold, silver, lead, and indium have been used for many years. Recent developments within the MoS$_2$ community have allowed for additional coatings to become qualified [104-107,102,108-110].

For this series of experiments a broad variety of MoS$_2$ based coatings were analyzed under varying environmental conditions to determine their wear performance. They are listed in Table 3-1. Some of the coatings are commonly found in space applications, while others are still being developed. The Air Force Research Laboratory developed the MoS$_2$/Sb$_2$O$_3$, MoS$_2$/Sb$_2$O$_3$/graphite, as well the MoS$_2$/Sb$_2$O$_3$/Au. Versions of both the coating containing graphite and gold are now commercially available from Tribologix Inc. Hohman Coatings also deposits a version of the molybdenum disulphide film containing gold. The pure MoS$_2$ coating studied was deposited by Tribologix Inc. The MoS$_2$/Ti coating was deposited by TEER Coatings Ltd.

Table 3-1. List of the coatings, their manufacturers, and the experiments they were used in.

<table>
<thead>
<tr>
<th>Coating Composition</th>
<th>Coating Provider</th>
<th>Experiments Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$+Ni</td>
<td>Hohman Coatings</td>
<td>In situ</td>
</tr>
<tr>
<td>MoS$_2$+Ti</td>
<td>TEER Coatings</td>
<td>In situ</td>
</tr>
<tr>
<td>MoS$_2$+Sb$_2$O$_3$</td>
<td>Air Force Research Labs</td>
<td>In situ</td>
</tr>
<tr>
<td>MoS$_2$+Sb$_2$O$_3$+graphite</td>
<td>Air Force Research Labs</td>
<td>In situ</td>
</tr>
<tr>
<td>MoS$_2$+Sb$_2$O$_3$+Au</td>
<td>Hohman Coatings</td>
<td>In situ</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>Tribologix Inc.</td>
<td>QCM</td>
</tr>
<tr>
<td></td>
<td>Tribologix Inc.</td>
<td>QCM</td>
</tr>
</tbody>
</table>
All commercial coatings were nominally 1 µm thick, unless otherwise stated in this work, although various deposition techniques were used to apply the coatings. MoS$_2$ with titanium was a layered coating created via sputtering a layer of pure titanium and then co-depositing a layer of MoS$_2$ and titanium, and finally applying a layer of pure MoS$_2$. The MoS$_2$ and nickel, pure MoS$_2$, and both MoS$_2$/Sb$_2$O$_3$/Au films were sputter deposited. The addition of other constituents besides the MoS$_2$ was to improve adhesion to the substrate, environmental stability, as well as add toughness to the coating. The Air Force Research Lab’s coatings are created via laser ablation of a target which is made of the desired constituents resulting in a coating of roughly the same composition as the target.

**Experimental Equipment**

Two types of equipment were used for these experiments: a tribometer and a quartz crystal microbalance. The tribometer used to perform testing was a linear reciprocator. Its functionality and design are discussed in this section.

**In Situ Linear Reciprocating Tribometer**

Wear track topography can vary greatly between samples which can potentially affect the wear life of a coating. It was for this reason an in situ linear reciprocating tribometer, depicted in Figure 3-1, was used to examine the wear occurring during experiments. This tribometer was described in detail by Bares et al. [111]. The in situ measurements were performed with a Zygo New View 5030 scanning white light interferometer (SWLI). The SWLI is capable of measuring surface heights of less than 1 nm up to 5000 µm in size.

The samples for the linear reciprocating portion of the tribometer were mounted on top of a linear stage while the force transducer was placed in the load path between the
pin and ground with a flexural component between them. This assembly was mounted
to a manual positioning stage which allowed the user to set a normal force up to a
maximum value of 10 N.

Figure 3-1. A schematic of the situ linear reciprocating tribometer with scanning white
light objective is shown. This tribometer is used to measure both friction and
wear rates of the coatings of interest.

This entire tribometer was situated within an acrylic environment chamber,
allowing for the gaseous environment to be varied. For the majority of experiments the
environment was either a dry nitrogen cover gas or 25% relative humidity (RH) air. Data
acquisition was recorded via a data acquisition card and LabVIEW where the normal
force, friction force, ambient temperature, temperature on the surface of the sample,
relative humidity, and stage position were all recorded.
Quartz Crystal Microbalance

The QCM system used for the room temperature experiments was an Inficon system. The controller was a XTM/2 which has the capability of measuring the frequency changes and thus associated mass per unit area values. The frequency range is 5 to 6 MHz +/-0.1 Hz. The recorder has an update rate of 4 Hz. The crystal holder was a front load standard single sensor holder with a maximum temperature range of 130 °C.

The system used for the thermal experiments was a Maxtech TM-400 monitor. The frequency resolution was 0.03 Hz for a 6 MHz crystal. The crystal holder was an Inficon cool drawer single sensor and a thermocouple was brazed to the back of the crystal holder to allow for in situ measurements of temperature changes.

The crystals were 13.97 mm diameter AT quartz crystals which are plano-convex contoured. The quartz crystal was coated with gold electrodes on either side of the crystal. Two types of crystals were used for these experiments, non-polished crystals from Inficon which have a base frequency range from 5.97 to 5.99 MHz and an average roughness of 1 to 5 µm. The other type used were polished crystals from Tangidyne LLC which also have a base frequency range of 5.97 to 5.99 MHz but an average roughness of better than 5 nm.

Experimental Setup

The emphasis of this work was to gain an understanding of the environmental factors that affect the wear of molybdenum disulphide films with a particular focus on the role water has on the tribological properties of MoS₂. The literature has demonstrated that the friction is affected by changing the relative humidity of the environment, yet there has not been a large focus on the wear of the coatings or the
general quantity of water that is required to affect the tribological properties. This section discusses experiments that provided insight into how wear is affected by the addition of water into the environment and how the quantities of water uptake change with varying water content. All experiments investigating the wear and friction in a humid compared to dry environment were performed at the University of Florida Tribology Laboratory. The experiments investigating the quantity of water uptake were performed at Sandia National Laboratories.

**Varying Humidity Friction and Wear Experiments**

One of the largest influential factors on the performance of molybdenum disulphide films is water in the environment. Water contamination has been a constant issue and its influence is not completely understood. The friction response of MoS$_2$-based coatings has been well documented for more than 60 years, yet studies on the wear process have been limited in the literature. The majority of the wear experiments have been ex situ after the coating has already failed. The goal of these experiments was to capture the evolution of the wear scar and thus the actual wear events as the test progressed.

As discussed previously, a SWLI is used to measure the wear of the coatings. By taking SWLI scans at regular time intervals at a consistent location near the middle of the wear track, the area loss at that particular region for each interval was measured, an example of which is depicted in Figure 3-2. As discussed in the theory section, the majority of the error in the volume loss calculations does not originate from the equipment, but in fact comes from the variation in wear that occurs throughout the wear track. Unfortunately for the in situ set of experiments, only one portion of the wear track was being measured, thus the variation in wear throughout the track cannot be
measured. It was assumed that the analyzed portion was a sufficient representative sample of the volume loss occurring throughout the wear track.

![Figure 3-2. Representative SWLI line scans taken at cycle 0 and cycle 2000 which are used to determine the area loss.](image)

The samples used for the in situ experiments were rectangular coupons of 1.50 in x1.00 in x0.19 in dimensions and were made of 304 stainless steel. Prior to being shipped for coating, the flats were polished to an average surface roughness better than 50 nm. The pin samples were 0.25 in diameter 6061-T6 aluminum spheres that were drilled and tapped to allow for a 4-40 screw. The spheres came polished with a mirror finish and were left unchanged prior to being sent for coating. Both coupons and pins were coated with MoS$_2$-based coatings, but these varied by constituents. The coatings used for these experiments are discussed in the first section of this chapter and are summarized in Table 3-1.

