EVAPORATIVE COOLING IN THE CONTACT LINE REGION

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to the required standard

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Abstract

Evaporative cooling of small, high power dissipating devices using thin liquid films is becoming an increasingly important field of research as the requirements for this technology grow. Understanding the mechanisms which cause liquid motion in the film and evaporation from the liquid surface is essential to the practical designer attempting to create a truly effective cooling scheme.

For liquid films of less than 1 \( \mu m \), previous experiments have confirmed the existence of an adsorbed layer where no evaporation occurs, plus a region of slightly increased thickness where limited evaporation takes place. A theory has been proposed for the non-evaporating region which modifies the thin liquid film pressure due to the molecular attraction of the underlying substrate. The pressure adjustment is termed the disjoining pressure and is thought to be the dominant driving force for liquid motion in this thin film region.

In order to test the validity of the disjoining pressure concept for an evaporating film, an experiment was designed which uses a dielectric liquid, FC-72, and a highly polished silicon substrate inclined at a 5\(^{\circ}\) angle from the horizontal to create an extended meniscus. A fluorescent light was used in an interferometer to provide increased film profile data and a specially designed focusing ellipsometer was used to measure film thicknesses in the adsorbed film region. Heat was supplied to the meniscus through a 400 \( \mu m \) wide boron diffused heater within the silicon substrate. Surface temperature and mass evaporation rates were also measured.
It was concluded from the results that the disjoining pressure model which had originally been developed for static non-evaporating thin films is equally applicable to evaporating thin film environments. The model proposes an inverse cubic relationship \((1/h^3)\) between the disjoining pressure and the adsorbed thickness. However, values of the Hamaker constant used in the relationship, inferred from the experiments were 4-5 times the theoretical value.

The corresponding heat and mass transfer models which employ the disjoining pressure require further study, as evidenced by their prediction of total heat and mass transfer rates at least one order of magnitude lower than those measured in the experiments. Improvement of the heater design and of the thin film profiling method are two very important areas to be considered for future work in this field.
Nomenclature

\( A \)  
Analyzer angle [degrees]

\( A \)  
Amplitude of Jones vector

\( A_{11} \)  
Hamaker constant, vapour-vapour [J]

\( A_{22} \)  
Hamaker constant, liquid-liquid [J]

\( A_{33} \)  
Hamaker constant, solid-solid [J]

\( A_{12} \)  
Hamaker constant, vapour-liquid-solid [J]

\( C \)  
Compensator angle [degrees]

\( d \)  
Distance difference of reflected waves in medium 0 [m]

\( E \)  
Amplitude of the Jones vector

\( E \)  
Jones vector

\( g \)  
Gravitational acceleration \([m^2/s]\)

\( h \)  
Film height [m]

\( h_p \)  
Planck's constant \( 6.626 \times 10^{-34} \) [J.s] (Eq.2.11, 2.12)

\( h_c \)  
Convective heat transfer coefficient \([W/m^2K]\)

\( h_e \)  
Evaporative heat transfer coefficient \([W/m^2K]\)

\( h_{fs} \)  
Heat of vapourization \([kJ/kg]\)

\( h_o \)  
Film height at the interline [m]

\( h_r \)  
Reference film height [m]

\( H \)  
Height above pool surface

\( i \)  
Imaginary component of complex number

\( I \)  
Light beam intensity

\( k \)  
Boltzmann's constant \( 1.380 \times 10^{-23} \) [J/K]
\(k_c\) Thermal conductivity \([W/m\cdot K]\)

\(K\) Curvature \([1/m]\)

\(m_e\) Evaporative mass flux from liquid-vapour interface \([kg/m^2s]\)

\(M\) Molecular weight

\(M_e\) Evaporation rate \([kg/s]\)

\(N\) Number of moles

\(n_s\) Index of refraction of the substrate

\(n_0\) Index of refraction in medium 0

\(n_1\) Index of refraction in medium 1

\(n_3\) Index of refraction in medium 3

\(P\) Pressure \([N/m^2]\)

\(P_d\) Disjoining pressure \([N/m^2]\)

\(P_e\) External hydrostatic pressure \([N/m^2]\)

\(P_t\) Pressure in a thin film \([N/m^2]\)

\(P_l\) Pressure in the liquid \([N/m^2]\)

\(P_{lv}\) Liquid pressure at a liquid-vapour interface \([N/m^2]\)

\(P_{lvls}\) Saturation pressure at a liquid-vapour interface \([N/m^2]\)

\(P_o\) Hydrostatic pressure at the pool surface

\(P_O\) Pressure in the bulk liquid forming the film \([N/m^2]\)

\(P_s\) Saturation vapour pressure of the bulk liquid \([N/m^2]\)

\(P_v\) Vapour pressure \([N/m^2]\)

\(P_N\) Normal pressure perpendicular to the liquid-vapour interface \([N/m^2]\)

\(P_T\) Normal pressure parallel to the liquid-vapour interface \([N/m^2]\)

\(r_B\) Radius of bubble

\(r_{01}\) Fresnel reflection coefficient between mediums 0 and 1
\( r_{12} \) Fresnel reflection coefficient between mediums 1 and 2

\( R \) Ratio of electric field components

\( \mathcal{R} \) Heater Resistance in Equation 4.1

\( s \) Specific entropy \( [\text{kJ/kgK}] \)

\( S \) Entropy \( [\text{kJ/K}] \)

\( S_0 \) First Stokes parameter

\( S_1 \) Second Stokes parameter

\( S_2 \) Third Stokes parameter

\( S_3 \) Fourth Stokes parameter

\( t \) Time \( [\text{s}] \)

\( T \) Temperature \( [\text{K}] \)

\( T_c \) Amplitude of complex compensator transmission ratio

\( T_{lv} \) Temperature at a liquid-vapour interface \( [\text{K}] \)

\( T_v \) Temperature of the vapour \( [\text{K}] \)

\( T_s \) Temperature of the substrate surface \( [\text{K}] \)

\( u \) u-velocity \( [\text{m/s}] \)

\( v \) Specific volume \( [\text{m}^3/\text{kg}] \)

\( V \) Volume \( [\text{m}^3] \)

\( x \) x-axis position \( [\text{m}] \)

\( x_0 \) Reference position along x-axis \( [\text{m}] \)

\( \chi \) Argument in determination of film thickness

\( y \) y-axis position \( [\text{m}] \)

\( z \) z-axis position \( [\text{m}] \)

**Greek**

vi
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Angle in the complex polarization ratio amplitude [rad]</td>
</tr>
<tr>
<td>αᵢ</td>
<td>α for the incident beam</td>
</tr>
<tr>
<td>αᵣ</td>
<td>α for the reflected beam</td>
</tr>
<tr>
<td>β</td>
<td>Phase difference of beam travelling in film [rad]</td>
</tr>
<tr>
<td>γ</td>
<td>Film tension [N/m]</td>
</tr>
<tr>
<td>Γ</td>
<td>Mass flow rate per unit width [kg/m·s]</td>
</tr>
<tr>
<td>Γₑ</td>
<td>Evaporation correction factor</td>
</tr>
<tr>
<td>Γₑᶠᵃ</td>
<td>Calculated mass flow rate per unit width [kg/m·s]</td>
</tr>
<tr>
<td>Γₑᵐᵉ</td>
<td>Measured mass flow rate per unit width [kg/m·s]</td>
</tr>
<tr>
<td>δ</td>
<td>Phase in the complex polarization ratio [rad]</td>
</tr>
<tr>
<td>δᵣ</td>
<td>Phase of the complex compensator ratio [rad]</td>
</tr>
<tr>
<td>δᵢ</td>
<td>δ of the incident beam</td>
</tr>
<tr>
<td>δᵣ</td>
<td>δ of the reflected beam</td>
</tr>
<tr>
<td>δₓ</td>
<td>Phase delay on x-axis [rad]</td>
</tr>
<tr>
<td>δᵧ</td>
<td>Phase delay on y-axis [rad]</td>
</tr>
<tr>
<td>Δ</td>
<td>Retardation in the ellipsometer [deg]</td>
</tr>
<tr>
<td>ε</td>
<td>Ratio of minor to major ellipse axes</td>
</tr>
<tr>
<td>ε₁</td>
<td>Dielectric permitivity of a vacuum</td>
</tr>
<tr>
<td>ε₃</td>
<td>Dielectric permitivity of a liquid</td>
</tr>
<tr>
<td>θ</td>
<td>Azimuth of the ellipse [rad]</td>
</tr>
<tr>
<td>θ₀</td>
<td>Angle of incidence in medium 0 [rad]</td>
</tr>
<tr>
<td>θ₁</td>
<td>Angle of incidence in medium 1 [rad]</td>
</tr>
<tr>
<td>Θ</td>
<td>Angle of substrate tilt from the horizontal</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength [m]</td>
</tr>
<tr>
<td>λ₀</td>
<td>Wavelength in medium 0 [m]</td>
</tr>
</tbody>
</table>
\( \lambda_i \) Wavelength in medium 1 [m]  
\( \lambda_p \) Wavelength along a path [m]  
\( \mu \) Dynamic viscosity [kg/ms]  
\( \mu_e \) Chemical potential [kJ/kgmole]  
\( \nu \) Kinematic viscosity \([m^2/s]\)  
\( \nu_e \) Characteristic absorption frequency [1/s]  
\( \rho \) Ratio of complex polarization ratios  
\( \rho_c \) Complex ratio of compensator axes  
\( \rho_i \) Density in the liquid  
\( \rho_v \) Density in the vapour  
\( \sigma \) Surface tension [N/m]  
\( \sigma_s \) Evaporation coefficient  
\( \tau_{yx} \) Shear stress at the liquid-vapour interface \([N/m^2]\)  
\( \phi \) Absolute Jones vector phase [rad]  
\( \psi \) Complex polarization ratio  
\( \psi_c \) Angle in the complex compensator ratio amplitude [rad]  
\( \psi_i \) Complex polarization ratio of the incident beam  
\( \psi_r \) Complex polarization ratio of the reflected beam  
\( \omega \) Angular frequency [rad/s]  

**Subscripts**  
i Incident upon the surface  
l Left hand polarization  
p Perpendicular to the plane of incidence  
r Reflected from the surface  
r Right hand polarization
$x$ Component along the $x$-axis

$x_0$ Amplitude along the $x$-axis

$y$ Component along the $x$-axis

$y_0$ Amplitude along the $y$-axis

$\frac{1}{4}\pi$ $x,y$ axes rotated $45^\circ$

$\frac{-1}{4}\pi$ $x,y$ axes rotated $-45^\circ$

**Superscripts**

', Stokes parameter after the analyzer

" Stokes parameter before the sample

"" Stokes parameter at the laser
# Table of Contents

Abstract ii  
Nomenclature iv  
Table of Contents x  
List of Tables xiv  
List of Figures xv  
Acknowledgement xviii  

1 Introduction 1  
1.1 Background ......................................... 1  
1.2 Research Motivation and Objectives ..................... 6  

2 Literature Review 8  
2.1 General ............................................. 8  
2.2 Disjoining Pressure ................................... 12  
2.3 Experiments with Heat and Mass Transfer in Thin Liquid Films .... 23  
2.4 Modeling of Heat and Mass Transfer in Thin Liquid Films ........... 28  
2.5 Synopsis ............................................. 34  

3 Experiment 36  
3.1 General ............................................. 36  


4.6 Surface Temperature Results ........................................ 92

5 Discussion of Results ............................................. 97
  5.1 Experimental Profile Comparison ............................... 97
  5.2 Unsteady Behaviour .......................................... 99
  5.3 "Lens" Formation .......................................... 103
  5.4 Adsorbed Thickness ...................................... 104
  5.5 Hydrodynamic Model ....................................... 112
  5.6 Heat and Mass Transfer .................................. 122
  5.7 Experimental Accuracy ..................................... 129
  5.8 Summary of Relevant Experimental Observations ........... 130

6 Conclusions ..................................................... 132

7 Future Work ..................................................... 135

Appendices .......................................................... 137

A Physical Description of the Stokes Parameters ............... 137
  A.1 The First Stokes' Parameter, $S_0$ .......................... 138
  A.2 The Second Stokes' Parameter, $S_1$ ....................... 138
  A.3 The Third Stokes' Parameter, $S_2$ ....................... 138
  A.4 The Fourth Stokes' Parameter, $S_3$ ....................... 139

B Stokes Parameter Description Using Ellipse Parameters .... 141

C Complex Polarization Ratio Determination .................... 144

D Description of Light Intensity at the Photodiode .......... 146
E  Determination of Compensator Imperfections  149

F  Estimate of Hamaker Constant Calculation Errors  151

Bibliography  153
List of Tables

3.1 Measured interference colour thickness values. .................. 55
3.2 Properties of test liquid, FC-72 [2]. ............................. 67
5.3 Experimentally calculated Hamaker constants. .................. 111
5.4 Experimental vs. calculated mass flow rates. ................... 125
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Heat flux levels for various microelectronic modules, Chu [1].</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>Effectiveness of direct contact cooling methods, [2].</td>
<td>2</td>
</tr>
<tr>
<td>1.3</td>
<td>Surface temperature profiles at a film edge, taken from Hirasawa and Hauptmann [3].</td>
<td>4</td>
</tr>
<tr>
<td>1.4</td>
<td>Illustration of an extended meniscus, showing the contact line region.</td>
<td>5</td>
</tr>
<tr>
<td>2.1</td>
<td>Thin liquid film pressure between two identical phases without overlap.</td>
<td>13</td>
</tr>
<tr>
<td>2.2</td>
<td>Thin liquid film pressure between two identical phases with overlap.</td>
<td>14</td>
</tr>
<tr>
<td>2.3</td>
<td>Thin liquid film pressure between two different phases without overlap.</td>
<td>16</td>
</tr>
<tr>
<td>2.4</td>
<td>Thin liquid film pressure between two different phases with overlap.</td>
<td>16</td>
</tr>
<tr>
<td>2.5</td>
<td>Disjoining pressure example 1.</td>
<td>18</td>
</tr>
<tr>
<td>2.6</td>
<td>Disjoining pressure example 2.</td>
<td>19</td>
</tr>
<tr>
<td>2.7</td>
<td>Notation for interfacial mass transfer.</td>
<td>31</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic of experimental design.</td>
<td>37</td>
</tr>
<tr>
<td>3.2</td>
<td>Travelling wave sinusoidal components.</td>
<td>40</td>
</tr>
<tr>
<td>3.3</td>
<td>Ellipse conventions.</td>
<td>42</td>
</tr>
<tr>
<td>3.4</td>
<td>Single reflection.</td>
<td>47</td>
</tr>
<tr>
<td>3.5</td>
<td>Multiple reflections.</td>
<td>48</td>
</tr>
<tr>
<td>3.6</td>
<td>Transverse plane ellipses for various thicknesses.</td>
<td>51</td>
</tr>
<tr>
<td>3.7</td>
<td>General Stokes parameter information for various transverse plane ellipses.</td>
<td>52</td>
</tr>
<tr>
<td>3.8</td>
<td>Boron Diffused Silicon Heater.</td>
<td>57</td>
</tr>
<tr>
<td>3.9</td>
<td>Schematic of the experimental chamber.</td>
<td>59</td>
</tr>
</tbody>
</table>
3.10 Photograph of the experimental chamber interior. 

3.11 Schematic of the ellipsometer-chamber setup. 

3.12 Experimental apparatus without microscope. 

3.13 Experimental apparatus with microscope. 

4.1 Experimental calibration of heater temperature vs. electrical resistance. 

4.2 Schematic description of photographic results. 

4.3 Photographic result for P=0 mW. 

4.4 Photographic result for P=4 mW. 

4.5 Photographic result for P=23 mW. 

4.6 Photographic result for P=59 mW. 

4.7 Photographic result for P=114 mW. 

4.8 Photographic result for P=185 mW. 

4.9 Liquid film profiles, averaged over 6 readings. 

4.10 Adsorbed thickness region profiles, averaged over 6 readings. 

4.11 Adsorbed thickness vs. power input. 

4.12 Mass Evaporation Rate vs. Power Input. 

4.13 Heater temperature rise vs. power input. 

5.1 Input power effect on liquid profiles, [30]. 

5.2 Normalized liquid profiles. 

5.3 Normalized liquid profiles, disjoining pressure region. 

5.4 Photograph of lens formation from Cook et al [30]. 

5.5 Comparison of adsorbed thickness vs. saturation pressure ratio, [21]. 

5.6 Comparison of non-dimensionalized adsorbed thickness vs. saturation pressure ratio, [21]. 

5.7 Adsorbed thickness vs. saturation pressure ratio, Equation 2.19. 

xvi
5.8 Polynomial curves fit to full profiles. ........................................ 113
5.9 Profile curvatures at relative positions. .................................... 115
5.10 Profile curvatures as a function of film thickness. ...................... 116
5.11 Evaporative mass flux for the full profile. .................................. 117
5.12 Curve fit to profiles in the disjoining pressure region. ................. 119
5.13 Disjoining pressure profiles. .................................................... 120
5.14 Evaporative mass flux in the disjoining pressure region. ............... 121
5.15 Heat transfer coefficient for the full profile. ............................... 123
5.16 Heat transfer coefficient in the disjoining pressure region. .......... 124
5.17 Evaporation coefficient for the full profile. ............................... 127
5.18 Evaporation coefficient in the disjoining pressure region. .......... 128
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Chapter 1

Introduction

1.1 Background

As technology produces new systems and devices which are smaller and more powerful than their predecessors, the requirements for effective cooling become greater. Figure 1.1 shows the heat flux levels which are produced by modules of various computers. Maintaining a cool and stable operating temperature for these components is becoming a greater challenge with this new technology. The benefits of cool and stable operating temperatures are greater microelectronic component reliability and the possibility of future increased power dissipation.