Prior to running any tests with this system, a calibration step was performed to verify that the objective lens of the Zygo was aligned with the wear track. A counterface and pin were mounted to the system and the counterface was moved directly below the Zygo lens. The Zygo stage was adjusted to align the counterface normal to the
objective axis. After the surface was brought into focus, the stage was returned to its initial position and the pin was loaded to 5N. The sample was run for 50 cycles on a 5 mm track to allow for a visible wear scar to be achieved. The pin was then unloaded and the stage was moved 0.5 mm at a time until the center of the wear scar was in the center of the field of view. This distance was then noted for future testing purposes.

The protocol for varying humidity environmental testing was established as a cyclic procedure. The two environments of interest were laboratory air conditions (RH>20%) and back-filling the acrylic chamber with dry nitrogen which provides a relative humidity of less than 2%. The sample was run for a total of 500 cycles in the dry environment with scans of the same portion of the wear track taken after cycles 0-20, 30, 40, 50, 100, 200, 300, 400, and 500 cycles. The chamber was then purged with laboratory air and the sample was run for another 500 cycles with the same scan frequency. This process was repeated for a total of 2000 sliding cycles, 1000 cycles total in each environment.

The next wear track run followed the same protocol but began in a laboratory air environment and transitioned to a dry nitrogen one afterwards. The goal of this data was to provide insight into how the system accommodates for a transition between the dry and humid environments where the friction coefficients are drastically different. It also aimed at understanding if the initial run in period in either a dry or humid environment will affect the future performance of the coating.

**Steady State Wear Experiments**

The varying humidity experiments provided insight into the evolution of wear and how the system accommodates changes in relative humidity, but it was not an ideal method for studying steady state wear of the coatings in each environment. Two
separate wear tracks were run on each sample, one for each environment. The tests were run for 10,000 cycles and SWLI scans of the wear track were taken every 1,000 cycles.

For these experiments a normal force of 5 N was applied between the counterface and the pin, a sliding speed of 10 mm/s, and a 5 mm wear track length was defined.

**Quartz Crystal Microbalance Experiments**

**Room temperature sorption**

As water has been shown to significantly affect the friction properties of molybdenum disulphide films, a better understanding of how the water is influencing these characteristics is still needed. The purpose of these experiments was to understand the quantities of water that the film sorbs during relative humidity cycling of the environment at room temperature.

The approach was to provide step changes in the relative humidity of the environment to analyze the diffusion rates into the films. This was accomplished by minimizing the volume surrounding the QCM. Two 250 mL beakers were used for the dry and wet environments with separate flows going into both. The dry beaker had dry nitrogen flowing into it at 3 liters per minute (LPM) which allows the entire volume to be replenished in 5 seconds. The wet environment consisted of a 3 LPM dry flow that splits with a portion flowing through a bubble humidification system before recombining. All flows are controlled with variable area flow meters which allowed for fine control of the desired relative humidity in each beaker. This system is depicted in Figure 3-3.

The QCM was rigidly fixed to a relative humidity probe for all experiments. This allowed for in situ measurement of both the relative humidity and environmental temperature in the beakers. The relative humidity probe was a Vaisala DRYCAP hand-
held dew point meter DM70. The probe has a dew point temperature range of -50 to +60 °C with an accuracy of +/-2 °C. The probe measures the relative humidity from 0 to 100% but the accuracy varies depending on the relative humidity range being read. For measurements less than 5% RH the accuracy is +/-0.025% RH +17% of the reading. For measurements greater than 5% the accuracy is +/-0.8% RH +2% of the reading. It has the capability of measuring the ambient temperature from -10 to +60 °C with an accuracy of +/-2 °C.

Figure 3-3. Experimental setup for step change in relative humidity experiments.

The procedure for these experiments was to mount the crystal into the holder, allow the QCM frequency to reach steady state in the ambient lab environment to verify that the electronics were warmed up and no electronic drift was occurring. Once a steady frequency value was read, the QCM and RH probe were placed into the dry nitrogen beaker and again allowed to equilibrate. After both the environment and the frequency had reached steady state (~1000+ seconds), the QCM and RH probe were removed from the dry beaker and placed immediately into the humidified environment beaker. While this was not a perfect step change in the relative humidity, the environment had reached a steady state relative humidity in about 5-10 seconds. This procedure was repeated numerous times for the various relative humidities of interest.
(5%, 10%, 20%, 30%, 40%, 50%, 60% and 70%). All experiments were performed at the ambient lab temperature which was recorded with the RH probe.

**Thermally activated desorption**

The next set of experiments sought to gain an understanding of the amount of water that can be removed after a thermal cycling procedure associated with the crystals after exposure to relative humidity environments. In order to accomplish this, the crystals were heated in an inert environment to remove the potential for oxidation of the film and analyze the quantities of water desorption from a thermal cycling process. This setup is depicted in Figure 3-4.

![Figure 3-4. Experimental setup for thermal desorption experiments.](image)

The QCM system used for this set of experiments was a Maxtech TM-400 monitor. The frequency resolution was 0.03 Hz for a 6 MHz crystal. The crystal holder was an Inficon cool drawer single sensor and a thermocouple was brazed to the back of the crystal holder to allow for in situ measurements of temperature changes. This assembly was welded to a CF40 feedthrough which attaches to one end of the furnace used.

A Thermo Electron Corporation Lindberg/Blue M tube furnace was used to heat the crystal. It has a maximum temperature of 1200 °C. The QCM assembly was suspended in the middle of the tube furnace to allow for heating to be established via radiant and convective methods. A flow through system was established through the
furnace. This consisted of a dry nitrogen flow at 4.5 LPM which was split into a pure dry flow and a wet flow through a bubble humidifier. Both the dry and wet flows are recombined prior to entering the chamber and have variable area flow meters which were used for fine control of the flows, thus allowing for relative humidity regulation in the furnace. The oxygen content and relative humidity of the flow was measured on the exhaust of the furnace. The exhaust was flowed through a General Eastern Hygro M4 chilled mirror and then through a Delta F Platinum Series Oxygen Analyzer. All heating experiments were performed under a dry nitrogen environment with oxygen content less than 5 ppm.

A LabVIEW program was used to read in the temperature and crystal resonant frequency data. The relative humidity and oxygen content was recorded by the user at regular intervals.

The experimental procedure was to mount the crystal into the chamber, establish a dry nitrogen flow through in the environment, and allow for the crystal’s frequency to reach a steady state value. Once a steady state frequency was established the furnace was turned on to heat the crystal to 110 °C. After holding the system at 110 °C for 3-10 hours, the furnace was turned off and allowed to cool down back to the ambient lab temperature. This was repeated 1-2 times to understand if additional water could be removed after the first heating/cooling cycle.

The last portion of this experimental procedure was to follow a similar protocol as that of the 110 °C heating, but heat the crystal to 170 °C to observe if additional mass loss will occur at the higher temperature.
**Microscopy**

Upon completion of the QCM experiments, various surface characterization techniques were performed on the crystals. Extreme high resolution scanning electron microscopy (HRSEM) was utilized to characterize the surface microstructure of the deposited films. The HRSEM work was performed at Sandia National Laboratories by Richard P. Grant on a FEI Magellan 400.

X-ray photoelectron spectroscopy (XPS) was performed at Sandia National Laboratories by Michael T. Brumbach. XPS was performed using a Kratos Axis Ultra DLD Instrument with a monochromatic Al Kα (1486.6 eV) source operated at 225 W and a base pressure less than 5x10^-9 torr. Full survey spectra were collected with an analyzer pass energy of 160 eV and step size of 900-1000 meV. High resolution spectra were collected with an analyzer pass energy of 40 eV and step size of 0.1 eV. The analyzed area was an ellipse with dimensions on the order of 300 μm by 700 μm. All spectra were analyzed using CasaXPS software. The quantifications were obtained from CasaXPS using the built-in relative sensitivity factors. The peaks were fit using a Shirley background and a Gaussian(70%)/Lorentzian(30%) line shape. The Mo 3p^{3/2} peak was fit using two unconstrained components. The low binding energy component is designated as MoS_2 while the higher binding energy component is associated with MoO_3.

The final characterization technique utilized an atomic force microscope (AFM) to acquire topographical images to determine the surface area of the films. This work was performed by Anna Trujillo and Tony Ohlhausen at Sandia National Laboratories on a Bruker Dimension Icon. Peak force tapping mode was performed with a 2 nm nominal
radius TESP-SS tip cantilever. Two scan sizes were analyzed, 5.0 x 5.0 µm and 500 x 500 nm.
CHAPTER 4
EXPERIMENTAL RESULTS

In Situ Wear Experiments

The in situ changing environment experiments were performed to gain a better understanding how the wear of molybdenum disulphide (MoS₂) coatings develop with changes in the water content in the environment. It has been shown throughout the literature that increasing the relative humidity of the environment leads to an increase in the friction coefficient. The goal of these experiments was to observe the wear with varying relative humidity and correlate the results to the previously understood friction coefficient trends.

The method used to estimate the wear volume occurring in these systems was discussed in Chapter 2. For this particular set of experiments, due to the nature of the experimental equipment, only one cross-sectional scan of the wear track could be made during testing. While the assumption was made that the wear was uniform throughout the wear scar, the uncertainty in the measurements is lower than if the variation in the wear track could have been taken into account.

The experimental data for all cyclic tests initiated in laboratory air environments can be seen in Figure 4-1. For most of the coatings the volume loss did not significantly change with the changing environment, but as expected the friction coefficient changed considerably. The only coating which exhibited a noticeable difference in volume loss during the tests was the MoS₂/Ni film. For this film, the wear rate was less in the dry nitrogen environment as compared to the humid air portions of the test.
Figure 4-1. Friction coefficient and volume loss of the coatings are plotted versus normal force times sliding distance for all cycled environment experiments initiated in laboratory air.
Figure 4-2. Friction coefficient and volume loss of the coatings are plotted versus normal force times sliding distance for all cycled environment experiments initiated in dry nitrogen.
Similar results can be seen from the tests initiated in dry nitrogen, which is depicted in Figure 4-2. Again, the only coating demonstrating a repeatable difference in wear rates between the environments is the MoS$_2$/Ni film.

While wear rate values could be estimated for each environment during these 2000 cycle tests, the quantity of volume loss was minimal for some of the films. This increases the uncertainty in the measurements as the SWLI used has an estimated repeatability of 10 nm and some of the films had a final wear depth of only 100-200 nm for the 2000 cycle tests. It is for this reason that further studies were required to look at the steady-state wear rate of each film.

**Steady State Wear Rate Experiments**

In order to study the steady state wear rate of each coating, tests were performed for 10,000 cycles in a single environment. Tests were performed on all of the composite films tested in the previous in situ section and the results are summarized in Figure 4-3.

The aim of the 10,000 cycle experiments was to explore if the humidity in the environment affected the steady-state wear rates of the composite films. In all instances, the friction coefficient was higher in humid air than dry nitrogen which follows the trends from the literature. The wear rate had a similar trend for all films, but some films had a more pronounced difference with the change in environment than others. The MoS$_2$ with Sb$_2$O$_3$ and graphite film had the smallest difference between the humid air and dry nitrogen environments. This is attributed to the addition of graphite which, as discussed in Chapter 2, exhibits its lubricious nature in a humid environment [109,82,93].
Quartz Crystal Microbalance Experiments

Quartz crystal microbalance experiments were performed to gain an understanding of the quantities of water uptake associated with changes in the environmental relative humidity. Isotherms of water sorption on MoS$_2$ powder have been shown in the literature, but studies have not been performed on thin films. The goal of these experiments was to determine the quantity of water sorbed by the MoS$_2$ film.

Step Changes in Relative Humidity Experiments

The first data of interest was the room temperature water uptake of the films due to step changes in the relative humidity of the environment. The data is presented in
units of mass per unit area which was determined via the Sauerbrey equation applied to
the raw resonant frequency data. In order to grasp a better mental model of what a
mass per unit area quantity meant these values were converted to monolayers of water
sorbed. This data is not meant to literally assume that the water uptake is in a
monolayer fashion, but rather provide a mental model for the reader to comprehend the
magnitude of these numbers.

Two methods were determined to calculate the number of monolayers of water
sorbed. The first relies on the density and thickness. The thickness of a monolayer of
water is assumed to be 3.1\times 10^{-10} \text{ m} and the density of water is 1\times 10^6 \text{ g/m}^3. The
measured mass per unit area is divided by both the density and thickness, as shown in
Equation 4-1.

\[
ML = \left( \frac{m}{A} \right) \frac{1}{\rho t}
\]  \hspace{1cm} (4-1)

The second method takes into account the area number density, molecular weight
of water, and Avogadro’s number. The area number density, \(n\), is assumed to be 10^{15}
molecules/cm^2, the molecular weight, \(M\), is 18 g/mol and Avogadro’s number, \(N_A\), is
6.023\times 10^{23} molecules/mol. This method is shown in Equation 4-2. Both methods
provide results on the same order of magnitude, thus the first method is chosen to
calculate the estimated monolayers of water for all tests.

\[
ML = \left( \frac{m}{A} \right) \frac{nM}{N_A}
\]  \hspace{1cm} (4-2)

Experimental data for a 0.1 \mu m thick pure MoS_2 film deposited on a rough
substrate is depicted in Figure 4-4a. This graph shows the mass per unit area changes
with time as the relative humidity of the environment is changed for a subset of the data.
The step changes can then be normalized with respect to time and compared to one another, which is depicted in Figure 4-4b. The sorption isotherm for each coating is measured from the individual step changes in mass per unit area.

Figure 4-4. Mass per unit area data for representative step change in relative humidity data for the 0.1 µm thick pure MoS$_2$ film. A) Mass per unit area versus time. B) Mass per unit area and monolayers of water versus normalized time for the step change portions of data.

Figure 4-5. Mass per unit area data for representative step change in relative humidity data for the 0.1 µm thick MoS$_2$/Sb$_2$O$_3$/Au film. A) Mass per unit area versus time. B) Mass per unit area and monolayers of water versus normalized time for the step change portions of data.
A similar representative data set for a 0.1 µm composite MoS$_2$/Sb$_2$O$_3$/Au film is shown in Figure 4-5. Again the sorption isotherm is determined from the step change in mass per unit area data.

Three different crystals, all coated during the same deposition process, were cycled through a similar step change in relative humidity to analyze the repeatability in the measurements. The normalized mass per unit area data is shown in Figure 4-6. Significant variability was shown in the mass per unit area for these three crystals. As all coatings were deposited in the same deposition run, this variability is assumed to be due to the roughness of the quartz crystal substrate.

![Figure 4-6](image.png)

**Figure 4-6.** Variability between three crystals coated in the same batch at similar relative humidity step changes.

These crystals were analyzed using a scanning electron microscope (SEM) and a scanning white light interferometer (SWLI). Variability in the average roughness values was found between each of the crystals depicted in Figure 4-6. This implies the surface area for each crystal varies and thus the sites available for water uptake to occur vary as well. In addition, SEM images showed that there were relatively large trenches formed during the deposition of the coatings on these rough surfaces. Between the roughness of the substrate and the trenches in the coating there are additional surface
area sites and thus additional pathways for water uptake to occur. Due to the surface area variability between samples, the pure MoS$_2$ and composite MoS$_2$/Sb$_2$O$_3$/Au coatings cannot be compared at this time, but the general magnitude of values can be noted for each film.