Minimizing the resistance to heat transfer between the component to be cooled and the cooling mechanism is one of the major goals of any practical cooling design. Direct contact cooling is the simplest method of reducing the thermal resistance between a device to be cooled and the coolant. Direct contact cooling with fluids may be accomplished with the familiar methods of free convection, forced convection and boiling or evaporation. Figure 1.2 shows the effectiveness of these various direct contact cooling methods.

Each direct contact method has its own positive and negative features when consideration is given to designing a practical cooling system. Forced or free convection cooling involving air is the easiest method if fabrication of the electronics packaging is the most important design parameter. However, due to the low density and the low thermal conductivity of air, the electronic components must be low power and situated in a low
Chapter 1. Introduction

Figure 1.1: Heat flux levels for various microelectronic modules, Chu [1].

Figure 1.2: Effectiveness of direct contact cooling methods, [2].
Chapter 1. Introduction

packaging density environment to avoid overheating.

Forced or free convection using a liquid provides at least one order of magnitude improvement in cooling capability due to the increased density and thermal conductivity compared with air. When using liquid as a coolant in microelectronic packaging, design difficulties are magnified compared to that for air cooling. Liquid circulation and the sealing of the cooling area are two difficult design considerations which must be overcome for a truly effective system.

The highest level of cooling effectiveness with direct contact cooling methods is that involving phase change. Either boiling or evaporation has been shown to provide the largest amount of localized cooling. This cooling benefit does not come without design drawbacks. High component surface temperatures compared with ambient conditions are normally required to initiate boiling, and even higher surface temperatures may occur if a dry-out situation develops within the boiling region. These high surface temperatures can adversely affect microelectronic component performance over a period of time. Also, a practical design limit to the condensate return rate must be overcome in any phase change cooling application.

Evaporative cooling does not require the high surface temperatures that boiling requires to initiate the process, but provides the same cooling benefits that change of phase supplies. Experimental investigations into film evaporation have demonstrated these large cooling effects, with particularly effective cooling existing near the film edge where the film is thinnest. Figure 1.3 shows the increased cooling levels near the contact line region (area at edge of film where apparent contact angle is measured). Practical use of the high cooling rates existing in evaporative film cooling has been made with the design of small wickless heat pipes and micro-grooved channels to cite just a couple of examples. In order to achieve maximum cooling benefit from film evaporation, investigations into the contact line region are required to provide an understanding of the area
Figure 1.3: Surface temperature profiles at a film edge, taken from Hirasawa and Hauptmann [3].

where the largest cooling rates occur.

Microscopic investigations into the contact line region of a wetting film show a gradually thinning film which eventually reaches a constant thickness, thus an actual zero contact angle. The constant thickness region is an adsorbed film (no evaporation from the interfacial surface) due to the presence of long range molecular forces from the underlying solid surface. The adsorbed layers are typically on the order of 100Å thick (1Å = 10^{-10}m), but some layers have been reported as thick as 600Å. As the film thickness increases, the effect of the molecular forces is reduced and evaporation occurs. The boundary between evaporating thin film and adsorbed film is called the interline. One method to produce an elongated contact line region is by situating a liquid pool at the bottom of a shallow sloping substrate. This design is shown schematically in Figure 1.4.

Studies into the contact line region show particular promise for microelectronic cooling. Two major factors, the presence of an optically smooth substrate and a dielectric
cooling liquid, exist in these applications and create a wide contact line region. These conditions are achieved with highly polished silicon wafers and electronic cooling liquids, such as FC-72 (perfluorohexane), available from 3M corporation.

Designing evaporative cooling schemes using film thicknesses in the contact line region requires a physical understanding of the relevant forces. The question then becomes how to incorporate these forces into fluid dynamic and heat transfer analysis.

A concept called “disjoining pressure” has been developed to account for the intermolecular forces important in films with thickness less than $1\mu m = 10^{-6} m$. The disjoining pressure ($P_d$) is used in equations of motion in the same manner as capillary or surface tension forces. Due to the nature of the size of the experimental apparatus, non-destructive measurement techniques are required to determine the effect of the pressures and validate existing theories. Two such thickness measuring techniques are interferometry and ellipsometry. Therefore, creating an extended meniscus with these measuring techniques should provide valuable insights into the contact line region.

Figure 1.4: Illustration of an extended meniscus, showing the contact line region.
1.2 Research Motivation and Objectives

Evaporative cooling appears to be very promising for small high power devices which are currently being designed and it appears these devices will be even more complicated in the future. The practical designer must be concerned with maintaining stable device operating temperatures within a room temperature environment. The most convenient evaporative cooling design will include very little liquid volume and maximum liquid-solid contact area, resulting in very thin liquid films. Also, packaging will include air mixed with vapour within the sealed cooling cell. With these expectations, it is necessary to understand the important physical factors in thin film cooling.

Considering the above factors, it was the general objective of this research to gain a fuller understanding of heat and mass transfer processes in the contact line region. With this understanding, a detailed evaluation of the existing models which use disjoining pressure and interfacial mass transfer models in the contact line region.

Specifically, the objectives of this research are itemized below.

1. To accurately measure the liquid film profiles in the contact line region, particularly in the region where the disjoining pressure is important, anticipated to be below 1\( \mu m \).

2. To measure interline temperature rise above the ambient surroundings.

3. To make overall heat and mass transfer measurements in the contact line region.

4. To use these experimental measurements to evaluate the analytical models which predict the heat and mass transfer in the contact line region with particular attention to the disjoining pressure dominated region.
5. To make an overall assessment of the effectiveness of using an evaporating thin liquid film for the cooling of microelectronic devices.

The procedure used to obtain the above objectives was to design and construct an experiment which localized the surface heat flux in the adsorbed film region and also gave an indication of the substrate surface temperature. A practical evaporation - condensation system was designed for a meniscus which exists on a sloping substrate. The film thickness in the contact line region was measured with greater resolution than in previous studies by the use of a focused ellipsometer beam in conjunction with a fluorescent light interferometer. This type of interferometer provided detailed profile information at thicknesses less than those which could be obtained using a monochromatic light source, and a spatial resolution not previously used for this application.
Chapter 2

Literature Review

2.1 General

With the miniaturization of technical components, most pronounced being the electronic micro-chip, highly effective dependable cooling systems become increasingly important. Bergles [4] provided a summary of the evolution of cooling for electronic equipment. The summary detailed cooling requirements from vacuum tubes in the 1950's to ultra large scale integration chips which have approximately 500,000 components on a chip of 0.25 $cm^2$ area. The IBM 3090 series chip, for example, produces almost 7 Watts of power. This indicates a definite need for reduced thermal resistance between the chip and the ambient environment, i.e. more effective cooling.

Many different methods have been reported in the literature. Chu [1] gave a good description of the current direct contact cooling methods being incorporated in electronics packaging today. The basic methods included free and forced convection, with both air and liquid, as well as phase change methods involving liquids. Studies into these methods are numerous, a select few will be discussed here to indicate the level of cooling effectiveness for each method.

Park and Bergles [5] examined natural convection heat transfer for simulated micro-electronic chips. They discovered that heat transfer could be enhanced by changing the configuration of the electronic chips, specifically stacking them in vertical arrays. Heat transfer coefficients as high as 600 $W/m^2K$ were measured, almost 100% greater than
Another cooling method which offers higher heat transfer coefficients than convection is boiling. However, large temperature superheats at the wall are normally required to initiate boiling unless a surface enhancement, such as an attached porous metal surface, is used to aid in nucleation. Bergles and Kim [6] studied the problem of reducing "temperature overshoots" (wall superheat above saturation required for boiling) in immersion cooling. Heat transfer coefficients in the range of 1,000-10,000 $W/m^2K$ were recorded with surface temperature superheats reduced from $30^\circ C$ to $8^\circ C$ by generating bubbles in the vicinity of the heated surface.

A variation of immersion cooling which creates thin films along the heat transfer surface was studied by Torii et al [7] using grooved fins and porous tunnels on tubes to augment heat transfer. Heat transfer coefficients as high as 7,280 $W/m^2K$ were obtained in an evaporation mode with superheats as low as $1.2^\circ C$. These studies have indicated the potential for large cooling rates using change of phase.

Evaporating liquid films have been shown to be another method of providing effective cooling. Many aspects of liquid film evaporation have been studied for films 1 $mm$ thick and less. Fujita and Ueda [8, 9] studied the flow of sub-cooled and saturated liquid films down the exterior of an electrically heated stainless steel tube. Wave formation in the liquid films was noted as power was increased with localized film thinning and eventual dry patch formation. For sub-cooled films, the surface tension variations due to temperature changes along the tube are shown to be important in causing dry patch formation. Local heat transfer coefficients dropped from approximately 2000 $W/m^2K$ to 500 $W/m^2K$ or less at the formation of a dry patch. For saturated films, boiling heat transfer coefficients in the range of 7000 $W/m^2K$ were measured.

A very informative study showing the cooling potential for large evaporation rates of thinning films and subsequent dry-out is given by Orell and Bankoff [10]. Nichrome strips
embedded in a horizontal plate were used to thin a pool of liquid. Higher heat transfer was noted as the film thinned but oscillating liquid behaviour of the contact line region was found as a dry patch formed. This important fact has subsequently been noted in wetting film evaporation studies and dry-out studies.

Sharon and Orell [11] studied heat transfer to flowing laminar liquids in a horizontal plastic channel with a smooth copper bottom. Isothermal and heated cases were considered. Liquid surface temperature measurements were made with a movable 25 \( \mu m \) diameter thermocouple to include thermocapillary effects in creating a critical heat flux model. Distilled water flowing over the smooth copper channel resulted in thin films, measured to within \( \pm 5 \mu m \) by a micrometer needle probe. Predicted profiles using capillary and thermocapillary forces in the equations of motion provided excellent agreement with the measured profiles, for film thicknesses on the order of 1 mm. Predictions of the critical heat flux were also very good with this method.

Hirasawa et al [12] examined surface tension effects in condensing laminar films formed in various sized small troughs. The most important effect noted was the surface tension changes in locally thinning areas of the film, which reduces the resistance to heat transfer and, therefore increases the heat transfer coefficient. At the thinnest section of the trough, the films were approximately 100\( \mu m \) thick. Calculations of condensation heat transfer coefficients based on experimentally verified thickness profiles range from 10,000 \( W/m^2K \) for R-113 to 100,000 \( W/m^2K \) for water.

Another area of interest which uses evaporative cooling with liquid films on the order of 1 mm thick is closed thermosyphons or wickless heat pipes. These heat pipes, generally on the order of 10 mm in diameter, return condensate by means of gravity or centrifugal force, and are used in gas turbine blade cooling, electronic component cooling or gas to gas heat exchangers. Studies by Imura et al [13], Reed and Tien [14], Chen et al [15] and Negishi and Sawada [16] have examined effects such as critical heat flux, dryout,
flooding, vapour shear effects, inclination etc. All the above mentioned studies show the driving forces in liquid films from $1\mu m$ to $10mm$ thickness. These heat pipes contain a complicated mix of phase change conditions ranging from evaporation to violent boiling, depending upon the design parameters. Studies into liquid film behaviours would benefit the understanding of the processes in these heat pipes.

The above cited papers [8]-[16] show the cooling potential available with evaporating liquid films but also show the adverse effect dry-out has on temperature. However, the behaviour of the contact line region is usually not considered for liquid films of approximately $1\ mm$ thickness. Studies in this region could provide valuable information on evaporative cooling and dry patch formation.

An important feature in films of $1\ mm$ thickness and less is the apparent contact angle of the evaporating liquid with the surface, which is used in hydrodynamic models of dry patch formation and stability. The contact angle is termed “apparent” due to the acknowledged presence of a very thin adsorbed portion of liquid at the interline. Hirasawas and Hauptmann [3] studied the apparent dynamic contact angle for a flowing rivulet between two heated patches using a colour schlieren method, and noted large heat transfer coefficients at the contact line region with films of the order $1\ \mu m$ or less. They pointed to the need for studying heat transfer in the area of very thin films, less than $1\ \mu m$, to determine heat transfer coefficients and important parameters describing the liquid motion.

Bankoff [17] gave a good account of the current state and future needs in thin film cooling. The previously mentioned macroscopic factors of stability, dry-out, boiling and contact line motion are mentioned as areas which require further detailed research. With respect to molecular forces and adsorbed liquid layers in the contact line region, Bankoff suggests that this is a “rich area for further research”.

2.2 Disjoining Pressure

The concept of disjoining pressure was first proposed for a thin liquid separating two plane, parallel solid surfaces by Derjaguin [18]. Derjaguin found experimentally that an additional force acting perpendicular to the plane of the surface was required to hold the surfaces in equilibrium at a fixed distance of separation. This force (either positive or negative depending on the combination of materials used) was in addition to that calculated from conventional hydrostatic pressure analysis for the liquid layer. The additional force required to maintain this separation distance between the two solid surfaces showed an increasing significance below $10^{-6}m$ separation distances. Dividing this additional force by the surface area of the solids in contact with the liquid gave a measure of the disjoining pressure in the thin film. The pressure distribution in the thin layer was assumed to be uniform through the layer with a pressure jump occurring at both liquid-solid interfaces. For a plane parallel case, the value of the jump at each face is identical.

The basic definition of disjoining pressure was originally given as (for the case of two solids separated by a thin liquid film)

$$P_d(h) = P_e - P_i,$$  \hspace{1cm} (2.1)

with $P_i$ being the pressure in the thin liquid layer assumed from conventional hydrostatic analysis and $P_e$ being the measured external pressure on the solids. Any anisotropy of pressure in the liquid was not considered during these initial investigations but was addressed by Derjaguin in later work as is discussed below. Derjaguin stressed the point that the pressure does not change with distance from the interface but is only a function of the liquid thickness, $h$, at each point. He states that the disjoining pressure “is allied to the concept of phase pressure but not of internal pressure”.
Gibbs interfacial theory [19] treats thermodynamic systems involving thin liquid films with interfacial zones as the sum of the bulk phase properties plus the properties of the interfacial regions between neighbouring phases. This approach assumes there exists a section between interfaces which contains liquid with bulk liquid properties as shown in Figure 2.1, for the symmetric case of a thin film bordered by two identical vapour phases (such as a thin soap film). The interfacial regions, which are anisotropic with respect to intermolecular forces near each interface, are assumed separated by a bulk liquid phase. Figure 2.1 also shows the pressure distribution which exists in a thin film which contains a bulk liquid region separating the two interfacial regions. The normal pressure, $P_N$, is everywhere equal to the surrounding normal pressure in the other bulk phases. The tangential pressure, $P_T$, varies in each interfacial zone but returns to an isotropic value (equal to $P_N$) in the bulk zone. The surface tension is a property of the interfacial region.
Figure 2.2: Thin liquid film pressure between two identical phases with overlap.

and is defined for this case by the Bakker equation as

$$\sigma = -\int_{0}^{+\infty} (P_T - P_N) \, dz = -\int_{0}^{+\infty} (P_T - P_0) \, dz, $$

(2.2)

where the integration is taken in the direction perpendicular to the interface, $z$, with the limits of integration being the region of influence on the tangential pressure. The film tension for this particular case will be the sum of the two individual surface tensions or

$$\gamma = -\int_{-\infty}^{+\infty} (P_T - P_N) \, dz = 2\sigma. $$

(2.3)

If sufficient thinning of the film occurs such that no region of bulk properties exists, the individual interfacial zones will overlap and this will significantly change the properties of the thin film, causing Gibbs’ approach to be invalid. This situation is shown in Figure 2.2. From the pressure distribution diagrams, it can be noted that the tangential pressure does not attain an isotropic value anywhere between the two interfacial regions.
The normal pressure also varies in a complex manner, $P_i'$, but is approximated by the disjoining pressure added to the surrounding isotropic pressure, the resultant shown as $P_i$ ($P_i = P_O + P_d$). For this symmetric case a relationship between the disjoining pressure and the film tension may be established using the film tension definition. Writing the film tension as

$$\gamma = -\int_{-\infty}^{+\infty} (P_T - P_O - P_N + P_O) \, dz,$$

and using the surface tension definition given by Equation 2.2 and the disjoining pressure definition, the film tension may be rewritten as

$$\gamma = 2\sigma + P_d h,$$

where $h$ is the height of the film, assumed to be equal to the integration limits for the thin film.