Figure 4-7. Surface area variability between rough and smooth surfaces. A) depicts a surface that has an average roughness of 8 nm from a SWLI (left) and SEM (right) and B) depicts a surface with an average roughness of 350 nm from a SWLI (left) and SEM (right).

The large surface roughness and voids formed during the deposition process led to the purchase of polished QCM crystals to limit these surface area differences as well as improve the uniformity of the coating during the deposition process. The previous crystals had an average roughness of approximately 250 nm. The polished crystals had
an average roughness of approximately 8 nm. Representative images from a SWLI and SEM of a rough coated crystal and a polished coated crystal are depicted in Figure 4-7.

Figure 4-8. SEM micrographs of the two pure MoS$_2$ samples. A) Depicts the 0.1 µm film’s topography and B) depicts the 0.9 µm film’s topography.

Further analysis of the coatings microstructural differences using high resolution SEM techniques exemplified the difference between the 0.1 µm and the 0.9 µm thick MoS$_2$ films. The high magnitude SEM images of the coating’s topography are shown in Figure 4-8.

Figure 4-9. Mass per unit area data for representative step change in relative humidity data for the 0.9 µm thick MoS$_2$ film. A) Mass per unit area versus time. B) Mass per unit area and monolayers of water versus normalized time for the step change portions of data.
The next set of experiments explored the difference in mass uptake for the variable thickness coatings. The samples of interest were the previously studied 0.1 µm thick MoS\textsubscript{2} coating on the rough crystal and a 0.9 µm thick MoS\textsubscript{2} coating on a polished crystal. A representative portion of the step change in relative humidity data for the 0.9 µm thick MoS\textsubscript{2} film is shown in Figure 4-9.

The data from all of the step change experiments is summarized in Figure 4-10. This figure depicts the sorption isotherms for the 0.9 µm thick MoS\textsubscript{2} sample, and the 0.1 µm thick MoS\textsubscript{2} and MoS\textsubscript{2}/Sb\textsubscript{2}O\textsubscript{3}/Au samples. This illustrates that the two 0.1 µm coatings had similar magnitudes of water uptake as compared to the 0.9 µm coating whose water sorption values increased by an order of magnitude.

Figure 4-10. Water sorption isotherms for both 0.1 µm and 0.9 µm MoS\textsubscript{2} films and the 0.1µm MoS\textsubscript{2}/Sb\textsubscript{2}O\textsubscript{3}/Au film.
Inert Heating Experiments

During the step change in relative humidity experiments the mass per unit area would not always approach the initial minimum value for a dry nitrogen environment. From this knowledge the following heating experiments were performed to determine if there was any additional water in the films that is not removed by solely removing the moisture in the environment.

The initial heating experiments were performed on the 0.1 µm thick pure MoS$_2$ and MoS$_2$/Sb$_2$O$_3$/Au films. Both samples went through numerous heat/cool cycles up to 110 °C. The mass per unit area data is shown in conjunction with the associated temperature data versus time for the MoS$_2$ film and the MoS$_2$/Sb$_2$O$_3$/Au film in Figure 4-11 and Figure 4-12 respectively. In both figures, the temperature change is shown on the top plot and the mass per unit area is shown on the bottom plot.

Due to the previously discussed temperature effects on the QCM crystal, only the relative changes in mass per unit area at room temperature, before and after heating, are compared. These changes in mass are labeled throughout the figures.

It was noted for both the MoS$_2$ and the MoS$_2$/Sb$_2$O$_3$/Au films, after going through one heat/cool cycle at 110 °C a large portion of mass was shown to be removed from the film. When the crystals went through another heat/cool cycle with the environment remaining dry (O$_2$<5 ppm) only negligible mass loss was observed. This implies that at 110 °C it was possible to thermally desorb a maximum amount of water with one heat/cool cycle.

The next set of experiments analyzed the potential for additional water removal by heating to 170 °C instead of 110 °C. The mass per unit area and temperature data is
again plotted versus time for both the 0.1 µm MoS$_2$ and the MoS$_2$/Sb$_2$O$_3$/Au films. This data is shown in Figures 4-13 and 4-14 respectively.

![Figure 4-11](image1)

Figure 4-11. Relative changes in mass per unit area are measured before and after each heat/cool cycle up to 110 °C for the thin MoS$_2$ film. A) depicts the temperature versus time and B) depicts the mass per unit area versus time.

![Figure 4-12](image2)

Figure 4-12. Relative changes in mass per unit area are measured before and after each heat/cool cycle up to 110 °C for the thin MoS$_2$/Sb$_2$O$_3$/Au film. A) depicts the temperature versus time and B) depicts the mass per unit area versus time.
Relative changes in mass per unit area are measured before and after each heat/cool cycle up to 170 °C for the thin MoS₂ film. A) depicts the temperature versus time and B) depicts the mass per unit area versus time.

Additional mass loss was observed upon heating to 170 °C for both of the 0.1 µm films. In both instances mass changes of about 0.1 µg/cm² were observed for all heat/cool cycles at 170 °C once the initial large quantity of thermally desorbed mass was removed. For the MoS₂ film, the first 170 °C heat/cool cycle which was held for ~3 hours prior to cooling had a mass loss of 0.13 µg/cm². Upon the next heat/cool cycle,
the temperature was held at 170 °C for ~15 hours and only observed a mass loss of 0.14 µg/cm². The MoS₂/Sb₂O₃/Au film exhibited identical mass loss values of 0.12 µg/cm² when held at 170 °C for 7 hours and then at 4.5 hours, which was the same order of magnitude as the MoS₂ film.

The final experiment performed a similar heat/cool procedure up to 110 °C and 170 °C for the 0.9 µm thick MoS₂ film. Numerous cycles could not be performed due to time constraints with the equipment, thus a heat/cool cycle to 110 °C immediately followed by a heat/cool cycle to 170 °C was performed. The heat/cool data for the 0.9 µm film is shown in Figure 4-15.

![Figure 4-15](image)

Figure 4-15. Relative changes in mass per unit area are measured before and after each heat/cool cycles up to 110 °C and 170 °C for the 0.9 µm MoS₂ film A) depicts the temperature versus time and B) depicts the mass per unit area versus time.

As additional mass loss was shown to occur at elevated temperatures, verification that oxidation was not contributing to the mass loss values was required. High
resolution x-ray photoelectron spectroscopy (XPS) was performed on three crystals for each 0.1 µm film, one that was as-deposited, one film that had seen relative humidity exposures, and a film that had seen relative humidity exposures and gone through thermal cycles. The goal of the high resolution XPS was to quantify the degree of degradation that has occurred in the films for either relative humidity exposure and/or thermal cycling. XPS data was acquired around the Mo 3p region, fits were performed on the data for the corresponding oxide and sulfide for Mo binding energies, and finally the data was deconvoluted into the respective oxide and sulfide species contributions. This same process could be used on the S 2p peak, but as MoO₃ is not volatile, the Mo 3p peak provides a more reliable measurement of the quantity of oxidation as compared to the S 2p region. The data is shown in Figure 4-16.

It was found that there was not a strong trend of oxidation occurring in the films. It was also seen that the amount of oxidation seems to be crystal dependent and thus it’s hard to conclude whether the increase in oxidation seen was due to the environments to which the samples were exposed or simply variability within the samples. This data further supports the idea that if oxidation is occurring, it is minimal and thus the majority, if not all of the mass per unit area values are due to water removal.
Figure 4-16. XPS spectral region for Mo 3p^{3/2} used to determine the amount of oxidation via the ratio of Mo oxide to sulfide for the 0.1 µm MoS_2 films. A1) A MoS_2 coated crystal that was as-deposited. A2) A MoS_2 coated crystal is depicted that had experienced step changes in relative humidity. A3) A MoS_2 coated crystal is depicted that had experienced both step changes in relative humidity and heat/cool cycling. B1) A composite MoS_2 coated crystal is depicted that was as-deposited. B2) A composite MoS_2 coated crystal is depicted that had experienced step changes in relative humidity. B3) A composite MoS_2 coated crystal is depicted that had experienced both step changes in relative humidity and heat/cool cycling.
CHAPTER 5
DISCUSSION

This chapter describes the three major conclusions of the water sorption experiments and presents a hypothesis explaining the phenomenological difference in the sorption mechanism for room temperature desorbable water and thermally desorbable water. The first section is a discussion of the evidence that water absorbs into, rather than adsorbing onto, the film. The second section presents various methods for the calculation of diffusion coefficients of water into films of MoS$_2$. The third section presents a discussion of the thermally desorbable water. Lastly, the fourth section examines hypothetical phenomenological mechanisms by which room temperature and elevated temperature desorption of water occurs.

**Evidence of Water Absorption**

A difference in the amounts of water uptake was observed at room temperature for the thick and thin pure MoS$_2$ films. The coating thickness was increased by a factor of 9 from 0.1 µm to 0.9 µm. The room temperature mass per unit area of sorbed water at various relative humidities are summarized in Table 5-1.

Two factors affect water uptake in the films: film thickness and surface roughness, where surface roughness exists on multiple length scales. Figure 5-1 summarizes the ratio of the rough to smooth crystal surface areas. As seen in Table 5.1, the ratio of water uptake between rough and polished crystals was approximately 1:40. The ratio of the rough to polished crystal surface area at the nanometer scale was quantified via AFM measurements and was found to be 1:4. This ratio is under estimating the surface area, as can be seen by the difference in resolution between the SEM image and AFM image shown in Figure 5-1C, but provide a general approximation. If the diffusion of
water was solely a film surface (adsorption) phenomenon, then film thickness would not affect the mass uptake and only the surface roughness would affect the measurement. If this was the case, the mass uptake should scale by 1:2, as compared to the measured 1:40 ratio measured. Thus, the film thickness must be influencing the water uptake into the film. If water permeation into the film (absorption) is assumed to occur, then the ratio of rough/thin to polished/thick coated crystal surface is greater than 1:18. This data suggests that the water is diffusing into the film (permeating the film).

Table 5-1. Mass per unit area room temperature sorption values for both the thick and thin MoS₂ films, corresponding to the data shown in Figure 4-10.

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Mass per Unit Area [µg/cm²]</th>
<th>Relative Humidity</th>
<th>Mass per Unit Area [µg/cm²]</th>
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<td>65</td>
<td>15.88</td>
</tr>
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<td>61</td>
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<td>54</td>
<td>13.67</td>
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<td>0.25</td>
<td>51</td>
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<td>37</td>
<td>11.44</td>
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<td>8.86</td>
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<tr>
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<td>0.10</td>
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</tr>
<tr>
<td>4</td>
<td>0.08</td>
<td>5</td>
<td>5.65</td>
</tr>
</tbody>
</table>

**Diffusivity of Water in Molybdenum Disulphide Films**

With the knowledge that the water absorbed at room temperature permeates into the film, the kinetics associated with the rate of reversible water uptake are of interest. From the step change experiments performed, the diffusivity of water into these films can be determined.
Figure 5-1. The differential ratio for various length scales between the coated rough and polished crystals. A) depicts the difference in film thickness, B) SEM and AFM images are shown which illustrate the difference in micrometer scale roughness which is measured using a SWLI and AFM to provide the 2:1 ratio. C) Both AFM and higher resolution SEM images are shown to exemplify the difference in nanometer scale microstructural roughness which was measured using an AFM.
Diffusion coefficients of gases or vapors into solids can be measured via a number of gravimetric analysis methods such as indirectly measuring changes in mass as a function of the resonant frequency of a quartz crystal with a quartz crystal microbalance (QCM) [112-114]. In order for accurate measurements to be made the sample must have a well-defined geometry, typically a thin film, and the weight gain of the sample is measured with respect to time in a maintained atmosphere of penetrant at constant temperature and pressure.

Crank derived solutions for one-dimensional diffusion through a plane sheet [114]. The derivation starts with Fick’s second law of diffusion which is shown in Equation 5-1.

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]  

(5-1)

The boundary conditions and initial condition are shown in Equations 5-2 through 5-4.

\[
C(x, 0) = C_1
\]  

(5-2)

\[
C(L, t) = C_0
\]  

(5-3)

\[
\frac{\partial C}{\partial x} (0, t) = 0
\]  

(5-4)

The initial condition, Equation 5-2, describes that at t=0 the film is at a uniform concentration of C\textsubscript{1}. The first boundary condition, Equation 5-3, describes the concentration at the surface of the film, x=L, as being constant, C\textsubscript{0}, at any time after the beginning of diffusion into the film. In order for this boundary condition to be satisfied, the environment surrounding the apparatus, in this case the quartz crystal microbalance, must be changed instantaneously and maintained at a constant value with no pressure or temperature changes. Equation 5-4 requires that there is no transport beyond the bottom of the film, at x=0. The solution of Equation 5-1 subjected
to these boundary and initial conditions is described by Crank and shown in Equation 5-5 [115,116]. This solution assumes that the diffusion coefficient is constant and the volume remains constant (the film does not swell).

\[
\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \left\{ -\frac{D(2m+1)^2 \pi^2 t}{L^2} \right\}
\]

Equation 5-5 assumes that the uptake is considered a diffusion process which is controlled by a constant diffusion coefficient, D. In this equation \(M_t\) is the total amount of vapor absorbed by the sheet at time \(t\), and \(M_\infty\) is the equilibrium sorption attained.

The key assumptions made in this derivation by Crank are that the diffusion of the penetrant into the film occurs in one dimension, the concentration of the penetrant at the surface of the film is maintained at a constant value, and the diffusion coefficient is a constant [115].

The first assumption is valid as the thickness is small in comparison to the surface area of the coated quartz crystal. The film thicknesses ranged from 0.1 to 0.9 µm while the diameters of the coatings were over 8 mm. The second assumption is valid as the concentration of the environment surrounding the QCM system was kept constant. The surrounding volume was minimized and the flow rates allowed the environment to reach a steady state value in less than 5 seconds and be maintained to the concentration of interest. The final assumption is verified by the experimental data.

Obtaining a sorption curve from the QCM frequency data is a typical application of a QCM system. As the penetrant diffuses into the film of interest, a computer is used to record the resonant frequency of the crystal as a function of time. As was shown in Figures 4-4, 4-5, and 4-9 there is a frequency response measured with a step change in
relative humidity. From the measured frequency response data, the ratio of \( M_t / M_\infty \) can be calculated and graphs of \( M_t / M_\infty \) versus time can be generated.

The mass change of penetrant is proportional to the associated frequency change, as was shown from the Sauerbrey equation in Equation 2-16. The ratio of \( M_t / M_\infty \) can be expressed as the ratio of the frequency changes which is shown in Equation 5-6. The mass after time \( t \), is defined as the difference between the frequency of the crystal at time \( t \) after the penetrant is allowed into the chamber, \( f_t \), and the frequency of coated crystal prior to addition of penetrant, \( f_1 \). The mass at equilibrium is defined as the difference between the frequency of the crystal at equilibrium, \( f_\infty \), and the frequency prior to the addition of penetrant.

\[
\frac{M_t}{M_\infty} = \frac{f_t - f_1}{f_\infty - f_1}
\] (5-6)

From the \( M_t / M_\infty \) data the associated diffusion coefficients can be estimated through numerous methods. The three methods of interest for this work are the half-time, limiting slope, and moment method [112,113,116,117].