For the case of a wetting thin film bordered by two different phases, namely a vapour phase and a solid phase, the pressure distribution will be quite different from the symmetric case. For a thin film without and with an overlapping interfacial region, the sketch and pressure diagram are given in Figure 2.3 Figure 2.4 respectively. The interfacial zones will be distinctly different from each other at the liquid-vapour and liquid-solid interfaces as compared with the identical values for the previous symmetric case. The interfacial tensions will also be much different at each phase boundary. Because the concept of film tension is not meaningful for the vapour-liquid-solid case, a direct relationship between the film tension and the disjoining pressure, such as Equation 2.5 does not exist for this case.

From the basic definitions presented, it is apparent that the disjoining pressure and surface tension are both functions of the height of the thin layer for cases with overlapping interfacial regions. However, the disjoining pressure concept is concerned solely with the forces acting normal to the interface and may be approximated with intermolecular force
Chapter 2. Literature Review

Figure 2.3: Thin liquid film pressure between two different phases without overlap.

Figure 2.4: Thin liquid film pressure between two different phases with overlap.
theory while the surface tension is more complex. Therefore, in wetting film analysis, the surface tension is assumed to be the calculated bulk value while the intermolecular effects are accounted for only in the disjoining pressure.

Using the anisotropic pressure description in a thin film, Derjaguin [20] recast the definition of disjoining pressure as

\[ P_d(h) = P_N - P_O, \]  

(2.6)

with \( P_O \) being the isotropic pressure in the bulk liquid from which the thin liquid was formed and \( P_N \) being the pressure component perpendicular to the interface within the thin liquid layer. The sign convention for the disjoining pressure term in Equation 2.6 is usually chosen such that a negative value will be obtained for a wetting film. This is the same sign convention as given in Equation 2.1 with a more defined description of the system pressures.

For thin film hydrodynamic calculations, the disjoining pressure given by Equation 2.6 is added to the existing pressure terms to give the net thin layer pressure. This net pressure is then taken as the isotropic pressure existing in the film under disjoining pressure theory analysis.

For the specific case of a solid-liquid-gas thin film system, two examples illustrate the disjoining pressure concept. The first is the case of a vapour bubble pressing against a solid surface creating a thin horizontal liquid film between the bubble and the solid, as shown in Figure 2.5. Assuming that the bubble is in thermodynamic equilibrium with the liquid and maintains a spherical shape except for the flat surface pressed against the solid, a uniform internal bubble pressure, which is higher than the surrounding liquid pressure by an amount given by the Laplace-Young equation, will create a uniform thin film between the bubble and the surface. Assuming mechanical equilibrium, the vapour pressure and the thin liquid pressure should be equal perpendicular to the horizontal
Figure 2.5: Disjoining pressure example 1.

interface. However, a higher pressure in the thin film with respect to the surrounding liquid would result in a flow outwards, toward the bulk liquid. Because this does not occur, the existence of a pressure jump at the liquid-vapour interface is inferred, indicating the existence of a disjoining pressure. Using the Laplace-Young equation to describe internal bubble pressure rise, the disjoining pressure is given as

\[ P_d(h) = P_N - P_O = P_l - P_v = \frac{-2\sigma}{r_B} = -K\sigma, \quad (2.7) \]

where \( r_B \) is the radius of curvature of the bubble and \( \sigma \) is the surface tension of the liquid. For an isothermal situation, an experiment varying the bubble size, and thus the curvature would give disjoining pressure variations with film thickness.

A second example is that of a vertical flat plate immersed in a liquid creating a meniscus as shown in Figure 2.6. On a microscopic scale for a wetting liquid, there is zero contact angle and the film is characterized by a plane parallel adsorbed film at the top of the extended meniscus. For an equilibrium situation, the pressure from the
horizontal liquid surface may be given as

\[ P_N = P_0 - \rho_l g H, \quad (2.8) \]
\[ P_O = P_0 - \rho_v g H. \quad (2.9) \]

Where \( \rho_l \) and \( \rho_v \) represent the liquid and vapour densities respectively. Therefore, the disjoining pressure is by definition

\[ P_d(h) = g(\rho_v - \rho_l)H. \quad (2.10) \]

In theoretical modeling, when evaporation causes a gradual thinning of the film, as in an extended meniscus, the basic disjoining pressure definition is used at each incremental position in the film to form a gradient of pressure in the liquid. In thin film hydrodynamics, the disjoining pressure is added to the local hydrodynamic pressure and used in the Navier-Stokes equations to determine liquid velocity and mass flux in the film. The
film must be a wetting film with slowly varying thickness because the disjoining pressure is assumed to be accurate at each incremental film height. Also, the composition of the film must be consistent because the disjoining pressure is generally unknown for mixtures. One inherent assumption that is made when using this disjoining pressure theory in hydrodynamics is that the pressure is isotropic in the thin liquid film and all pressure components are affected by the disjoining pressure. No separate theoretical description of the pressure parallel to the interface is utilized within the disjoining pressure term.

From the definition of disjoining pressure, if the gradient of disjoining pressure with thickness is less than zero,

\[ \frac{dP_d}{dh} < 0, \quad (2.11) \]

the disjoining pressure will aid the stability of the flow causing the liquid to flow towards the thinner section resulting in a wetting film. This corresponds to the condition of molecular attraction between the liquid and the solid as opposed to repulsion.

Using the condition of chemical equilibrium, Derjaguin and Zorin [21] calculated the disjoining pressure for a one-component thin film in terms of the corresponding saturation pressures. For a single component system, the Gibbs-Duhem relation gives

\[ SdT - VdP + Nd\mu = 0, \quad (2.12) \]

or

\[ d\mu = -sdT + vdP \quad (2.13) \]

For a constant temperature liquid, \( T_l \), the change in chemical potential may be written as

\[ \left( \frac{\partial \mu}{\partial P} \right)_{T_l} = v_l, \quad (2.14) \]

For the case of a change of liquid pressure from the thin liquid value, \( P \), to the bulk saturation value of the same liquid, \( P_s \), integrating to determine the change in chemical
potential the relation may be written based on the disjoining pressure definition as

\[ \Delta \mu_l = \nu_l (P - P_2) = \nu_l (P_d). \]  

(2.15)

Using the same analysis for a vapour at a constant temperature, \( T_v \), the chemical potential may be written

\[ \left( \frac{\partial \mu}{\partial P} \right)_{T_v} = \nu_v = \frac{RT_v}{MP_g}, \]

(2.16)

and integrating between the same pressure conditions gives

\[ \Delta \mu_v = \left( \frac{RT_v}{M} \right) \ln \left( \frac{P}{P_s} \right). \]

(2.17)

If the vapour and liquid are in equilibrium, the chemical potentials at each state must be equal and hence also the change, therefore the relation may be written as

\[ P_d(h) = \left( \frac{RT_v \rho_l}{M} \right) \ln \left( \frac{P}{P_s} \right), \]

(2.18)

with \( P \) and \( P_s \) being the pressure in the thin liquid film and the saturation pressure which would occur in the bulk liquid at the same temperature conditions as the thin film respectively.

Based on experimental data, Derjaguin and Zorin [21] further proposed the relationship

\[ P_d(h) = \left( \frac{RT_v \rho_l}{M} \right) \ln \left( \frac{P}{P_s} \right) \approx \frac{1}{6\pi} \frac{A_{12}}{h^3}, \]

(2.19)

using the molecular interaction of van der Waals dispersion forces only. This dependency was also derived theoretically by Frenkel [22], showing the disjoining pressure dependency of \( \frac{1}{h^3} \) for non-polar liquids using dispersion force interaction. Equation 2.19 was compared with experimental data for non-polar liquids and concluded to be in agreement, "albeit by a rather long stretch" [21].

A different form of Equation 2.19 was given by Wayner et al [23] and was used in a majority of Wayner's subsequent contact line studies (work to be described in detail.
later in this chapter). The different form of the disjoining pressure equation presented by Wayner et al [23] gives the potential to calculate the disjoining pressure based on temperature difference measurements as opposed to pressure.

Van der Waals dispersion forces may be taken as the dominant intermolecular force for non-polar molecules. The forces are the result of the creation of a temporary dipole moment in a molecule due to the instantaneous position of the electrons which then polarize neighbouring molecules. The attraction is classified as long-range with effects being important at distances of greater than 100 Å. The attraction has been shown theoretically to depend inversely on the distance to the sixth power. Frenkel [22] indicated that experimentally measured values show effects at distances 20 times larger than the calculated values.

If the molecular separation becomes too large, retardation effects occur due to the reflection of the temporary polarization back to the original site, now possessing a dipole oriented differently. The effect of this phenomenon is to reduce the attraction between distant molecules.

The Hamaker constant, $A_{12}$, is dependent upon the type of liquid and substrate for the case of a wetting film. Churaev [24] and Wayner [25] proposed methods of calculating the Hamaker constant based upon known relationships for the electromagnetic frequency dependent dielectric constants of the materials involved. However, these frequency dependent properties are unknown for the liquid used in this study, FC-72; therefore a more approximate method proposed by Israelachvili [26] may be used. Israelachvili uses a combination of Hamaker constants derived from molecular attraction of identical substances across a vacuum to create an overall system constant. The relationship is given as

$$A_{12} = (\sqrt{A_{22}} - \sqrt{A_{11}})(\sqrt{A_{00}} - \sqrt{A_{11}}),$$  \hspace{1cm} (2.20)
where the subscripts 2, 1, and 0 refer to the solid, liquid and vapour phases respectively. The individual Hamaker constants for the solid and liquid are given in terms of bulk properties. For a liquid, the constant is

$$A_{11} = \frac{3}{4}kT \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right)^2 + \frac{3h_p\nu_e (n_1^2 - n_3^2)^2}{16\sqrt{2}(n_1^2 + n_3^2)^3}, \tag{2.21}$$

where the subscript 3 refers to a vacuum. For a solid, the constant is

$$A_{22} = \left( \frac{3}{16}\sqrt{2} \right) h_p\nu_e. \tag{2.22}$$

The dielectric permitivities, $\varepsilon$, are taken at zero frequency, the refractive indices, $n$, are values in the visible frequency range, and $\nu_e$ is the main absorption frequency.

For non-polar liquids, the Hamaker constants calculated by Israelachvili typically range from $-0.4\times10^{-19}$ to $-4\times10^{-19}$J. Israelachvili [26] showed good agreement between values calculated using the approximate theory presented above and the more complex analytical theories (i.e. Churaev [24]), errors typically less than 5%. Comparisons of both analytical theory values with the limited experimental values available show differences as much as 2-3 times the calculated value. Using the approximate method, the Hamaker constant for FC-72 on a silicon dioxide covered surface is $-9.8\times10^{-20}$J. The data for the liquid was obtained from the manufacturer, 3M [2], while the data for the $SiO_2$ covered silicon surface was obtained from Gregory [27].

### 2.3 Experiments with Heat and Mass Transfer in Thin Liquid Films

The theoretical equations for heat and mass transfer are of practical design use if they can be verified by direct or indirect experimental observation. Obtaining experimental verification is necessary if thin liquid film analysis is to be used with confidence in analytical and numerical models.
Derjaguin and Zorin [21] were amongst the first experimenters to attempt to determine disjoining pressure variation with liquid thickness. Equilibrium adsorbed film thicknesses were measured, using an ellipsometer, on a superheated glass substrate using polar and non-polar liquids along with the surface and vapour temperatures. The data were fit to the equation

\[ P_d(h) = \frac{RT\rho_l}{M} \ln\left(\frac{P_{in}}{P_{vap}}\right) \approx \frac{1}{6\pi} \frac{A_{12}}{h_0^3}. \]  

(2.23)

The Hamaker constant was reported to be in the range of \( A_{12} \approx -10^{-12} \text{ergs} \) (\( \text{erg} = 10^{-7} \text{J} \)) for non-polar liquids. Gee et al. [28] measured adsorbed thicknesses of n-alkanes on quartz using ellipsometry for various vapour pressures. Control of the vapour pressure, measured by a transducer, proved difficult although the same disjoining pressure model as Derjaguin, Equation 2.23 provided good agreement with experimental results. Experiments of this nature have proven the existence of the intermolecular forces described by the disjoining pressure concept. Both studies used an ellipsometer to measure the film thicknesses, all below 100 Å thickness.

Experiments using the disjoining pressure concept to predict equilibrium thin liquid film profiles and thin liquid film transport processes have become more frequent the past two decades. Wayner [29]-[32], [35]-[40] has been a leading researcher in this area since 1970, conducting experiments with extended menisci developed at the contact line region of a non-polar liquid and an optically smooth solid.

Renk and Wayner [29] used monochromatic light interference through a glass slide to observe meniscus profiles of ethanol varying with heat flux levels. The profiles were fitted with a fourth order polynomial from which the profile curvatures were calculated. In an evaporating meniscus, the calculated change of curvature was taken as a measure of the pressure differences in the film (normally associated with capillary forces) which cause the liquid to flow into the evaporating region. The results indicate that the curvature
increased towards the interline for an evaporating meniscus and the degree of curvature increased with increasing heat flux. It appeared that capillary forces were the dominant driving force for liquid flow into the evaporating region for film thicknesses greater than approximately 1000 Å. Because the first interference fringe was at 1120 Å, no direct measurement of either the thin film region where disjoining pressure becomes dominant or the adsorbed film region was possible.

Cook et al [30] measured meniscus profiles of non-polar decane on silicon in an extended meniscus formed by a 6° tilt of the substrate from horizontal. An improvement of the interference technique was achieved through the use of a scanning microphotometer. Again, the meniscus profile curvature was found to increase with increased heat flux, thus shortening the contact line region. This was attributed to the increased capillary forces required to provide more liquid for the higher evaporation rates. Two substantial observations were that the meniscus vibrated at high heat fluxes and “lenses” were present in the photographic results, concluded to be dust particles or distillation effects of an impure liquid. For this system, the disjoining pressure was assumed to be important below approximately 5000 Å. Using capillary and disjoining pressure theory, the profiles were used to calculate a theoretical heat flux due to evaporation which agreed well with the overall heat flux inferred from twelve 130 μm thermocouples attached on the back side of the substrate. The results showed that the evaporation region was estimated to begin at a liquid thickness of between 7 μm and 10 μm.

Wayner et al [31] used basically the same setup to study the effects of composition changes on the meniscus profiles. Results indicate a more drawn out, shallower meniscus, concluded to be due to distillation within the liquid. This resulted in a small profile curvature with decreasing purity indicating a different physiochemical process occurring in the contact line region. For the case of 98% hexane and 2% octane, the maximum curvature occurs at much larger film thicknesses than the tests with a higher percentage
of hexane. This was taken as a clear indication of additional mechanisms contributing to liquid flow. Again, an oscillatory motion of the meniscus and lens formation were noted at higher heat fluxes.

Truong and Wayner [32] measured transport properties near the interline directly for films less than 100 Å. An ellipsometer was used to measure liquid profiles of a decane on silicon extended meniscus system for varying heat fluxes. Ellipsometer measurements, with a measuring area of the order 200 μm x 200 μm, were taken. Using quadratic regression analysis to fit the data, theoretical analysis based on disjoining pressure theory indicated a heat transfer coefficient of 10,000 W/m²K in the contact line region, specifically near the interline. Again, thermocouple size and spacing on the opposite side of the substrate made thermal verification difficult in the contact line region, although global measurements are in good agreement. Adsorbed films between 36 Å and 55 Å were measured. Beaglehole [33] used a microscopic imaging ellipsometer to examine the rate of spreading of a wetting film of siloxane oil on various surfaces. Leger [34] measured the thin film ahead of a spreading drop using a focusing ellipsometer and 2-axis scanner. Adsorbed films of a few hundred angstroms or less were found for polydimethylsiloxane on silicon.

Combination of the above interferometry and ellipsometry was used by Truong and Wayner [35] to measure equilibrium wetting film profiles of hexane and octane on silicon. Film thicknesses between 200 Å - 10,000 Å were measured, studying the region where both capillary forces and disjoining pressure terms are important. Adsorbed thicknesses of 250 Å and 195 Å were reported using ellipsometry. Theoretical equilibrium liquid film profile calculations using disjoining pressure and capillary forces did not accurately predict the film thicknesses in the adsorbed region. However, results in the capillary force region (10,000 Å) were very good.

Sujanani and Wayner [36] also used ellipsometry combined with interferometry to
analyze draining films of non-polar liquids on silicon nitride covered silicon surfaces. Equilibrium thicknesses of approximately 50% less than those predicted by theoretical calculations using only van der Waals dispersion forces were found. The changing rate of drainage was linked with surface tension changes due to impurities of liquid or in the cleanliness of the sample. These were taken as very important.