**Half-Time Method**

The half-time method is the simplest of the three that will be described for estimating the diffusion coefficient. The data is plotted in a similar fashion as the representative data shown in Figure 5-2. From this plot, the time at which \( M_t / M_\infty = 0.5 \) is determined. The diffusion coefficient is then found from Equation 5-7 [116,117].

\[
\left( \frac{t}{L^2} \right)_{1/2} = -\frac{4}{\pi^2 D} \ln \left[ \frac{\pi^2}{16} - \frac{1}{9} \left( \frac{\pi^2}{16} \right)^9 \right]
\] (5-7)

This equation can be simplified to solve for the diffusion coefficient as shown in Equation 5-8 [117].
\[ D \approx \frac{0.049L^2}{t_{1/2}} \]  \hspace{1cm} (5-8)

Figure 5-2. Example of calculating the time when \( M_t/M_\infty \) is 0.5 by the half-time method.

The associated error for Equation 5-8 was calculated via the law of propagation of uncertainty which is shown in Equation 5-9.

\[ u(D) = \sqrt{\left( \frac{0.049L^2}{t_{1/2}} \right)^2 u(t)^2 + \left( \frac{0.098L}{t_{1/2}} \right)^2 u(L)^2} \]  \hspace{1cm} (5-9)

**Moment Method**

The moment method requires the use of the entire sorption curve. The first moment, \( \tau_s \), is calculated via numerical integration as shown in Equation 5-10.

\[ \tau_s = \int_0^\infty \left( 1 - \frac{M_t}{M_\infty} \right) dt \]  \hspace{1cm} (5-10)

The first moment is determined from the plot of \( 1 - M_t/M_\infty \) versus time a representative graph is shown in Figure 5-3. The first moment is measured via numerical integration of the area under the curve, shown in Figure 5-3. The equation
for the average diffusion coefficient is then found from Equation 5-11 which is derived in detail by Willoughby [116].

\[ D \approx \frac{L^2}{3\tau_s} \]  
(5-11)

Figure 5-3. Example of calculating \( \tau_s \) by the moment method.

The associated error for Equation 5-11 was calculated via the law of propagation of uncertainty which is shown in Equation 5-12.

\[
u(D) = \sqrt{\left[ -\frac{L^2}{3\tau_s} \right]^2 u(\tau_s)^2 + \left[ \frac{2L^2}{3\tau_s} \right]^2 u(L)^2} \]  
(5-12)

**Limiting Slope Method**

The limiting slope method [112] is based off of the first-term in the series from Equation 5-5 at sufficiently long times. This approximation is simplified and shown in Equation 5-13.

\[
\ln \left( \frac{1 - M_t}{M_{\infty}} \right) = \ln \left( \frac{8}{\pi^2} \right) - \frac{\pi^2 Dt}{L^2} 
\]  
(5-13)
At large times, a plot of $\ln(1 - M_t/M_\infty)$ versus time will approach a straight line and
the diffusion coefficient, $D$, can be calculated by Equation 5-14. An example of
determining the limiting slope is shown in Figure 5-4.

$$D \approx -\frac{4RL^2}{\pi^2}$$

(5-14)

In Equation 5-13, $R$ represents the limiting slope of the previously described plot.
This limiting slope it typically found by performing a linear regression from $M_t/M_\infty=0.980-$
0.999.

Figure 5-4. Example of calculating $R$ by the moment method. A) is an example of the
thick sample in which the method is valid and B) is an example of the thin
sample in which the resolution of the instrument does not allow for this
method to be used.

The limiting slope method is not a good fit for this data set. This is due to the
increase in the relative error as there is an increased need for finer resolution with these
relatively small mass change values in comparison to literature results. The values of
the mass change per unit area become too small to resolve when $M_t/M_\infty$ is on the order
of 0.98 for thinner film data sets, as is seen Figure 5-4B.
**Diffusivity Results**

Data from all three films were studied to compare the difference in diffusivity between sample thickness and composition. For reasons discussed previously only the half-time and moment methods are used to calculate the diffusion coefficients of water into MoS$_2$. Table 5-2 summarizes the diffusivity results found from these experiments. The two methods provided values on the same order of magnitude, but the uncertainty in the moment method was greater thus for this discussion the half-time method diffusivity values were used and are summarized in Figure 5-5.

![Graph showing diffusivity results](image)

**Figure 5-5.** A comparison of the diffusivity of water into various MoS$_2$ films. The error bars represent the uncertainty in the data due to the use of the half time method.

The diffusion coefficient is not dependent upon the relative humidity of the environment which validates the assumption of a constant diffusion. The composite and pure 0.1 µm MoS$_2$ films were found to be of similar magnitudes while the diffusivity of water in the thicker pure MoS$_2$ film was found to have a faster rate.
Table 5-2. Calculated diffusivity values for the MoS$_2$ films. A) is the 0.9 µm pure sample, B) is the 0.1 µm pure sample, and C) is the 0.1µm composite.

<table>
<thead>
<tr>
<th></th>
<th>A 0.9 µm MoS$_2$ film</th>
<th></th>
<th>B 0.1 µm MoS$_2$ film</th>
<th></th>
<th>C 0.01 µm MoS$_2$/Sb$_2$O$_3$/Au film</th>
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<td>uncertainty of moment method [m$^2$/s]</td>
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<td>1.6E-16</td>
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</table>

The topographical differences, as shown in the SEM micrographs depicted in Figure 4-8, is hypothesized to be the potential cause in the change in diffusivity values between the varying thickness samples. The surface area availability for water uptake in the thick sample with the thin columnar-like topographical structure would be larger than that of the topography shown for the thin sample. While at this point in time this
hypothesis can’t be proven there is potential for further studies to analyze the surface area/internal porosity of the films using BET sorption isotherm methods.

**Thermally Activated Desorption**

**Continuous Mass Loss – Oxidation?**

During the inert heating experiments it was determined that relatively large changes in mass per unit area were observed after the first heat/cool cycle. This change in mass per unit area has since been referred to as thermally activated desorption. Two regimes of mass per unit area loss were observed, one at 110 °C and another at 170 °C.

Upon heating to 110 °C, a considerable amount of mass per unit area loss was measured, approximately twice the quantity observed during the room temperature absorption experiments. After further heat/cool cycles, minimal additional quantities of mass removal per unit area were found, ~0.007µg/cm². Yet, when the same procedure was repeated for 170 °C continuous larger changes in mass per unit area were observed, ~0.12 µg/cm². As these temperatures are not high enough to be affecting the quartz crystal’s mechanical properties, the only other potential explanation is the film is oxidizing causing these mass losses, with the rate of oxidation being less at 110 °C as compared to 170 °C.

In order to determine the potential for environmental impurities being the culprit for this continuous loss of mass per unit area, the impingement rate of water onto the coating surface was studied. The detailed analysis is described in Appendix A, a brief explanation follows here. This method is an attempt to provide an upper bound for the potential for environmental oxidation that could occur in the film.
The quantity of impurities in the ultra-high purity nitrogen gaseous flow is less than 5 ppm and thus a value of 1 ppm of water was assumed to interact with the coating for these upper bound calculations. The partial pressure of impurities in the environment is calculated from which the flux of impurities impacting per area per second is found. This flux can then be used to determine the total number of molecules of oxygen landing on the surface per area for the duration of the heat cycle. If the balanced chemical equation for oxidation of MoS$_2$ is analyzed, which is shown in Equation 5-14, 3.5 impacting impurities are required to convert one MoS$_2$ molecule to MoO$_3$ [118].

$$MoS_2 + 3.5O_2 \rightarrow MoO_3 + 2SO_2$$  \hspace{1cm} (5-14)

These calculations assume that every 3.5 impurities impacting the surface will lead to the oxidation of one MoS$_2$ to MoO$_3$. This is an upper bound on the problem as it is not likely that every impact will participate in the oxidation chemistry. The film is also assumed to be completely dry after being heated to 110 °C and thus only environmental impurities are the source for oxidation. The change in mass per unit area associated with this upper bound method was on the order of 1000 µg/cm$^2$. The values thought to be due to oxidation that were observed during testing were at most 0.14 µg/cm$^2$. Thus, it is very possible that environmental oxidation could be an explanation for this continuous mass loss occurring at both 110°C and 170 °C.

An attempt at quantifying the degradation of the film was made using x-ray photoelectron spectroscopy (XPS). As discussed previously in the experimental results section, the XPS data did not show a strong trend of oxidation of the films. Also, as a single crystal was not used for all XPS measurements, variability was found and no strong statements as to the degree of oxidation can be made. However, as there was
not a significant increase in the MoO$_3$ area of the Mo 3p peak, this suggests that the amount of oxidation occurring is minimal to nonexistent.

To further exemplify this fact calculations were made to determine what the change in fractional percentage of MoO$_3$ would be required for the measured mass loss per unit area at 170 °C. The detailed analysis is shown in Appendix B. It was found that the fractional percentage of MoO$_3$ would increase by ~3% with a mass loss of 0.12 µg/cm$^2$ for a film that is 0.1 µm thick. For the 0.9 µm thick film, the fractional percentage of MoO$_3$ drops to 0.3%. With such minimal changes in the quantity of oxidation, the variability of the oxidation between crystals masks the potential to measure the amount of oxidation occurring within the films.

**Ratio of Water to MoS$_2$ in the Film**

A comparison of the maximum quantity of mass per unit area thermally desorbed at 110 °C for all three films was made. Table 5-3 summarizes the results found, during the experimentation for both of the 0.1 µm films. These values were shown to be repeatable if the coating had been exposed for a sufficient time.

Table 5-3. Maximum thermally desorbed mass per unit area values at 110 °C

<table>
<thead>
<tr>
<th>Thickness</th>
<th>MoS$_2$</th>
<th>MoS$_2$/Sb$_2$O$_3$/Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>µm</td>
<td>[µg/cm$^2$]</td>
<td>[µg/cm$^2$]</td>
</tr>
<tr>
<td>0.9</td>
<td>8.53</td>
<td>0.82</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1</td>
<td>0.98</td>
</tr>
</tbody>
</table>

The thermally desorbed quantities of mass per unit area for the two 0.1 µm films were on the same order of magnitude while the thicker film had a value 10 times greater. The thermally desorbed mass per unit area scaled with the thickness, similar to the room temperature absorption values discussed earlier. It was of interest to
determine what moles per area (mol/area) of H$_2$O to mol/area of MoS$_2$ this would be associated with.

The method for determining the ratio of the mol/area for water to molybdenum disulphide is described in detail in Appendix C. This ratio will be referred to as the molar ratio for the purposes of this discussion. The mol/area of MoS$_2$ is determined from the molecular weight of MoS$_2$, density of MoS$_2$, and thickness of the film. The mol/area of water was determined from the measured mass per unit area loss and the molecular weight of water.

The molar ratios for 0.1 µm and 0.9 µm pure MoS$_2$ films were found to be similar, 0.14 and 0.16 respectively. This constant molar ratio of water to MoS$_2$ further supports the idea that the quantity of the thermally desorbed water scales with the film thickness.

**Hypothesis of Water Diffusion Locations**

With the knowledge that there are both room temperature sorption and thermally activated desorption processes occurring within these films, the hypothesis is that there are two diffusion processes taking place. The thermally desorbed quantities of water are the first to diffuse into a completely dry film. The water preferentially physisors to defects within the film, essentially capping the sites, which allows the water to be at a lower energy state than in the vapor phase leading to the necessity for additional energy to remove the water molecules. The next diffusion process occurs once the defects sites are capped and the water begins to stack up within the film. The water absorbed during this process does not require additional energy to be removed, thus the mass per unit area of water within the film will change with partial pressure of water changes.

As the 0.9 µm and 0.1 µm MoS$_2$ films were deposited by the same process, it would be anticipated that the ratio of the number of defect sites to the volume of MoS$_2$
deposited would scale with the film thickness. This appears to be a valid assumption as the molar ratios are both approximately 0.15 water to MoS$_2$. It is known from microprobe analysis that the films are not stoichiometric but closer to MoS$_{1.6}$. Thus, on top of the typical defects that occur during deposition sulfur vacancies could be another potential site for the physisorbed water that requires an energetic input to be removed.
CHAPTER 6
CONCLUSIONS

Water has been shown to significantly impact the tribological properties of molybdenum disulphide films. Both the friction coefficient and wear rates of the films were shown to increase with an increase in the moisture in the environment. While the wear rates followed the same trend, it was not to the same magnitude as the increase seen in the friction coefficient results.

Through the use of a quartz crystal microbalance water was shown to be absorbed into the film. Two different quantities of water were found, room temperature sorption and water that required an energetic input in order for desorption to occur. The thermally activated desorption quantities were found to have constant molar ratios of water to molybdenum disulphide for both film thicknesses. The room temperature sorption values linearly increased with an increasing film thickness, but the molar ratios were not constant.

The films were found to be sub-stoichiometric and thus further studies on a stoichiometric film would be of interest to determine if limiting the number of sulfur deficiencies will minimize the quantity of water that requires thermal energy to be removed. It is also of interest to determine how a tribologically run-in film, with oriented surface layers, would affect the diffusivity of water into the film. Another study of interest would be to have comparable thickness pure and composite MoS$_2$ films deposited on polished crystals to compare their change in diffusivity and water uptake quantities and potentially relate the differences back to the density differences of the films. Finally, determining the internal surface area through BET isotherm measurements would allow
a direct comparison between the films and water uptake without having to account for microstructural differences.
APPENDIX A
IMPINGEMENT AND OXIDATION RATES

This section presents a derivation of the impingement rates of impurities from the gas stream on the molybdenum disulphide coating surface during the heating experiments. These experiments were run with ultra-high purity nitrogen gas flow-through system.

As ultra-high purity nitrogen is known to have up to 5% impurities present in the gas, a conservative estimate of 1 part per million (ppm) of these impurities having the potential to lead to oxidation of the coating is made. It is then assumed that one tenth of these oxidizing impurities would impact the surface of the coating. From this the partial pressure of water, $P_{H_2O}$, present in the nitrogen can be calculated from atmospheric pressure, $P_{atm}$, and the fraction of impurities, $n$. This calculation is shown in Equation A-1 (shorthand is used in the remaining derivation to refer to equations, such as A-1 for Equation A-1).

$$P_{H_2O} = P_1 = P_{atm}n = 1.01 \times 10^5 \left( \frac{1}{1 \times 10^6} \right) \left( \frac{1}{10} \right) = 0.010 Pa$$  \hspace{1cm} (A-1)

The nitrogen gas was flowing through a heated tube furnace thus the relative partial pressure of the impurities, $P_2$, is calculated from the pressure at room temperature found via A-1, $P_1$, and the associated temperatures, $T_1$ and $T_2$, which are input into the ideal gas law.

$$P_2 = P_1 \left( \frac{T_2}{T_1} \right) = 0.010 \left( \frac{373}{298} \right) = 0.013 Pa$$  \hspace{1cm} (A-2)
The number of impurity molecules impacting the surface per unit area per second, \( f \), is determined from the relative pressure, molecular weight of water, \( M \), and the temperature of the gas stream and is shown in A-3.

\[
f = 2.63E20 \left( \frac{P}{\sqrt{MT^2}} \right) = 2.63 \times 10^{20} \left( \frac{0.013}{\sqrt{18.373}} \right) = 4.06 \times 10^{16} \text{ molecules} \frac{\text{cm}^2}{\text{s}}
\]  

(A-3)

Assuming a period of time, \( t \), and the knowledge that it will take a minimum of 3.5 impurities to convert one molybdenum disulphide molecule to one molybdenum trioxide molecule, the number of moles oxidized per area, \( m \), is found from A-4.