Sujanani and Wayner [37], Wayner et al [38], DasGupta et al [39] all used a slightly modified version of the microphotometer based interferometry combined with ellipsometry to provide increased liquid film profile accuracy. Ellipsometer spot measurements of 200 μm x 200 μm were used in the disjoining pressure dominated region. In the capillary dominated meniscus region, a microcomputer was used to digitize the monochromatic microscopy image obtained from the meniscus. Having every pixel graduated for light intensity levels provides resolution for 0.625 μm x 0.625 μm areas in the capillary dominated meniscus region. Sujanani and Wayner [37] used octane on silicon as an extended meniscus inside a sealed glass cell which also contained air at atmospheric pressure. The results were termed as “near equilibrium” because of the difficulty of achieving stable equilibrium due to the sensitivity of the entire system to small temperature changes. The adsorbed thickness changed with time, from 50 Å to 600 Å over 30 minutes, indicating the possibility of condensation at the interline for small changes in temperature. DasGupta et al [39] used a meniscus formed at the exit of a circular capillary feeder in a closed cell with external liquid supply to measure the evaporation rate of heptane on silicon. From the measured thickness profiles, the maximum curvature was found to exist at liquid thicknesses of approximately 1200 Å for equilibrium cases and as low as 500 Å for evaporating cases. Again, backside thermocouples were used for the temperature profiles from which heat transfer rates in the evaporating region were calculated. Good macroscopic heat transfer agreement was achieved using the thermocouple measurements in a one-dimensional conduction model of the silicon substrate as compared with the measured
evaporation rate. Major observations from all these microcomputer enhanced profile studies indicated that the meniscus length shortened and adsorbed film layer thickness decreased with increasing power until eventually the meniscus displayed an oscillatory behaviour with respect to position. The adsorbed thickness appeared to approach some asymptotic value as the heat flux increased before oscillation was observed.

Sujanani and Wayner [40] used the enhanced microscopy on an inclined silicon plate for an extended meniscus of 1,1,2-trichlorotrifluoroethane. The measurements indicate that the capillary dominated region ends at 500 Å with the disjoining pressure being important below this thickness. Again, an oscillating meniscus behaviour was observed.

Very few experiments have been done with the experimental apparatus approximating that of a practical cooling application. Xu and Carey [41] conducted an experimental and analytical investigation of a copper slab with small V-shaped grooves cut in the surface (64 μm wide x 190 μm deep x 25.4 mm long). With one end in a methanol pool and the other heated, capillary action drew liquid up the length of the groove while disjoining pressure action carried the liquid up the groove sides. Three thermocouples transverse to the groove length were embedded in the copper at five separate locations along the groove. Heat transfer coefficients at the edge of the film were estimated from thermocouple readings to be as high as 40,000 W/m²K.

2.4 Modeling of Heat and Mass Transfer in Thin Liquid Films

Theoretical analyses of heat and mass transfer in the contact line region which included disjoining pressure theory have been presented in a few different forms but these theories still require experimental verification. Ruckenstein and Jain [42], Miller and Ruckenstein [43], and Frenkel [22] incorporated the molecular attraction into a body force term for analysis. However, most researchers used the disjoining pressure approach
in their analysis.

Combining the disjoining pressure term into the fluid dynamics equations is straightforward. Due to the small evaporation area and the low power inputs to avoid meniscus oscillations, the rate of evaporation is very small. Therefore, the lubrication approximation is used. This approximation is given in numerous sources, such as Probstein [44],

\[
\frac{d^2u}{dy^2} = \frac{1}{\mu} \frac{dP_l}{dx} - \frac{g}{\nu} \sin \Theta. \tag{2.24}
\]

Using boundary conditions of no-slip at the substrate surface and no-shear at the liquid-vapour interface,

\[
y = 0, \ u = 0, \tag{2.25}
\]

\[
y = h, \ \tau_{yx} = 0, \tag{2.26}
\]

the resulting equation for the u-velocity in the thin layer is simply

\[
u = \left( \frac{1}{\mu} \frac{dP_l}{dx} - \frac{g}{\nu} \sin \Theta \right) \left( \frac{y^2}{2} - hy \right), \tag{2.27}
\]

While it is not necessarily true for a thin liquid film that the surface tension forces at the liquid-vapour interface may be neglected, very few experiments have had the capability of measuring any surface tension changes due either to composition or temperature differences, thus no surface tension driven motion is usually considered.

Taking the important fluid driving forces in the contact line region as capillary forces, \(\sigma K\), disjoining pressure forces, \(P_d\), and gravity, and using a force balance at the liquid-vapour interface, the pressure in the liquid may be expressed as

\[
P_l - P_v = P_d - \sigma K + \rho_l g (h - y) \cos \Theta, \tag{2.28}
\]

where the curvature for a very shallow change in height with distance along the substrate is approximated by

\[
K = \frac{d^2h}{dx^2}. \tag{2.29}
\]
and the disjoining pressure is given by Equation 2.19. Integrating across the film gives the mass flow rate (per unit width) as

$$\Gamma(x) = \frac{h^3}{3\nu} \left( \sigma \frac{d^3h}{dx^3} + \frac{3A_{12}}{6\pi h^4} \frac{dh}{dx} + \rho g \sin \Theta - \rho g \frac{dh}{dx} \cos \Theta \right). \quad (2.30)$$

For an extended meniscus, the last two terms on the right hand side of Equation 2.30, the gravity force terms, have been shown to be orders of magnitude smaller than the other two. Neglecting these two terms results in the equation

$$\Gamma(x) = \frac{h^3}{3\nu} \left( \frac{\sigma}{\nu} \frac{d^3h}{dx^3} + \frac{3A_{12}}{6\pi \nu h^4} \frac{dh}{dx} \right). \quad (2.31)$$

The change in the mass flow rate per unit width in the liquid represents mass which is added or lost from the liquid-vapour surface. This mass evaporation rate per unit surface area (as opposed to condensation for this experiment) is given by

$$\dot{m}_e = -\frac{d\Gamma}{dx} = -\frac{\sigma}{3\nu} \left( h^3 \frac{d^4h}{dx^4} + 3h^2 \frac{dh}{dx} \frac{d^3h}{dx^3} \right) - \frac{A_{12}}{6\pi \nu} \left( \frac{1}{h} \frac{d^2h}{dx^2} - \frac{1}{h^2} \left( \frac{dh}{dx} \right)^2 \right). \quad (2.32)$$

Theoretical predictions of heat and mass transfer in the contact line region require a statement of the system parameters, most notably the temperature difference between the heated surface and the surroundings. This temperature difference will cause evaporation of the liquid. A sketch showing the model most frequently used for heat and mass transfer analysis is shown in Figure 2.7. Combining the temperature difference and the evaporative mass flux given in Equation 2.32, the heat transfer coefficient for evaporation from the liquid-vapour interface may be calculated using the equation

$$h_e = \frac{\dot{m}_e h_{fg}}{T_{lv} - T_v}. \quad (2.33)$$

The most often cited equation used for predicting the amount of interphase mass transfer is that given by Schrage [45]. Schrage’s basic mass transfer equation is derived from the kinetic theory of gases. For an equilibrium condition between a liquid and a
vapour, the number of molecules passing between phases is identical. Therefore, using a Maxwell velocity distribution for gas molecules near the interface, an absolute vapourization rate \( (w_{s+}) \) is given based on the number of molecules passing through a plane as

\[
w_{s+} = P_s \sqrt{\frac{M}{2\pi RT_{lv}}}. \tag{2.34}
\]

The absolute vapourization rate must be modified by a factor which accounts for the fraction of molecules which are reflected at the surface and do not vapourize \( (\sigma_s) \). A similar analysis may be conducted for the absolute rate of condensation. For a net evaporation or condensation to be occurring, a local movement of the vapour away from or toward the interface will occur. Accounting for this movement, the absolute condensation \( (w_{o^-}) \) is given as

\[
w_{o^-} = - \left( \frac{\rho_{lv}}{\rho_s} \right) \left( \frac{T_{lv}}{T_v} \right)^{1/2} \Gamma_c w_{s+}. \tag{2.35}
\]
Again, correcting for reflection, the net interfacial mass transfer may be written as

\[ \dot{m}_e = \sigma_e \sqrt{\frac{M}{2\pi R}} \left[ \frac{P_v}{T_{lv}^\frac{3}{2}} - \Gamma_c \frac{P_u}{T_v^\frac{3}{2}} \right]. \] (2.36)

The evaporation correction factor, \( \Gamma_c \), is a function of the overall velocity of the vapour. For a case where equilibrium exists, the value will be \( \Gamma_c = 1.0 \). For an evaporating case, there will be a net movement of vapour away from the liquid-vapour interface. Collier [46] adjusted the interphase mass transfer, Equation 2.36, for a small net motion away from the surface to give the modified interphase equation as

\[ \dot{m}_e = \left( \frac{2\sigma_e}{2 - \sigma_e} \right) \sqrt{\frac{M}{2\pi R}} \left[ \frac{P_{lv}}{T_{lv}^\frac{1}{2}} - \frac{P_v}{T_v^\frac{1}{2}} \right]. \] (2.37)

The pressure at the liquid-vapour interface must be adjusted from the normal bulk liquid saturation vapour pressure, \( P_{lv,s} \), at the interfacial temperature, \( T_{lv} \), to account for the effects of disjoining pressure and curvature. The correction is from Equation 2.23 plus the addition of the interfacial pressure difference effects due to the presence of a curved surface

\[ P_{lv} = P_{lv,s} \exp \left[ \frac{(P_d - \sigma K)M}{R \rho T_{lv}} \right]. \] (2.38)

One of the least investigated but most important aspects of the interphase mass transfer equation, Equation 2.37, is the evaporation coefficient, \( \sigma_e \). Schrage [45] indicated that the theoretical value of \( \sigma_e = 1.0 \) has not always been consistent with experimental results. The ideal experiment would include knowing the exact temperature of the liquid surface and the vapour temperature within less than one molecular mean free path, plus having the condensing surface also within one mean free path from the evaporating surface. When dealing with macroscopic experiments with thin films, the liquid-vapour surface temperature may be approximated using a simple one-dimensional heat conduction model through the thin film, neglecting the liquid motion in an evaporating film, with corresponding evaporation and natural convection heat transfer from
the liquid-vapour interface. An order of magnitude calculation for the natural convection heat transfer coefficient \(h_c\) for this particular experimental design gives a coefficient of \(h_c = 5 W/m^2 K\). The interfacial temperature may then be calculated from the substrate surface temperature, \(T_s\), by the equation

\[
T_{lv} = \left( \frac{k_c}{h_c} + h_c \right) \left( \frac{k_c T_s}{h} - \bar{m}_e h_f + h_c T_v \right).
\] (2.39)

However, the vapour temperature of practical design interest is located within the chamber interior, many orders of magnitude distance greater than the ideal theoretical molecular mean free path. An added difficulty is the presence of any non-condensables. Indications of the uncertainty in the value of \(\sigma_e\) are given by Merte [47], who reports experimental results of \(\sigma_e\) for water from 0.006 to 1.0. Collier [46] reports \(\sigma_e\) for various liquids from 0.04 to 1.0.

Mirzamoghadan and Catton [48] used these basic equations in the theoretical analysis of an extended meniscus on a sloping surface with varying degrees of incline. Maximum heat transfer was predicted for plate tilt angles of between 20° and 30°.

Holm and Goplen [49] also used these equations to predict that 80% of the heat transfer for liquid filled capillary grooves in a plate occurred in the capillary force dominated region. Only 8% of the heat transfer occurred in the disjoining pressure dominated region.

Wayner, in his theoretical investigations [50]-[52] and in his previously described experimental investigations, used these basic equations to predict the heat and mass transfer in the contact line region. Wayner’s most frequent method involves equating Equations 2.31 and 2.37 and adjusting the equation parameters, mainly the temperature difference until a best fit with the experimental profiles is achieved. Subsequently calculated interfacial temperature differences, \(T_{lv} - T_v\), are typically \(10^{-3}-10^{-5}\) K. These are not measurable experimentally, so verification is difficult.
The above investigations assume $\sigma_e = 1.0$, which could lead to large differences in mass flows and temperature differences if surface contamination or non-condensables seriously affect the value of $\sigma_e$.

2.5 Synopsis

Highly effective cooling has been demonstrated using evaporating thin films in wetting film configurations. The most obvious use of this cooling technique has been in the area of micro-electronics. However, many aspects of the transport behaviour and cooling potential of thin films remain unknown for the practical designer.

At the leading edge of a thin wetting film, it has been experimentally proven that a thin adsorbed, non-evaporating film is present due to the molecular interaction between the liquid and the solid substrate on which the thin film resides. A theory converting the molecular attraction forces into a modification of the liquid pressure has received much attention in the literature in recent years. This modification, termed "disjoining pressure", has been shown to significantly affect equilibrium thin liquid film profiles and liquid transport in evaporating thin films. Analytical predictions of the disjoining pressure involve two separate theories, one describing the change of disjoining pressure with film thickness, $1/h^3$, and the second in the magnitude of the attractive forces between the liquid and the solid. Experimental results have reasonably shown the $1/h^3$ behaviour to be a good approximation for equilibrium adsorbed films while the Hamaker constant, representing the molecular attraction is difficult to verify. The behaviour of both of these theories requires more investigation for evaporating thin liquid films, particularly in the area of surface temperature effects because only small surface temperature rises are possible before instabilities in the interline region occur. The region of interest begins as thin liquid films become less than 1 $\mu m$. 
Many excellent studies have been reported for thin film evaporation with thin film thicknesses in the range from 10 \( \mu m \) to 0.1 \( \mu m \), where the main contribution to fluid dynamic motion is due to capillary forces. However, detailed experimental studies into the disjoining pressure dominated region are few because of the inherent difficulties in measuring accurate thin film profiles in this region due to various factors such as measuring technique and film stability. Previous investigations have shown the apparent accuracy of the fluid dynamics modelling, including the disjoining pressure, by good agreement between the predicted and measured profiles. However, independent confirmation of the interline temperature rise and an accurate measurement of the contact line region mass transfer have not been reported. Therefore, a need exists for detailed information in the disjoining pressure dominated region to validate fluid dynamic and mass transfer models for use on a macroscopic scale.

Particular information is required in the region near the interline with respect to the temperature difference between the surface and the surroundings so local heat transfer coefficients may be calculated and compared. Closely related to this measurement is a need for increased liquid film profile information in the contact line region to validate the disjoining pressure model. One additional experimental measurement which is lacking in the literature but is very difficult to obtain is the isolation of heat transfer and mass transfer directly into the interline region with the subsequent mass transfer measurements pertaining to this region exclusively.
Chapter 3

Experiment

3.1 General

Studying the heat and mass transfer in the contact line region of an evaporating meniscus requires an experiment which provides the largest contact line region possible so measurement techniques can adequately assess the parameters. From the previously discussed modeling equations for a thin liquid film, the thickness profile in the contact line region is a necessary measurement. Also, the heat flux into the region, the surface temperature in the contact line region and the ambient surrounding conditions are required to estimate heat and mass transfer. Creating a sealed environment which is in a steady state situation allows the direct measurement of mass transfer if the condensate return is calibrated. The entire experiment is shown schematically in Figure 3.1.

This experiment uses the method of Truong and Wayner [32] for creating an extended meniscus. A highly polished pure silicon wafer is tilted at 5° to the horizontal and a dielectric cooling liquid is placed in a pool at the bottom end. The liquid then forms an extended meniscus on the wafer due to molecular attraction forces. Because the adsorbed thicknesses are anticipated to be of the order of 100Å or less, the silicon must be highly polished so the surface roughness is less than 100Å. This also aids in the profile measurement using optical devices due to the high reflectivity of the polished surface.

The choice of experimental fluid was determined by the nature of the experimental investigation. The most prominent cooling application for thin film heat transfer is
Figure 3.1: Schematic of experimental design.
micro-electronics. With this application as the main criterion for choosing a liquid, a commercially available electronic cooling liquid which is a dielectric and has low surface tension was desired. FC-72 from 3M corporation was a logical choice. One additional favourable aspect of FC-72 is the ability of the experimental designer to use standard silicone rubber as a sealant because FC-72 does not dissolve silicone.

The basic idea for the experiment was to construct an embedded heater in the silicon wafer to act as a localized heat source and a electrical resistance temperature gauge. The contact line region would then be placed as close as possible to the heater. This would provide heat flux and surface temperature measurements locally.

The profile measurements were made by a combination of ellipsometry and interferometry. The interferometer used a fluorescent light source since the interference of the various colours provided additional thickness details, thus higher resolution than a monochromatic source at thicknesses below approximately 3000Å. The ellipsometer contained focusing lenses that reduce the ellipsometer spot measuring size to a width of less than 20µm. This represents an improvement over standard ellipsometer designs that have spot widths 10 times this size.

The mass transfer measurements were accomplished by counting and calibrating the condensate return drops. These drops were created by making a preferential condensation face which was cooler than the surrounding chamber interior. Locating the return over the liquid pool created an evaporation - condensation situation.

3.2 Ellipsometry

3.2.1 Background

If we assume that a chamber exists which isolates a thin liquid film in a steady state condition with its own vapour, an accurate method of measuring liquid thickness to a
depth of $10^{-8}$–$10^{-9}$ m is by the use of an ellipsometer as described by McCrackin et al [53]. An ellipsometer is a useful tool to measure liquid thickness because it is generally a non-intrusive technique. If the laser power is kept low, a highly reflective surface will absorb very little energy, a definite requirement for evaporation studies of thin films.

The most economical ellipsometer available is the nulling ellipsometer, which is very simple to operate. If a polarized light beam is thought of as consisting as a combination of two Cartesian component individual waves, judiciously set combinations of input polarization and retardation will create a linearly polarized light beam after reflection from a sample. This may be verified by having another polarizer crossed with the output beam as observed visually. Analysis of the angular positions of the ellipsometer components plus the known sample refractive properties allows a thickness determination. A slight variation of this nulling ellipsometer method was used in this experiment to ease use and fabrication. Because ellipsometry measures thickness through the change in polarization states of a monochromatic coherent light beam, a method of describing the polarization state completely upon reflection is required for this method.

3.2.2 Theory and Operation

3.2.2.1 Methods of Describing the Polarization State of Light

In general, if a propagating light beam exhibits polarization characteristics, the position of the electric field vector in the transverse plane will describe an ellipse with time. Specific cases of linear and circular polarization arise from the general ellipse. A polarized light beam may be described in an $x$–$y$–$z$ co-ordinate system, with $z$ being the direction of propagation, by creating two sinusoidal components in the $x$–$z$ and $y$–$z$ planes as shown in Figure 3.2. The $x$ and $y$ vector components may be written as

$$E_x = E_{xo} \cos(\omega t - \frac{2\pi z}{\lambda} + \delta_x),$$
Choosing \( z = 0 \) as any transverse plane of interest, the components become

\[
\begin{align*}
E_x &= E_{x0} \cos(\omega t + \delta_x), \\
E_y &= E_{y0} \cos(\omega t + \delta_y).
\end{align*}
\]  

(3.1)  

(3.2)

Eliminating time, \( t \),

\[
\frac{E_x^2}{E_{x0}^2} + \frac{E_y^2}{E_{y0}^2} - \frac{2E_x E_y \cos(\delta_y - \delta_x)}{E_{x0} E_{y0}} = \sin^2(\delta_y - \delta_x). 
\]  

(3.3)

Equation 3.3 indicates that, in general, an ellipse will be described in a transverse plane for a coherent monochromatic light beam. Knowing \( E_{x0}, E_{y0}, \delta_x, \delta_y \) completely describes the ellipse. However, measuring \( E_{x0}, E_{y0}, \delta_x, \delta_y \) directly is not straightforward, therefore an alternative method of describing the elliptic state is required to correlate with measurements.

Four physical quantities which are measurable in terms of light beam intensity are known as the Stokes parameters and are described in Clarke and Grainger [54]. The
parameters are

\[ S_0 = E_{zo}^2 + E_{yo}^2, \]
\[ S_1 = E_{zo}^2 - E_{yo}^2, \]
\[ S_2 = 2E_{zo}E_{yo}\cos(\delta_y - \delta_x), \]
\[ S_3 = 2E_{zo}E_{yo}\sin(\delta_y - \delta_x). \] (3.4)

The four parameters are calculable by measuring the physical quantities listed below and described in Appendix A.

\begin{align*}
S_0 & = \text{total intensity of light}, \\
S_1 & = \text{difference between } x\text{-coordinate intensity} \\
& \quad \text{and } y\text{-coordinate intensity}, \\
S_2 & = \text{difference between } +1/4\pi \text{ coordinate intensity} \\
& \quad \text{and } -1/4\pi \text{ coordinate intensity}, \\
S_3 & = \text{difference between right-handed circular polarization} \\
& \quad \text{intensity and left-handed circular polarization intensity}.
\end{align*}

A more convenient method of describing an ellipse is shown in Figure 3.3. The four defining parameters are azimuth, \( \theta \), ratio of minor to major axis of the ellipse, \( \tan |\epsilon| \), the sign of \( \epsilon \), and the absolute ellipse size. The convention for measuring \( \theta \) and \( \epsilon \) as given by Hauge et al [55] is \( \theta \) positive measured counter clockwise from the \( x\)-axis when viewing the source and \( \epsilon \) is positive for right-handed polarization. Relating the ellipse description quantities to the measured Stokes parameters, as shown in Appendix B, the relations are

\begin{align*}
S_0 & = I = E_{zo}^2 + E_{yo}^2, \\
S_1 & = S_0 \cos 2\epsilon \cos 2\theta,
\end{align*}
Figure 3.3: Ellipse conventions.

\[ S_2 = S_0 \cos 2\epsilon \sin 2\theta, \]
\[ S_3 = S_0 \sin 2\epsilon. \]  
(3.5)

In subsequent analysis, it is shown that the absolute value of the light beam intensity, \( S_0 \), is not a necessary factor in thickness and refractive index calculations. Therefore, using Equation 3.5, the ellipse is fully described for our purposes by

\[ \theta = \frac{1}{2} \tan^{-1} \frac{S_2}{S_1}, \]
\[ \epsilon = \frac{1}{2} \sin^{-1} \frac{S_3}{S_1}, \]  
(3.6)

along with the sign of \( \epsilon \).

Knowing the elliptic representation as given by Equation 3.6, this information must be converted to a thickness measurement using reflection theory. The thickness theory is based on complex Fresnel reflection coefficients parallel and perpendicular to the plane of incidence. Therefore, the previously described ellipse parameters must be related to complex polarization components of mutually perpendicular planes (choose \( x \) and \( y \)
components) which may be aligned with the directions parallel and perpendicular to the plane of incidence. Using the Jones vector as phasor representation of a totally polarized light wave as given in Clarke and Grainger [54], the x and y components may be written as

\[ E = \begin{bmatrix} E_x \\ E_y \end{bmatrix} = \begin{bmatrix} E_{x0} e^{i\delta_x} \\ E_{y0} e^{i\delta_y} \end{bmatrix} = A e^{i\phi} \begin{bmatrix} \cos \theta \cos \epsilon - i \sin \theta \sin \epsilon \\ \sin \theta \cos \epsilon + i \cos \theta \sin \epsilon \end{bmatrix}. \] (3.7)

Azzam and Bashara [56] create a complex polarization ratio, \( \psi \),

\[ \psi = \frac{E_x}{E_y} = \frac{E_{x0} e^{i(\delta_x - \delta_y)}}{E_{y0}} = \tan \alpha e^{i\delta}, \] (3.8)

which suppresses the absolute amplitude and phase information. This is acceptable provided the change in polarization is the information of primary interest as it is here.

Using Equation 3.7, the complex polarization ratio for mutually perpendicular phasor components becomes

\[ \psi = \frac{\sin \theta \cos \epsilon + i \sin \epsilon \cos \theta}{\cos \theta \sin \epsilon - i \sin \epsilon \sin \theta} = \frac{\tan \theta + i \tan \epsilon}{1 - i \tan \theta \tan \epsilon}. \] (3.9)

Equating 3.8 and 3.9 allows determination of \( \alpha \) and \( \delta \) and thus \( \psi \) in terms of the ellipse description parameters, as detailed in Appendix C,

\[ \cos 2\alpha = \cos 2\epsilon \cos 2\theta, \]

\[ \tan \delta = \frac{\tan 2\epsilon}{\sin 2\theta}. \] (3.10)

Consequently, measuring the four Stokes parameters and using Equations 3.6 and 3.10 results in complete description of the complex polarization ratio, \( \psi \).
3.2.2.2 Determining the Stokes Parameters from a Nulling Ellipsometer

Knowing the polarization state before and after the interaction of the light beam with a sample allows the calculation of the change in polarization. From the previous section, knowing $\psi$ before and after interaction would suffice for calculating the change in polarization. This requires knowledge of the Stokes parameters immediately before and after sample interaction. Providing an input of known polarization may be readily accomplished with specific optical components. However, the polarization after sample reflection may assume any polarization state. In order to obtain thickness results, the measured light intensities must be related directly to the Stokes parameters following reflection and before any optical components used in the intensity measurement.

Hauge [57] describes a method of determining the reflected polarization state using an ellipsometer in the polarizer–sample–compensator–analyzer (PCSA) setting. The intensity reaching the detector in terms of $S_0$, $S_1$, $S_2$, $S_3$, (the four Stokes parameters after the sample but before the compensator) is given by

$$I(C, A, \Delta) = \frac{1}{2} [S_0 + (S_1 \cos 2C + S_2 \sin 2C) \cos 2(A - C) (S_2 \cos 2C - S_1 \sin 2C) \sin 2(A - C) \cos \Delta S_3 \sin 2(A - C) \sin \Delta].$$

(3.11)

Using a quarter wave retarder plate, $\Delta = 90^\circ$, the Stokes parameters are obtained with the following intensity readings $I(C, A)$, $C$ and $A$ measured in degrees counterclockwise from the x-axis,

$$S_0 = I(0, 0) + I(90, 90),$$

$$S_1 = I(0, 0) - I(90, 90),$$

$$S_3 = I(45, 45) - I(135, 135),$$

$$S_4 = I(0, 45) - I(0, 135).$$

(3.12)
The first three readings may be taken without the compensator in-line because the compensator’s effect is restricted to phase differential. This is assuming a perfect quarter-wave retarder with ideal transmission along both axes.

For a compensator in general, the complex ratio of the amplitude and phase of the fast transmission axis compared to the slow transmission axis is

\[ \rho_c = \tan \psi_c e^{-i\delta_c} = T_c e^{-i\delta_c}. \]  

(3.13)

Using this representation of the compensator effects, the intensity at the detector may now be written as (Appendix D)

\[
I(C, A, \delta_c) = S_0 [\cos 2\psi_c \cos(2C - 2A) + 1] \\
+ S_1 [\cos 2C \cos(2C - 2A) + \cos 2C \cos 2\psi_c] \\
+ \sin 2C \sin(2C - 2A) \sin 2\psi_c \cos \delta_c \\
+ S_2 [\sin 2C \cos(2C - 2A) + \cos 2\psi_c \sin 2C] \\
- \cos 2C \sin(2C - 2A) \sin 2\psi_c \cos \delta_c \\
+ S_3 [-\sin 2\psi_c \sin \delta_c \sin(2C - 2A)].
\]

(3.14)

Using the same settings as the previous determination of the Stokes parameters, the four quantities become

\[
S_0 = \frac{[I(0, 0) + I(90, 90)]}{[\cos 2\psi_c + 1]}, \\
S_1 = \frac{[I(0, 0) - I(90, 90)]}{[\cos 2\psi_c + 1]}, \\
S_2 = \frac{[I(45, 45) - I(135, 135)]}{S_2 \sin 2\psi_c \cos \delta_c}, \\
S_3 = \frac{[I(0, 45) - I(0, 135)] - S_2 \sin 2\psi_c \cos \delta_c}{\sin 2\psi_c \sin \delta_c}.
\]

(3.15)

Obviously the values of \( \psi_c \) and \( \delta_c \) must be determined in order to obtain the elliptical state using the Stokes parameters.
The compensator imperfections may be found by removing the sample and setting the input linear polarization angle coinciding with the x-axis, as detailed in Appendix E. Measuring the intensity at the detector in the form $I(C,A)$, the compensator values are found to be

$$\cos 2\psi_c = \frac{I(0,0) - I(90,0)}{I(0,0) + I(90,0)},$$

$$\frac{1 - \sin 2\psi_c \cos \delta_c}{2} = \frac{I(0,0) - 2I(45,0) + I(90,0)}{I(0,0) + I(90,0)}.$$  

This information allows the complete determination of the four Stokes parameters and thus the complex polarization ratio $\psi$ immediately upon reflection from the sample.

### 3.2.2.3 Determination of Liquid Thickness Using the Complex Polarization Ratio

The complex polarization ratio which determines the elliptic state of a polarized light beam may be written for the incident and reflected beams from a sample. The two ratios may be written as

$$\psi_i = \tan \alpha_i e^{i\delta_i},$$

$$\psi_r = \tan \alpha_r e^{i\delta_r}.$$  

Experimentally given these ratios, the theoretical description of light reflecting from a thin liquid covered surface must also be presented as the ratio of two electric field components for mutually orthogonal planes.

For an electromagnetic wave incident upon a solid surface with a thin film present, the reflected component will be a summation of an initial reflected component from the film surface plus multiple reflections from the solid–film and film–air interfaces. A phase difference due to the film and dependent upon the thickness (as well as refractive
indices) will be introduced. Figure 3.4 illustrates the phase difference for an ideal case of one reflection. The phase difference for a reflection is given by

\[ \text{phase difference} = \frac{2\pi}{\lambda_p} \times \text{path difference}. \]  

(3.19)

For the geometry in Figure 3.4 the path difference may be written as

\[
\text{path difference} = 2 \left( \frac{h}{\cos \theta_1} \right) - d \\
= \left[ 2 \left( \frac{h}{\cos \theta_1} \right) \right]_{\text{medium 1}} - [2h \tan \theta_1 \sin \theta_0]_{\text{medium 0}}. \]  

(3.20)

Combining Equation 3.20 into Equation 3.19

\[
\text{phase difference} = \frac{2\pi}{\lambda_1} \left( \frac{2h}{\cos \theta_1} \right) - \frac{2\pi}{\lambda_0} (2h \tan \theta_1 \sin \theta_0) \\
= \frac{4\pi}{\lambda \cos \theta_1} \left( n_1 - n_0 \sin \theta_1 \sin \theta_0 \right). \]  

(3.21)

Using Snell’s Law,

\[ n_0 \sin \theta_0 = n_1 \sin \theta_1, \]  

(3.22)
the phase difference becomes

\[
\text{phase difference} = \frac{4\pi h n_1}{\lambda \cos \theta_1} \left( 1 - \sin^2 \theta_1 \right)
\]

\[
= \frac{4\pi h}{\lambda} n_1 \cos \theta_1.
\]

Therefore, for a beam travelling from the liquid surface to the solid surface, a phase difference of

\[
\beta = \frac{2\pi h}{\lambda} n_1 \cos \theta_1,
\]

is introduced. Figure 3.5 shows the general case of multiple reflections from an incident electromagnetic wave. The amplitude reduction due to multiple reflection and the introduced phase lags due to multiple path differences are shown. The total reflected wave will consist of all components due to multiple reflection. The ratio of the reflected electric field component to incident electric field component is

\[
\frac{E_r}{E_i} = r_{01} + (1 - r_{01}^2)r_{12}e^{-2j\beta} + (1 - r_{01}^2)(-r_{01})r_{12}^2e^{-4j\beta} + \cdots
\]

\[
= r_{01}(1 - r_{01}^2)r_{12}e^{-2j\beta} \left[ 1 - (r_{01}r_{12}e^{-2j\beta}) + (r_{01}r_{12}e^{-2j\beta})^2 + \cdots \right]
\]
Chapter 3. Experiment

\[ r_{01} + \frac{(1 - r_{01}^2)r_{12}e^{-2j\beta}}{(1 + r_{01}r_{12}e^{-2j\beta})} = \]

\[ \frac{r_{01} + r_{12}e^{-2j\beta}}{1 + r_{01}r_{12}e^{-2j\beta}}, \quad (3.25) \]

where \( r_{01} = \frac{n_1 \cos \theta_0 - n_0 \cos \theta_1}{n_1 \cos \theta_0 + n_0 \cos \theta_1}, \)

\( r_{12} = \frac{n_2 \cos \theta_1 - n_1 \cos \theta_2}{n_2 \cos \theta_1 + n_1 \cos \theta_2}. \)

The preceding analysis is correct for both the components, parallel and perpendicular, to the plane of incidence. Letting \( p \) denote the parallel plane and \( s \) denote the perpendicular plane, the reflection coefficients are

\[ R_p = \frac{E_{sp}}{E_{ip}} = \frac{r_{01p} + r_{12p}e^{-2j\beta}}{1 + r_{01p}r_{12p}e^{-2j\beta}}, \]

\[ R_s = \frac{E_{rs}}{E_{is}} = \frac{r_{01s} + r_{12s}e^{-2j\beta}}{1 + r_{01s}r_{12s}e^{-2j\beta}}. \quad (3.26) \]

If the x–plane in the nulling ellipsometer discussion coincides with the plane parallel to the plane of incidence and the y–plane with the perpendicular plane, the ellipsometer complex polarization ratios and the reflection coefficients are related by

\[ \rho = \frac{R_p}{R_s} = \frac{E_{sp} E_{is}}{E_{ip} E_{rs}} = \frac{E_{x\rho} E_{y\rho}}{E_{x\tau} E_{y\tau}} = \frac{E_{y\rho} E_{x\rho}}{E_{x\tau} E_{y\tau}} = \frac{\psi_i}{\psi_r}. \quad (3.27) \]

Solving Equation 3.27 for the thickness, \( h \), gives (Appendix E)

\[ h = \left[ j(4\pi)^{-1}(n_1^2 - n_0^2 \sin^2 \theta_0)^{-1/2} \ln \chi \right] \lambda, \quad (3.28) \]

\[ \chi = \left[ -(r_{01p}r_{01s}r_{12s} + r_{12p} - r_{01s}r_{01p}r_{12p} \rho - r_{12s} \rho) \right] + \left[ (r_{01p}r_{01s}r_{12s} + r_{12p} - r_{01s}r_{01p}r_{12p} \rho - r_{12s} \rho)^2 \right] \]
\[-4(\tau_{12p}\tau_{01s}\tau_{12a} - \tau_{12a}\tau_{01p}\tau_{12p}\rho)(\tau_{01p} - \tau_{01s}\rho) \right)^{1/2} \]
\[\div2(\tau_{12p}\tau_{01s}\tau_{12a} - \tau_{12a}\tau_{01p}\tau_{12p}\rho).\]

The real solution to the above quadratic will be the thickness providing the refractive indices are known.