\[
m = \frac{ft}{3.5} \left( \frac{1}{6.023 \times 10^{23}} \right) = 4.06 \times 10^{20} \cdot 3.600 \left( \frac{1}{6.023 \times 10^{23}} \right) = 1.46 \times 10^2 \text{ molecules} \frac{\text{cm}^2}{\text{s}}
\]  

(A-4)

The associated grams per area is then calculated for both molybdenum disulphide and molybdenum trioxide by taking \( m \) and dividing by the molecular weight, \( M \), of either molybdenum disulphide or molybdenum trioxide, shown in A-5 and A-6 respectively.

\[
\frac{m}{M_{\text{MoS}_2}} = \frac{1.46 \times 10^{20}}{160} = 0.011 \frac{\text{g}}{\text{cm}^2}
\]  

(A-5)

\[
\frac{m}{M_{\text{MoO}_3}} = \frac{1.46 \times 10^{20}}{145} = 0.010 \frac{\text{g}}{\text{cm}^2}
\]  

(A-6)

The change in mass per area is then found by the subtraction of the two values and converting to \( \mu \text{g/cm}^2 \) which is shown in A-7.

\[
\left( \frac{m}{M_{\text{MoS}_2}} - \frac{m}{M_{\text{MoO}_3}} \right) \cdot 1 \times 10^6 = (0.011 - 0.010) \cdot 1 \times 10^6 = 1119 \frac{\mu \text{g}}{\text{cm}^2}
\]  

(A-7)
APPENDIX B
FRACTIONAL INCREASE IN OXIDATION DUE TO MASS PER UNIT AREA LOSS AT 170°C

The derivation of the fractional change of molybdenum trioxide (MoO₃) is based on the continuous mass per unit area loss observed at 170 °C. The fraction of MoO₃ prior to heating is designated as \( f_1 \) and the fraction of MoO₃ after heating is \( f_2 \). The densities of the system, \( \rho \), before and after heating are defined in Equation B-1 and B-2 respectively (shorthand is used in the remaining derivation to refer to equations, such as B-1 for Equation B-1).

\[
\rho_1 = f_1 \rho_{\text{MoO}_3} + (1-f_1) \rho_{\text{MoS}_2} = f_1 \cdot 4.69 + (1-f_1) \cdot 5.06 \quad \text{(B-1)}
\]

\[
\rho_2 = f_2 \rho_{\text{MoO}_3} + (1-f_2) \rho_{\text{MoS}_2} = f_2 \cdot 4.69 + (1-f_2) \cdot 5.06 \quad \text{(B-2)}
\]

The difference between the initial and final system densities would equal the measured change in mass per unit area, \( \frac{dm}{A} \), observed divided by the thickness of the film, \( L \), which is shown in B-3.

\[
\rho_2 - \rho_1 = \frac{dm}{A} \cdot \frac{1}{L} = -0.12 \left( \frac{1}{1 \times 10^{-5}} \right) = -1.3 \times 10^{-2} = (f_2 - f_1) (\rho_{\text{MoO}_3} - \rho_{\text{MoS}_2}) \quad \text{(B-3)}
\]

From B-3 the change in the fractional percentage of MoO₃ can be determined as shown in B-4.

\[
(f_2 - f_1) = \frac{-1.3 \times 10^{-2}}{(\rho_2 - \rho_1)} = \frac{-1.3 \times 10^{-2}}{(4.69 - 5.06)} = 0.032 \quad \text{(B-4)}
\]
APPENDIX C
MOLAR RATIO CALCULATIONS

This section presents a derivation of the ratio of moles of water to the moles of molybdenum disulphide, MoS₂, from the mass per unit area, m/A, measurements made. The theoretical moles per area, mol/A within the film is found from the density, ρ_{MoS₂}, and molecular weight of MoS₂, M_{MoS₂}, and the thickness of the film, L. This is shown for the thick film in Equation C-1 (shorthand is used in the remaining derivation to refer to equations, such as C-1 for Equation C-1) and thin film in C-2.

\[
\left( \frac{\text{mol}}{A} \right)_{\text{MoS₂}} = \frac{\rho_{\text{MoS₂}} L_{\text{thick}}}{M_{\text{MoS₂}}} = \frac{5.06 \cdot 9 \times 10^{-5}}{160} = 2.84 \times 10^{-6} \text{ mol/cm}^2 \tag{C-1}
\]

\[
\left( \frac{\text{mol}}{A} \right)_{\text{MoS₂}} = \frac{\rho_{\text{MoS₂}} L_{\text{thin}}}{M_{\text{MoS₂}}} = \frac{5.06 \cdot 1 \times 10^{-5}}{160} = 3.16 \times 10^{-7} \text{ mol/cm}^2 \tag{C-2}
\]

The moles per area of water for the thick and thin samples is calculated from the associated measured mass change per area, m/A, and the molecular weight of water, M_{H₂O}. This is shown in C-3 and C-4 respectively.

\[
\left( \frac{\text{mol}}{A} \right)_{\text{H₂O}} = \frac{m}{A} \frac{1}{M_{\text{H₂O}}} = 8.53 \left( \frac{1}{18} \right) = 4.73 \times 10^{-7} \text{ mol/cm}^2 \tag{C-3}
\]

\[
\left( \frac{\text{mol}}{A} \right)_{\text{H₂O}} = \frac{m}{A} \frac{1}{M_{\text{H₂O}}} = 0.82 \left( \frac{1}{18} \right) = 4.55 \times 10^{-8} \text{ mol/cm}^2 \tag{C-4}
\]

The ratio of the moles per water to the moles of molybdenum disulphide is calculated by taking the ratio of C-3 to C-1 which is shown in C-5 and C-4 to C-2 which is shown in C-6.
\[ \frac{\text{mol}}{A} \bigg| _{\text{H}_2\text{O-thick}} = \frac{4.73 \times 10^{-7} \text{mol}}{\text{cm}^2} = 0.16 \]

\[ \frac{\text{mol}}{A} \bigg| _{\text{MoS}_2-thick} = \frac{2.84 \times 10^{-6} \text{mol}}{\text{cm}^2} \]

\[ \frac{\text{mol}}{A} \bigg| _{\text{H}_2\text{O-thin}} = \frac{4.55 \times 10^{-8} \text{mol}}{\text{cm}^2} = 0.14 \]

\[ \frac{\text{mol}}{A} \bigg| _{\text{MoS}_2-thin} = \frac{3.16 \times 10^{-7} \text{mol}}{\text{cm}^2} \]

(C-5)
FUNDING SOURCES

Financial support for this work was provided in part by Harris Corporation, an AFOSR-MURI grant, and Sandia National Laboratories.

Any opinions, finding, and conclusions or recommendations expressed in this material are those of the author and do not necessarily reflect the views of the Air Force Office of Scientific Research.

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LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Rachel Sarah Colbert was born in Gainesville, Florida. She graduated in 2003 from the International Baccalaureate Program at Eastside High School. She was accepted at the University of Florida with a full scholarship from Florida Bright Futures Program. In 2007 she graduated with a Bachelor of Science degree in Mechanical Engineering. She was then admitted to the graduate program at the University of Florida where she completed her Master of Science (2009) and Doctor of Philosophy (2012) in the field of mechanical engineering. She researched under the direction of Professor W. Gregory Sawyer from 2007 – 2012 where her research focus was on the environmental effects on the tribological properties of solid lubricants. From July 2011 until December 2012 she interned at Sandia National Laboratories under the mentorship of Dr. Michael T. Dugger. During this time she continued to study solid lubricants but began to focus primarily on the role of water. Rachel was also very active in societies. She was a founding member of the Graduate Student Council for the Mechanical and Aerospace Engineering Department, serving as chair of the council from 2009-2010. She continued her involvement as a member of the Society of Tribologists and Lubrication Engineers where she took on leadership positions in the Materials Tribology and the Early Career Tribologists Committees.