### 3.2.2.4 Fortran Program

The solution of the complex quadratic equation for the film thickness was written following the general outline of McCrackin [58]. The program solves for a thickness given all the system inputs including the refractive index of the film. Using the Stokes parameter determination of Hauge [57], modifications from the basic nulling ellipsometer input angles must be incorporated so the proper thickness solutions are obtained. This involves setting the complex polarization ratio angles of \(\psi\) and \(\Delta\) into the proper quadrant to provide all possible thickness values as potential solutions. To facilitate an understanding of the proper required quadrants, the full range of thicknesses must be related to the complex polarization ratio, \(\rho\), and the Stokes parameters \((S_0, S_1, S_2, S_3)\). This was accomplished by writing a reverse Fortran program which provided complex polarization ratios given film thickness as an input. Figure 3.6 shows the various transverse plane ellipses for given thicknesses. Figure 3.7 generalizes this information into quadrants plus gives the corresponding azimuths, \(\theta\), and Stokes parameter signs (+ or -). Note that the first Stokes parameter, \(S_0\), is always positive as it is a measure of total intensity.

Using this information, the Fortran program was written to ensure the solution to the equations observed the above limitations. Achieving the above restraints required writing corrections into the program for Equations 3.6 and 3.10. Based on the signs of \(S_1, S_2, S_3\), the solutions to the tangent function were maintained in value but placed into the appropriate quadrant. Another correction which was required was in the solution of
Figure 3.6: Transverse plane ellipses for various thicknesses.
Figure 3.7: General Stokes parameter information for various transverse plane ellipses.
Equation 3.28. Again, to maintain the full range of thickness values, the solution to $X$ requires that the solution angle be measured counterclockwise for increasing thickness.

### 3.2.2.5 Focusing Lenses

Due to the extremely small size of the interline region even in an extended meniscus, a standard laser beam size of 5mm diameter is much too wide to be of use. When ellipsometry is combined with a form of interferometry as was done here, the last visible fringe is approximately 400Å thick. The distance between colours is in the range of 50μm or less so the thickness changes rapidly with distance. Therefore, the smallest possible ellipsometer spot is desirable.

Focusing of an ellipsometer beam is not a new technology although application to profile measurement in the contact line region has not been made previously. Derjaguin and Zorin [21] used a focusing ellipsometer to study disjoining pressure isotherms in 1957. Theories describing the accuracy of focusing the ellipsometer are given in Svitashev et al [59, 60], and Baruskov et al [61, 62]. The conclusions of these studies are that any errors result from a small change in the angle of incidence of various parts of the beam due to focusing. However, the zones converge so the errors tend to cancel and the accuracy is preserved.

### 3.3 Interferometer

As the meniscus increases in thickness away from the interline, the ellipsometer ceases to be effective due to the limited range of readings before repetition of the calculated film thickness occurred and the rate of thickness change within the ellipsometer spot size resulted in meaningless readings. Therefore, in this experiment, perpendicular fluorescent lighting was used in conjunction with a 30X magnification microscope following the
method of Plishkin and Conrad [63] to identify the area in which the ellipsometer was useful, and also to provide an interference pattern to identify the profile shape. The thickness colour chart for SiO$_2$ was adjusted for index of refraction differences between SiO$_2$ and FC-72. Table 3.1 lists the values used in the fringe pattern analysis.

Using this colour interference pattern provides an increased number of data points as the rate of change of thickness with position is very small close to the interline. The very beginning appearance of the colour tan is approximately 400 Å. This is an improvement over monochromatic fringes where the first order dark fringe occurs at roughly 1000 Å. Uncertainties exist in this method from a combination of the estimated thickness and subjective interpretation of the colour. Table 3.1 indicates the thickness at a corresponding colour plus the thickness at a boundary between two colours.

With the present combination of liquid and substrate, the ellipsometer cycles itself at approximately 3800 Å. Knowing this, a verification was devised to check the colour thickness pattern given in Table 3.1. Inside a sealed chamber, drops of FC-72 were placed on a silicon wafer under saturated conditions. The drops spread out on the silicon so the colour pattern was well defined. Using the ellipsometer and translation stage, the ellipsometer spot was positioned over the various colours using a microscope. A series of three readings were taken and averaged. The results are also listed in Table 3.1. The range of measurement variation was less than 10% for each colour. The results show good agreement between the theoretical and measured values, well within the limits of error due to colour interpretation and ellipsometer spot positioning.

Past 4000 Å, it was impossible to accurately position the spot due to the rapidly changing colour pattern. The bright fringes past this point were pink or purple, therefore, the mid-point of each succeeding red fringe from theory was taken as the thickness of each fringe.
### Measured Interference Colour Thicknesses

<table>
<thead>
<tr>
<th>Fringe No.</th>
<th>Colour (Theoretical)</th>
<th>Thickness, Å (Theoretical)</th>
<th>Thickness, Å (Ellipsometer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Clear-Tan</td>
<td>&lt;580</td>
<td>370</td>
</tr>
<tr>
<td></td>
<td>Tan</td>
<td>580</td>
<td>573</td>
</tr>
<tr>
<td></td>
<td>Brown</td>
<td>820</td>
<td>853</td>
</tr>
<tr>
<td></td>
<td>Brown-Blue</td>
<td>1170</td>
<td>1121</td>
</tr>
<tr>
<td></td>
<td>Blue</td>
<td>1400</td>
<td>1379</td>
</tr>
<tr>
<td></td>
<td>Blue-Light Blue</td>
<td>1575</td>
<td>1670</td>
</tr>
<tr>
<td></td>
<td>Light Blue</td>
<td>1870</td>
<td>1962</td>
</tr>
<tr>
<td></td>
<td>Light Blue-Gold</td>
<td>2330</td>
<td>2360</td>
</tr>
<tr>
<td></td>
<td>Gold</td>
<td>2567</td>
<td>2760</td>
</tr>
<tr>
<td>2</td>
<td>Purple</td>
<td>3326</td>
<td>3499</td>
</tr>
<tr>
<td></td>
<td>Blue-Green</td>
<td>3850</td>
<td>4240</td>
</tr>
<tr>
<td></td>
<td>Yellow</td>
<td>4376</td>
<td>4631</td>
</tr>
<tr>
<td>3</td>
<td>Purple</td>
<td>5368</td>
<td>5213</td>
</tr>
<tr>
<td>4</td>
<td>Purple</td>
<td>7400</td>
<td>N/A</td>
</tr>
<tr>
<td>5</td>
<td>Purple</td>
<td>9740</td>
<td>N/A</td>
</tr>
<tr>
<td>6</td>
<td>Purple</td>
<td>12080</td>
<td>N/A</td>
</tr>
<tr>
<td>7</td>
<td>Purple</td>
<td>14420</td>
<td>N/A</td>
</tr>
<tr>
<td>8</td>
<td>Purple</td>
<td>16760</td>
<td>N/A</td>
</tr>
<tr>
<td>9</td>
<td>Purple</td>
<td>19100</td>
<td>N/A</td>
</tr>
<tr>
<td>10</td>
<td>Purple</td>
<td>21440</td>
<td>N/A</td>
</tr>
<tr>
<td>11</td>
<td>Purple</td>
<td>23780</td>
<td>N/A</td>
</tr>
<tr>
<td>12</td>
<td>Purple</td>
<td>26120</td>
<td>N/A</td>
</tr>
<tr>
<td>13</td>
<td>Purple</td>
<td>28460</td>
<td>N/A</td>
</tr>
<tr>
<td>14</td>
<td>Purple</td>
<td>30800</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 3.1: Measured interference colour thickness values.
3.4 Apparatus

3.4.1 Heater

The desire to simulate a two-dimensional micro-electronic chip was the starting point for the heater design. To aid in ellipsometric measurements, a highly polished and optically flat surface was required. Parameswaran et al [64] have done extensive work in boron doping of silicon surfaces. Dr. Paramaswaran agreed to provide two-dimensional rectangular heaters created in a piece of polished silicon substrate as per our design. The heater design is shown in Figure 3.8.

Five thin rectangular boron atom heaters were thermally diffused into a 10 cm diameter piece of high resistivity n-type silicon wafer. (40-60 ohm – cm) The heaters were 3 cm long with widths varying from 200 μm to 600 μm. The diffusion process consisted of thermally growing a layer of SiO₂ in the silicon, then using a precision mask to open rectangles in the oxide to match the heater pattern. The sample was then placed in a diffusion oven with a boron source for 90 minutes, a time determined by trial and error to be the maximum exposure time which still prevented diffusion through the oxide to unwanted locations. The entire process was then repeated to achieve greater diffusion depth and density, thus the lowest possible resistance. The wafer was then trimmed to a 5 cm x 5 cm square to easily fit the translation stage and chamber dimensions.

A problem arose in attempting to make consistent electrical connection to the enlarged boron diffused end squares. Therefore, a thin layer of aluminum was vapor deposited over the boron squares. Small brass posts were held in contact with the aluminum squares using a pair of microscope slide spring clamps. The clamps were attached to wires leading to a BNC connector fitted in the chamber wall. Care was required once the experiment was assembled because movement of the clamps caused a small change in the resistance readings, however, the reading was stable if no apparatus adjustment occurred after the
Figure 3.8: Boron Diffused Silicon Heater.
chamber was sealed. Over the silicon wafer and posts, an acrylic cover with a $3.75 \text{ cm} \times 2.5 \text{ cm}$ cut-out was fitted over the silicon wafer with the inside edge sealed with a silicone bead. This rectangular space, $6 \text{ mm}$ high, was the containment volume for the liquid. The silicon heater fastened in place inside the chamber is shown in Figure 3.10. Five heaters of various widths were constructed in a single silicon substrate to provide a range of resistances and insurance in the event of a failure. However, the middle heater produced a stable resistance without failure and was used for the duration of the experiments.

### 3.4.2 Chamber

Figure 3.9 shows a schematic of the chamber with the microscope positioned above the optical window located in the chamber top. The translation stage provides relative motion between the laser and the meniscus position. Figure 3.10 is a photograph of the chamber interior without the top in place. The silicon wafer with thin embedded heaters is visible in the center of the photograph. The microscope clamps which provide the electrical connection to the heater are also evident on top of the acrylic plate that provides the liquid containment area. The acrylic piece that extends from the vertical wall in the bottom of the photograph is the return mechanism for the condensate. The two focusing lenses and the tuberculin syringe are also visible.

The sample chamber was milled from a solid aluminum block. Two exterior side walls were perpendicular to the base with the other two machined at a $20^\circ$ incline from perpendicular. The inclined sides are thus perpendicular to the incident and reflected paths of the ellipsometer laser. The inner walls are all perpendicular to the base with interior dimensions of $85 \text{ mm} \times 120 \text{ mm} \times 60 \text{ mm}$.

Two $25 \text{ mm}$ diameter low birefringent windows were located in the inclined walls to allow laser beam passage into and out of the sealed chamber. A $75 \text{ mm}$ diameter window
Figure 3.9: Schematic of the experimental chamber.
Figure 3.10: Photograph of the experimental chamber interior.
was fixed in the chamber lid for liquid viewing. The windows were Melles Griot models 02 WLQ 105 and 02 WBK 007 respectively.

In one of the perpendicular outer walls, a 40 mm diameter hole was drilled through and fitted with a hollow cylindrical insert penetrating 10 mm into the chamber. A thermoelectric cooler, Marlow Industries model MI1022T was installed in the insert and connected to a series of cooling fins via a cooper cylinder. A variable voltage source from 0–3.5 Volts was available for the cooler.

An Oriel Model 16122 7.5 cm x 8.75 cm translation stage was fastened to the interior chamber floor and connected to an externally mounted Mitutoyo model 151-255 micrometer head with 0.01 mm graduation. The translation stage surface was removed and replaced with an acrylic cover with a 3.75 cm x 2.5 cm cut-out in the middle. This provided an insulating airspace under the actual heaters so as to approximate an insulated condition. All chamber openings were fitted with 1.8 mm rubber gaskets plus the micrometer shaft was complete with an O-ring seal fitted in the mounting shoulder. Also, all edges were sealed with silicone and allowed to cure once assembly was completed.

3.4.3 Ellipsometer

A basic nulling type ellipsometer, arranged as Polarizer–Sample–Compensator–Analyzer, (PSCA) was designed to measure the film thickness. In addition, focusing lenses were used immediately preceding and following the sample to provide the smallest measurement area possible.

The basis of the ellipsometer is a 1 mW Melles Griot Model 05 LPL 340-065 polarized He–Ne laser. The red laser beam is at a wavelength of 6328 Å. A polarized laser was chosen based on Hauge and Dill [65] in order to eliminate intensity variations due to switching between polarization modes.

Using lens focusing theory [66], the focused spot size is inversely proportional to the
input beam diameter. Therefore, to minimize the spot size to diffraction limits an expansion of the 0.59 \(mm\) diameter standard laser beam output was achieved using a Melles Griot 8–X beam expander Model 09 LBC 003. This resulted in a beam approximately 5 \(mm\) in diameter.

The polarizer and analyzer were 20.6 \(mm\) diameter dichroic sheet polarizers with extinction ratios of 10\(^{-4}\) (Melles Griot Model 03 FPG 001). The focusing lenses are 30 \(mm\) diameter, 100 \(mm\) focal length lenses to correspond to the chamber design. A single layer MgF\(_2\) anti-reflection coating was used on the Melles Griot Model 01 LPX 178/066 lenses. The compensator is a 1/4 wave mica retardation plate specifically designed for a 6328 Å red light laser, model number Melles Griot 02 WRM 015.

All the optical components were mounted with optical post holders and posts fastened to two Melles Griot mini-rail carriers (Model 07 ORM 007). The rail carriers were fixed to an aluminum platform at an angle of 70° from the platform normal axis. This angle provides a maximum in ellipsometer reading sensitivity according to McCrackin et al [53]. The entire ellipsometer configuration is shown schematically in Figure 3.11.

The optic holders for the polarizer, compensator and analyzer were required to rotate to four fixed positions each, thus rotatable mounts were fabricated using fixed Melles Griot component mounts for 30 \(mm\) diameter components (and adapters if necessary) and machined aluminum rings. The mounts were scribed to an accuracy of \(\pm 0.025^\circ\).

A silicon photodiode was used as a measuring device for the ellipsometer output because unlike a true nulling ellipsometer, the light intensity reading levels were required. However, the absolute intensity was not required only the relative intensity of the various readings. Therefore, absolute detector calibration was not imperative. The detector is an Oriel model 7182 silicon photodiode with 100 \(mm^2\) sensitive area. In order to prevent any polarization dependent tendencies of the detector, the analyzer output was focussed into a fibre optic bundle which uses multiple internal reflection inside between 50–200
Figure 3.11: Schematic of the ellipsometer-chamber setup.
bundles to essentially eliminate polarization effects [67]. The fibre optic bundle is an Oril model 77521. The signal was amplified and output to a digital voltmeter.

3.4.4 Stand, Microscope and Camera

Figure 3.12 shows a photograph of the overall view of the apparatus, including the liquid insertion method through a tuberculin syringe. The thermoelectric cooler fins are evident in the front wall of the chamber. Figure 3.13 shows the apparatus complete with the microscope in position above the chamber. The RTD temperature probe can be seen in the back wall of the chamber.

The ellipsometer and chamber, complete with a space for the microscope, were assembled on a 36" x 12" rectangular aluminum platform with four adjustable legs. The accuracy of the adjusting screws was one full turn per one-half degree incline. A levelling bubble was attached to ensure the stand was level in the direction perpendicular to the incline axis.

The microscope was an Edmund Scientific Industrial Microscope model A37,659 with 30X magnification and a 75 mm working distance. A fluorescent light ring was fitted around the microscope objective to supply perpendicular fluorescent light. A Yashica 35 mm camera was fitted over the microscope eye piece for still photographs.

3.4.5 Resistance, Power Input and Temperature Measurement

The temperature of the vapour inside the chamber was measured with a platinum RTD probe inserted through the chamber wall and secured with a compression fitting. The probe was located about mid-chamber height approximately 1 cm from a side wall. The location was chosen to approximate the bulk vapour temperature while not interfering with the laser beam. The probe and digital readout was an Omega model PR-13-2-100-1/8-51/2-E with an accuracy of 0.1 °C.
Figure 3.12: Experimental apparatus without microscope.
Figure 3.13: Experimental apparatus with microscope.
### Liquid Properties of FC-72 and Water at 25°C

<table>
<thead>
<tr>
<th>Property</th>
<th>FC-72</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>340</td>
<td>18</td>
</tr>
<tr>
<td>Surface Tension (dynes/cm)</td>
<td>12</td>
<td>72</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.252</td>
<td>1.333</td>
</tr>
<tr>
<td>Vapour Pressure (torr)</td>
<td>232</td>
<td>23.7</td>
</tr>
<tr>
<td>Solubility of air (ml/100ml)</td>
<td>48</td>
<td>1.9</td>
</tr>
<tr>
<td>Density (g/ml)</td>
<td>1.68</td>
<td>1.0</td>
</tr>
<tr>
<td>Viscosity (cs)</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Heat of Vapourization (cal/g)</td>
<td>21</td>
<td>540</td>
</tr>
<tr>
<td>Conductivity (mW/cm°C)</td>
<td>0.57</td>
<td>5.86</td>
</tr>
<tr>
<td>Dielectric Constant (1Hz)</td>
<td>1.76</td>
<td>78</td>
</tr>
</tbody>
</table>

Table 3.2: Properties of test liquid, FC-72 [2].

The heater power was supplied by a constant current source variable from 4-100 mA. The current through and resistance across the heater were measured by 5-1/2 digit multimeters.

#### 3.4.6 Dielectric Test Liquid

The cooling liquid used to create the thin film was 3–M Fluorinert FC–72. The composition of the liquid is $C_6F_{14}$, known as perfluorohexane. Typical bulk liquid properties are given in Table 3.2. As a comparison the properties of water are also included. Injection into the chamber was accomplished with a 1.0 cc tuberculin syringe with a 4 inch long needle fitted through a rubber stopper and inserted through a side wall. The 3M representative established the fact that the liquid was tested with a silicone rubber seal for a 6 month period with less than 1% variation in properties.
3.5 Procedure

The pre-testing procedure involved cleaning the chamber and sample as thoroughly as possible, then assembling and sealing the chamber. The silicon wafer was put into a dilute HF solution to remove the SiO$_2$ layer which was deposited during fabrication. The wafer was then washed with de-ionized water, dried with compressed $N_2$ then further dried in an inert gas oven. As it is impossible to keep a small oxide layer from growing when exposed to normal atmospheric conditions, it was accepted that a thin oxide layer was present during testing. The wafer was handled with a lint-free cloth covering the test surface until the final assembly stage.

The chamber and all parts associated with it were washed with alcohol, rinsed with de-ionized water and air dried. Once assembled, before the silicon wafer was placed inside, the interior was rinsed with the test liquid and allowed to dry. The wafer was then inserted and the entire chamber sealed. Before liquid was introduced, calibration readings were taken with a dry surface. Ellipsometer readings in the vicinity of the heater were taken to determine the native oxide layer thickness as well as the surface reflectance to be used in ellipsometer thickness calculations. Power was introduced to the heater for a short time to check for changes in substrate refractive index with temperature. The temperature-resistance calibration of the heater strip was accomplished by wrapping an electrical resistance heating strip around the chamber and setting various power levels to obtain a range of ambient chamber temperature conditions. Temperatures were limited to between 20 °C-30 °C as these would sufficiently cover the test range.

Finally, liquid was introduced into the test area to a level near the heater with both the heater and interline being in the field of view of the microscope. With the thermoelectric cooler activated, liquid was continually introduced until the return rate maintained the interline near the heater, a visual measure of steady state. The apparatus was left for a
period of 24 hours prior to the beginning of a series of tests. A test was initiated by setting an input current level and monitoring the heater resistance level and the interline position relative to the heater. Once a steady state situation was noted for a minimum of 2 hours, the microscope and camera were positioned above the heater and a photograph taken. The chamber ambient temperature, heat input, and return rate of condensation drops were measured as data. After these steps, the ellipsometer spot was located above the last visible brown fringe and the micrometer adjusted to find a constant reading in this region. The reading was then monitored for approximately 5 minutes for any sign of changes. After recording the ellipsometer data, power was removed from the heater and the resistance was monitored until the wafer cooled to equilibrium with the chamber temperature. The resistance change was recorded as a measure of the wafer temperature rise above ambient.

The tests were terminated at a power level which introduced more vapour than could be condensed with the cooler alone and condensate appeared on the chamber floor. Once the tests were complete the condensate return from the cooler was positioned away from the test area and a range of tests repeated. The equilibrium liquid supply was introduced through the syringe thus calibrating the return rate as the return drops were counted and timed.
4.1 Preliminary Operation and Calibration

An initial set of tests was done to verify the accuracy of the ellipsometer. Two silicon wafers with $SiO_2$ layers of known thickness, measured by two separate ellipsometers at the Micro-Electronic Research Centre at the University of Alberta (U. of A.), were measured with the ellipsometer with and without the focusing lenses. The measurements without the lenses were accurate to within 0.2% of the values measured by U. of A. With the focusing lenses in position, the present ellipsometer measured values were slightly higher than the values without the lenses, but the estimated error remained less than 1%. These errors are small compared with the uncertainty associated with manual positioning of the ellipsometer components as is discussed later.

Due to the extremely thin nature of the liquid film and the small length of the two-dimensional evaporating region, the most difficult obstacle to overcome was achievement of a steady-state situation. A stable ambient environment for the duration of the experiments was attained by conducting the experiments at night in a photographic dark room. During the experiments, use of the fluorescent microscope ring and laser was kept to the minimum required to obtain the measured results. If left on for any duration of time other than that required for immediate observations and photographs, it was noticed that the fluorescent light ring caused a rise in the temperature inside the chamber. No noticeable effect on the internal temperature from use of the laser was detected but the
beam was blocked when not in use as a precaution. With the cell wall thickness currently used and no significant changes of the ambient conditions in the room during the night, the vapour temperature in the cell was measured to within ±0.1°C and was very stable during each test run.

Equation 3.28 gives the quadratic solution used to obtain the film thickness from the ellipsometer readings. The refractive index of the vapour, liquid and surface are required within this equation to obtain the thickness. The refractive index of the vapour is taken to be 1.0, the liquid taken as that of the bulk liquid, 1.251, but the refractive index of the silicon wafer with a native surface oxide layer is unknown. Therefore, in order to use the ellipsometer, refractive index readings of the bare silicon substrate with native SiO₂ layer were required. The readings were taken at the location just below heater No. 3, shown in Figure 3.8, the designed location of the adsorbed film during a test. Five separate readings were averaged to give a complex refractive index of \( n_0 = 4.24 - 0.05i \). Using the value of Palik [87] for pure silicon of \( n_0 = 3.882 - 0.019i \), a native surface oxide thickness was calculated to be 18 Å, ±5 Å. The estimate of error was determined by recording the change of ellipsometer reading with each individual setting of the compensator and analyzer. The maximum possible error was then calculated for the oxide thickness results. Therefore, the experimental substrate is actually pure silicon with a thin SiO₂ layer on the pure silicon surface to be considered.

The determination of the surface temperature of the boron heater required a calibration of heater temperature versus heater electrical resistance. The RTD probe used to measure the vapour temperature was used to measure the ambient temperature in the chamber while the chamber was heated externally with an electric resistance heating strip. The chamber contained no liquid during the calibration, therefore evaporation did not influence the calibration. Figure 5.8 shows the results of the calibration. The
resistance was measured to within ±0.001 ohms and a linear least squares regression gave

\[ R = 225.466 + 0.539T_s, \]  

(4.1)

with \( R \) measured in ohms (\( \Omega \)) and \( T_s \) in degrees Kelvin, K. This calibration was repeated after the experiments were completed. The results were similar with a resulting temperature-resistance curve slope of 0.59, slightly less than a 10% variation from the original. The original calibration was used to calculate temperatures because it was taken before any movement or adjustment was made to the experimental setup.

Once the heater calibration was completed, the test liquid was introduced into the sealed chamber through the tuberculin syringe. The liquid level was set below the test heater (No. 3 in Figure 3.8) and allowed to evaporate. Liquid input was continued until isothermal saturation was achieved. The liquid level was then microscopically set so the interference colour (beige) was just below the test heater. This would situate the adsorbed film on the heater. Once the liquid level was set, the thermoelectric cooler voltage was set by trial and error. Initially, 2.0 volts was set across the cooler. Observation through the microscope showed a large condensation rate at the cooler face for a saturated chamber condition. This resulted in an oscillatory motion of the contact line region without power having been supplied to the heater. Oscillations toward and away from the heater were noticed plus waves travelling along the interline from one edge of the heater (where the heater and acrylic cover intersect) to the other edge. The voltage was reduced to 0.75 volts and this provided a steady interline and low condensation rate at the cooler face. This level was chosen for use during all of the experiments. The power input to the cooler was not quantified for use in the results.

With the cooler level set, the experiments were taken at steady-state. The assumption of steady-state was not strictly correct as it was noticed that all the liquid would disappear in 7-10 days if the system was allowed to run continuously. Because an entire test would
Figure 4.1: Experimental calibration of heater temperature vs. electrical resistance.
be completed within 2 nights, this fact was noted but would have to be addressed if any duration type tests were done in the future.

Due to the very specific design of the experiment with respect to the liquid condensation and return path, power input to the heater could not be increased arbitrarily without encountering a situation where the thermoelectric cooler face could not condense at a rate equivalent with the evaporation rate. This would cause condensation on the chamber bottom and walls thus eliminating the condensation-evaporation steady-state system, and making the mass transfer measurements unreliable. By trial and error, this heater power level was found to be anything greater than 0.2 Watts. Therefore, between 0 and 0.2 Watts, 6 separate power settings were chosen for each experimental set. Two photographs, 15 minutes apart, at each power setting were taken during each experimental run and three complete experimental sets done. This resulted in 6 experimental profiles for each power setting, a total of 36 individual interference photograph profiles.

4.2 Interferometry Photographs

Figure 4.2 shows a sketch which explains the features of the following photographic results. The photographs are approximately a 40X magnification of the area after photographic enlargement is included. Horizontally in the z direction, each photograph encompasses 16% of the width of the heater. Each photograph is the result of a minimum of 2 hours of continuous steadystate operation at the stated power level. The fluorescent light ring was activated and the photograph taken immediately and the light deactivated in order to avoid any thermal changes to the system while measurements were being taken. The colour fringes correspond to various liquid thicknesses as described in Chapter 3.

Figures 4.3 through 4.8 show one typical set of interferometric photographic results for the 6 different heater power settings which comprised an experimental set.
Figure 4.2: Schematic description of photographic results.
Chapter 4. Experimental Results and Observations

Figure 4.3: Photographic result for $P=0$ mW.
Figure 4.4: Photographic result for P=4 mW.
Figure 4.5: Photographic result for P = 23 mW.
Figure 4.6: Photographic result for P=59 mW.
Figure 4.7: Photographic result for $P=114$ mW.
Figure 4.8: Photographic result for $P=185$ mW.
Referring to Figure 4.3, a case with no heat flux input, the edge of the beige or brown initial fringe is approximately 400 Å, with the thickness reducing towards the heater and eventually the constant thickness adsorbed layer (clear, no interference pattern) which is located on the heater for each case. The beginning of the adsorbed layer is located at a different distance from the brown edge depending on the heater power level. As can be seen from Figure 4.3, the fringe pattern is almost parallel to the heater in the range photographed. This parallel pattern exists for over 90% of the heater length indicating the two-dimensional nature of the experiment. The fringes deviate from the horizontal pattern only at the edges where capillary action draws the meniscus higher. This is not shown in the photographs. Toward the liquid pool end of the photograph, the fringes disappear into the liquid pool which becomes 2-3 mm thick at the deepest section, the pool edge at the acrylic cover.

The first 8 or 9 colour bands are easily distinguishable by the change of colours, given in Table 3.1 (i.e. brown to blue to light blue to gold to purple to etc.) and the determination of film thickness is straightforward. Past these distinguishable colour bands, a series of red (pink) and green closely spaced fringes is evident. The fringe pattern becomes similar to monochromatic interference with the middle of the bright fringe taken as the thickness reference point for position measuring purposes. Due to different colour wavelengths which contribute to constructive and destructive interference, examination of the bright fringes shows a change from pink to purple as the thickness increases. These minor variations in the bright fringe colour were ignored and the main colour for the bright fringe was assumed to be red. Therefore the wavelength 6328 Å was used to determine the thickness after the ninth distinguishable colour band, or the first purple fringe (fringe No.1) as shown in Table 3.1.

It is observed from the photographs that the evaporating meniscus becomes smaller and the fringe pattern closer together as the power input is increased from 0 - 185 mW
in Figures 4.3 - 4.8. The last visible fringe in Figure 4.8 is at a thickness of approximately 30,000 Å or 3 μm. This represents the power setting with the least number of distinct visible fringes. In comparison, Figure 4.3 has 6 additional distinguishable fringes. In the photographs, faint horizontal and vertical lines may be observed, these are the microscopic cross-hairs used for measuring and positioning.

Examination of the individual photographs shows some interesting details which may be qualitatively described by comparing the various pictures. In Figure 4.3, large lenses are visible on the heater edge away from the liquid film. Microscopic impurities are evident in the middle of these lenses. This photograph was taken without power input to the heater, and the only source of evaporation is due to the condensation of the vapour on the cooler face. This results in a vapour pressure below the saturation level and causes evaporation from the liquid interface. At the first appearance of interference fringes, bubbles or lenses appear parallel to the heater and of varied size. These bubbles only appeared after the cooler was activated and surface evaporation commenced. The bubbles were always present once evaporation began, regardless of the power input level.

Comparing Figure 4.4 to Figure 4.3, it is apparent that the brown colour band is thinner in the former. Between these two tests, no additional liquid was added to the chamber for positioning purposes, however, the heater was activated and with P=4mW of power being input. The edge of the brown fringe is now further away from the heater and close examination shows that the bright fringe spacing beyond fringe No. 1 is closer. This indicates a higher evaporation rate and accounts for the difference in distance from the meniscus edge to the heater. The same bubble pattern is evident in Figure 4.4 as in Figure 4.3. The clarity of Figure 4.4 shows a disturbed fringe pattern near the bubbles at the centre of the photograph. It is apparent that these bubbles disturb the flow in their immediate vicinity while the bubbles on the left of the photograph do not appear to influence the flow.
Figure 4.5 is the first result where additional liquid was introduced into the chamber to position the adsorbed film directly over the heater. The additional liquid was necessary because the increased evaporation rate shortened the meniscus to an extent that the edge of the colour bands was between 2-3 heater widths from the heater edge. At this power input level, $P=23\text{mW}$, a significant compressing of the fringe pattern above fringe No. 3 is clearly shown. This is a result of the increased evaporation rate for this case. The bubbles which exist between the fringes and the pool are, on average, smaller in size than the previous two cases, but one additional large bubble appeared. One obvious feature of this photograph is the small size of the brown colour band. However, the size of the colour bands between brown and the fringe No. 3 does not appear to have changed noticeably.

The results from Figure 4.5 which show the decreased fringe spacing above fringe No. 3 and constant colour band size between this fringe and the heater is very clearly presented in Figure 4.6. The fringe spacing becomes very small by comparison to the previous cases. The bubble size appears very similar to Figure 4.5 but the centre bubble appears to be causing a slight disturbance in the liquid locally, as is evident by the slight bowing of the fringe pattern near this bubble. Again, liquid was introduced to maintain the adsorbed layer over the heater, therefore, relative positioning may not be considered.

Figures 4.7 and 4.8 show the exact same trends as detailed in the description of Figure 4.6. The fringe spacing at liquid thicknesses greater than those at fringe No. 3 becomes very close while the colour bands between this fringe and the heater appear to maintain the same constant spacing as is evident throughout all the photographs. In Figure 4.7 the local perturbation near the large bubble is clearly shown, but the overall bubble size remains close to the same size as shown in Figures 4.5 and 4.6.

The result in Figure 4.8 shows a much different aspect than all the previous photographs. The bubbles between the fringes and the liquid pool appear to be connected
by a wave-like feature. This exact feature was also apparent at higher power input levels, which produced meniscus oscillation and condensation on the chamber floor.

The presence and formation of the lenses between the liquid pool and the fringes were examined closely. When the chamber was filled with liquid, without the cooler operating and without power to the heater, the entire fringe pattern was very small, with fringe spacing so close that the resulting photograph could not distinguish the separate fringes. Also, no lenses were present in the liquid. However, once the cooler was activated resulting in condensation and corresponding evaporation, these lenses appeared as shown in Figure 4.3. Deactivating the cooler would eventually result in the disappearance of the lenses but they would return upon reactivation. The lenses were present for every heater power level used and would remain in the photographed location for the duration of each experimental run. Disassembling the experiment, cleaning, and re-sealing the chamber between experimental sets would not change the appearance or behaviour of the lenses. It was noted that the large lenses near the pool, at least one of which is present in every photograph, would eventually move through the fringes and migrate upwards past the heater and reside above the heater. It would take more than 2 hours for this to occur. The location of the lenses was not consistent in terms of liquid thickness. In the lower power range, Figures 4.3 - 4.5, the lenses were centred approximately at the 12th purple fringe while for the higher settings, Figures 4.6-4.8, the centre location was approximately the 15th purple fringe.

Figures 4.7 and 4.8 show the sensitivity of the entire experimental system to changes in the setup. With the sensitivity of the constant current source feeding power to the heater, there is much greater control at the lower power settings. Increasing the power may be accomplished slowly at the lower settings; however, at the higher settings the increase is accomplished within larger increments. This rapid increase causes surges in the meniscus which produce a wave which propagates up the substrate toward the heater
from the liquid pool. A small remnant is seen in Figure 4.7 located on the heater while Figure 4.8 shows a much more noticeable wave. These waves eventually migrate to the opposite side of the heater from the liquid pool. This resulted in waiting for the meniscus to resume a stable shape before measurements were taken. This same behaviour resulted from movement of the translation stage. Once the wave migrated away from the meniscus visible edge it was assumed to have negligible effect on the steady state evaporating system.

4.3 Liquid Film Profiles

Calculation of the liquid film profiles was accomplished using the photographic results and the thicknesses of Chapter 3. The colour fringe position was analyzed through a 30X magnification microscope on a 0.01 mm graduated translation stage. Each of the 6 power settings had 6 photographic results which were all analyzed at the centre of the photograph. The x-axis positions of each fringe were averaged for each power setting, and the profiles are presented in Figures 4.9 and 4.10.

The effect of increasing the power input to the heater is evident in the length of the evaporating meniscus as shown in Figure 4.9. The slope of the profile increases dramatically with increased power input. The relative position of the x-axis, x, was determined by finding the last visible red fringe on the photograph of the highest power level, Figure 4.8, the result with the least number of visible fringes. This red fringe, number 13, was then taken as the reference position of all the other test cases, with distances were measured from this fringe to the interline, x₀. For the red fringes, the centre location was taken for the distance measurement. Once individual colours became distinguishable, the mid-point of the colour was measured along with the boundary between two adjacent colours. The photographic measurements ended at the visible edge of the beige fringe.
Chapter 4. Experimental Results and Observations

Figure 4.9: Liquid film profiles, averaged over 6 readings.
Figure 4.10: Adsorbed thickness region profiles, averaged over 6 readings.
The last point of each data set is the adsorbed thickness and position as measured with the ellipsometer. The adsorbed thickness was measured by locating the laser into the region above the last visible remnants of the beige fringe and moving the translation stage while monitoring the ellipsometer reading until no change was noted. After monitoring the ellipsometer reading in this location for approximately 15 minutes to ensure no variation, the reading was taken. After the reading was noted, the translation stage was moved towards the beige fringe and the translation position noted when the ellipsometer reading began to deviate from the equilibrium adsorbed thickness reading. The distance from this point to the visible edge of the beige fringe was recorded. This method had to be performed quickly because translation stage motion caused waves in the meniscus, therefore the distance had to be determined before equilibrium was disturbed. The present design precluded a slow profiling method using the ellipsometer because the meniscus was highly sensitive to translation stage motion. Although a detailed ellipsometer profile between the beige fringe edge and the adsorbed film was desired, (one measurement every 10 \( \mu m \) along the x-axis) the variation in adsorbed layer position with power input was still obtained with this alternate method.

An expanded view of the adsorbed layer position from Figure 4.9 is shown in Figure 4.10. The primary reason the curve points are not perfectly smooth is due to the subjective interpretation of the colours and related thickness as discussed in Chapter 3. The results show that the adsorbed thickness layer begins approximately 350 \( \mu m \) from the visible beige edge in the case without power to the heater and this same measurement is only 50 \( \mu m \) in the highest power case, \( P=185 \) mW. Figure 4.9 clearly shows the shortening of the meniscus as the power is increased. The initial slope is much steeper at \( P=185 \) mW than the other power levels. Figure 4.10 illustrates the point that below the second purple fringe (\( \approx 5000\AA \)) the profiles are fairly constant in slope. The change near the adsorbed thickness reflects the widths of the beige fringe in the photographs.
4.4 Adsorbed Thickness

While the photographic results were limited to 6 power input settings throughout the experimental range, as the power was increased incrementally through the test range, adsorbed thickness, evaporation rate, and heater temperature were all measured at each increment. This resulted in 14 different measurements for each of these three parameters. The 14 measurements were averaged for the 3 experimental runs. The average values for the adsorbed thickness change with power input are shown in Figure 4.11.

Each adsorbed film thickness measurement was made after the laser was determined to be situated in the adsorbed region using the consistency in ellipsometer readings as an indicator as the ellipsometer spot was situated at the interline visually and subsequently moved toward the adsorbed film region using the micrometer. A minimum of 15 minutes was allowed to monitor the reading for any possible variations with time. The points in Figure 4.11 represent an average of the three experimental runs. Variations of less than 10% of the value at each condition were noted. For readings in this range of the ellipsometer (<150Å), the estimated human error in reproducing the analyzer and compensator positions for each reading is ±5Å. This estimate was achieved by using one of the SiO2 samples from the University of Alberta as a test sample, and then recording the sensitivity of each ellipsometer component to 1 degree changes in measurement position (the estimate of repeatability of positioning with the current design). Using these sensitivity results in the computer program, the maximum variation in calculated thickness was computed. The calculated variation represents approximately 25% of the adsorbed thickness value at the highest power inputs. The two most notable parts of Figure 4.11 are the lack of variation in adsorbed thickness past 100 mW input power and the rapid change in steady-state adsorbed thickness below 50 mW input power. The adsorbed thickness ranged from 138Å at P=0 mW to 40Å at P=185 mW.
Figure 4.11: Adsorbed thickness vs. power input.
4.5 Evaporation Rate

Figure 4.12 shows the mass evaporation rate as a function of the input power. The mass evaporation measurements involved timing the return rate of liquid drops at steady-state. The drops were timed to within $\pm 0.5\, \text{seconds}$, leading to an error of less than 3 % of the calculated evaporation rate.

The mass evaporation rate was calculated relative to the background evaporation determined from the evaporation result from the $P=0\, \text{mW}$ case. The evaporation for this particular case was caused solely by the thermoelectric cooler condensing the vapour and resulting in a vapour space below saturation pressure. As the cooler voltage was held constant throughout the tests, the evaporation due to the cooler was assumed to be constant for all the tests. Therefore, this evaporation rate was subtracted from all the cases where the heater was activated. This should provide information on the evaporation caused only by the heater. The background evaporation comprised 90% of the total evaporation measured for the $P=4\, \text{mW}$ case and only 31% for the $P=185\, \text{mW}$ case. The assumption was made that the internal chamber conditions were constant throughout the test causing the background evaporation to be steady at the pre-test measured level. The net mass transfer results (total minus background) were constant to within less than 5% variation when comparing the individual test runs.

4.6 Surface Temperature Results

The surface temperature change with power input is shown in Figure 4.13. The temperature results were averaged over the three experimental sets; however, variation of the temperature readings at each power level was less than 5%.

The heater temperature rise was measured by recording the electrical resistance before and after a test, then disconnecting the power supply and monitoring the electrical
Figure 4.12: Mass Evaporation Rate vs. Power Input.
Figure 4.13: Heater temperature rise vs. power input.
resistance until the heater attained thermal equilibrium with the chamber interior. The electrical resistance was then recorded again and the difference was taken as a measure of the heater temperature rise above the chamber temperature. Determining when the heater was in thermal equilibrium with the chamber was the most difficult aspect of the reading. However, the results were very consistent over the three experimental runs and it was estimated that the error in the resistance measurement was less than 5% of the reading and much lower at the higher power settings. The estimate was calculated by recording the uncertainty in the electrical resistance measurement while monitoring the reading to determine exactly when thermal equilibrium with the chamber was achieved. The one exception to the above error estimate was the temperature reading at the lowest power input level, 4 mW. The change in electrical resistance was very small and therefore, determining when thermal equilibrium occurred was extremely important. Estimation of this error was difficult, however, errors as large as 25% could be possible. The relative change in the electrical resistance reading for the other power settings was sufficiently large so that the determination of thermal equilibrium was not as crucial. These errors combined with the slight scatter in the calibration data resulted in a temperature rise error estimates of no greater than 10% of the calculated result and much less at the higher power levels.

The adsorbed thickness, mass evaporation and temperature rise measurements were repeated on 2 additional experimental runs after the complete experimental set with results consistent with the ones shown, within the experimental accuracies. The extra runs were conducted mainly to check the adsorbed thickness results. Surface contamination would alter the adsorbed thickness readings dramatically, so the test surface was cleaned with the test fluid and a lint free cloth before each of the additional runs. Refractive index readings of the surface were taken before both tests and the average reading was a 20 Å layer of SiO2, compared with the average reading of 18 Å before the tests. This was
an indication that practically no surface contamination was present during the additional tests.
Chapter 5

Discussion of Results

5.1 Experimental Profile Comparison

Comparing experimental extended menisci thin liquid film profiles is difficult due to the variety of geometries and materials used in research of interline heat and mass transfer. While silicon is a common substrate among wetting film researchers because of the smoothness of the surface and high reflectivity, interline dimensions and experimental liquids vary depending upon the individual experimental setup. One common factor among researchers is the use of non-polar liquids leading to theoretical analyses which use only London van der Waals dispersion forces as the only significant contributions to the intermolecular attraction between the liquid and substrate. One experiment that provides a useful comparison to the results presented here was that of Cook et al [30]. Figure 5.1 shows the present results which indicate the effect of increased input power on the profile shape. Figure 5.1 also shows the results of Cook, who had a similar experimental setup but used decane as a working fluid. The effect of increasing the input power is similar in both experiments. The meniscus length shortens and the slope becomes steeper in each case. This indicates that an increased evaporation level creates forces within the meniscus, the result of which shortened the length.

Further examination of Figure 5.1 indicates the possibility of comparing the current experimental film profiles by attempting to eliminate the effect of power input. Normalizing the profile length by dividing the relative position, $(x - x_0)$, by the individual
Effects of Increasing Power Input on Film Profiles

Figure 5.1: Input power effect on liquid profiles, [30].
meniscus length (reference position to the interline \((x_i - x_o)\)), the six individual profiles may be compared. Figure 5.2 shows the normalized profiles plots. It appears that the normalized profiles are very similar from the thickest portion, 30,000 Å, down to approximately 5000 Å. This indicates that the meniscus length in this part of the profile is dependent upon the power input almost exclusively. However, below 5000 Å the profiles do not appear similar. Below 5000 Å, where the disjoining pressure forces become important, the expanded view profile plots presented in Figure 4.10 are normalized in the same manner as previously described and shown in Figure 5.3. This Figure illustrates more clearly the previous observation that the normalized profiles are not similar in this region. It can be clearly seen that the profile slopes down to 400 Å are almost identical but the major differences occur in the region from the 400 Å level to the interline. This could indicate that the power input is not the most important factor in determining the meniscus shape in this thickness range. One additional consideration is the fact that the distance from the edge of the beige fringe to the interline was the singularly most difficult measurement to obtain in the experiment. This may account for significant errors in the normalized profile; a more precise experimental design is needed to accurately examine this region.

5.2 Unsteady Behaviour

Initially at very high cooler background voltage settings or at high power settings, meniscus oscillations toward and away from the interline were noted. The oscillations were comparable to a wave motion on a shoreline when viewed from above. This behaviour was noted in many of Wayner's experimental works. [30], [31], [39], [38]. Wayner noted that the profile shape remained constant (determined by observation of the fringe pattern) while the meniscus advanced towards and receded from the interline. These
Figure 5.2: Normalized liquid profiles.
Figure 5.3: Normalized liquid profiles, disjoining pressure region.
previous experiments used monochromatic light with a first dark fringe of approximately 1000Å thickness. The oscillations were evident by the position of the leading fringe. The oscillations were noted but were never quantified in terms of frequency.

With the current experimental setup using a fluorescent light ring as a source, a variation of colours beginning at approximately 400Å thicknesses provided greater detail for the liquid profiles plus added insight into the behaviour of the meniscus during oscillations. It was observed during oscillations that the leading edge colour would vary between the colour extremes of tan and light blue over a period of time (plus intermediate colours between). At thicknesses greater that 2000Å (light blue), no variation of the meniscus pattern was noticeable. Upon meniscus advancement towards the heater, the leading edge would appear light blue followed by the clear adsorbed region. During a cycle of between 5-10 seconds, the light blue would change to blue, from blue to brown, from brown to tan followed by a return to light blue only. It appears that at high evaporation rates, a smooth supply of liquid into the evaporating zone is not possible so a small dry-out and rewetting situation is created. Analysis of this periodic condition was beyond the scope of this investigation, other than to note the appearance and behaviour.

While the meniscus could be approximated as two-dimensional for greater than 90% of width of the silicon substrate, the meniscus did wick further up the substrate, towards the heater, at the edges where the substrate joined the acrylic cover and was sealed with silicone rubber. This appears to cause an interesting action at high evaporation rates. When oscillatory meniscus behaviour appeared at a high power inputs, waves travelling parallel to the interline were observed. It appears that liquid was drawn into the evaporating region from the side edges as well as from the liquid pool below. This effect was not apparent if no oscillations were present.
one order of magnitude in area). Both the previous papers attribute the lenses to the presence of microscopic dust particles. Their behaviour was similar to that noticed in this experiment in that some of the lenses slowly coalesced over time and propagated towards the heat source. Because the results indicate that larger lenses near the heater have microscopic particles visible while the bubbles between the fringes and the pool have no apparent particles, it is not certain that all the lenses (or bubbles) are necessarily created by particles. The experiment was disassembled and cleaned on five separate occasions but the bubbles returned in the same location every time evaporation began upon activation of the heater.

One possibility for the bubble formation is the dissolution of air into the liquid FC-72, since air is extremely soluble in FC-72, 48% air by volume at 25°C. The dissolved air may begin to come out of solution as the meniscus begins to thin dramatically and different forces are introduced locally into the meniscus. This would explain the constant presence of the bubbles in the same location over a period of hours and days. One aspect which can be concluded not to cause the bubble formation is nucleation due to boiling. Reeber and Frieser [88] used a smooth silicon substrate with FC-72 as a cooling liquid in superheated plate tests with a superheat of 30°C without producing any nucleation. This superheat is at least 20 times greater than that of the highest substrate superheat produced in this experiment, therefore no nucleation should appear.

5.4 Adsorbed Thickness

In an effort to test the proposed disjoining pressure relationship, Equation 2.19, the measured adsorbed thickness was plotted versus the saturation pressure ratio (calculated from measured temperatures), and is shown in Figure 5.5 along with the data of Derjaguin and Zorin [21] for comparison. Derjaguin and Zorin measured adsorption thicknesses
Figure 5.5: Comparison of adsorbed thickness vs. saturation pressure ratio, [21].
of various polar and non-polar liquids on superheated plates in a static non-evaporating environment. The shape of the curve containing the present experimental data compares favourably with the non-polar data, CCl₄, for values of P/Pₘ near 1.0, although the absolute levels are different most notably at the lower saturation pressure ratios. This could be a function of the different material properties used in the two experiments. The polar liquid, butyl alcohol is shown to indicate that the results for all polar liquids intersected the saturation pressure ratio P/Pₘ = 1.0 axis while the non-polar fluids became tangent to this axis, as did the present experimental results.

Direct comparison of the different experimental results reported above can be achieved by rearranging Equation 2.19 to non-dimensionalize the adsorbed thickness by the remaining terms in the equation which account for the variations in substrates and liquids among the experiments. Equation 2.19 may be written as

\[
\ln \left( \frac{P}{P_s} \right) = \left( \frac{A_{12}}{6\pi} \right) \left( \frac{M}{RT_v \rho_l} \right) h_0^3. 
\]

(5.1)

Defining a reference thickness as

\[
h_r^2 = \left( \frac{A_{12}}{6\pi} \right) \left( \frac{M}{RT_v \rho_l} \right),
\]

(5.2)

Equation 2.19 may be written as

\[
\ln \left( \frac{P}{P_s} \right) = \frac{1}{(h_r \rho_s)^3}.
\]

(5.3)

Evaluating the terms in \( h_r \) for each particular fluid and substrate in Figure 5.5 (from theoretical bulk values), the non-dimensionalized thicknesses are replotted versus the saturation pressure ratio in Figure 5.6. The results show very good agreement with the data of Derjaguin and Zorin [21] for the non-polar liquids. This result indicates that the adsorbed thickness behaviour of different non-polar liquids is similar when non-dimensionalized using Equation 5.3. This supports the use of Equation 2.19 for predicting
of various polar and non-polar liquids on superheated plates in a static non-evaporating environment. The shape of the curve containing the present experimental data compares favourably with the non-polar data, CCl₄, for values of P/Pₛ near 1.0, although the absolute levels are different most notably at the lower saturation pressure ratios. This could be a function of the different material properties used in the two experiments. The polar liquid, butyl alcohol is shown to indicate that the results for all polar liquids intersected the saturation pressure ratio P/Pₛ = 1.0 axis while the non-polar fluids became tangent to this axis, as did the present experimental results.

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\[
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\]  

(5.1)

Defining a reference thickness as

\[
h_r^3 = \left( \frac{A_{12}}{6\pi} \right) \left( \frac{M}{RT_v \rho_l} \right),
\]  

(5.2)

Equation 2.19 may be written as

\[
\ln \left( \frac{P}{P_s} \right) = \frac{1}{\left( \frac{h}{h_r} \right)^3}.
\]  

(5.3)

Evaluating the terms in h_r for each particular fluid and substrate in Figure 5.5 (from theoretical bulk values), the non-dimensionalized thicknesses are replotted versus the saturation pressure ratio in Figure 5.6. The results show very good agreement with the data of Derjaguin and Zorin [21] for the non-polar liquids. This result indicates that the adsorbed thickness behaviour of different non-polar liquids is similar when non-dimensionalized using Equation 5.3. This supports the use of Equation 2.19 for predicting
Figure 5.6: Comparison of non-dimensionalized adsorbed thickness vs. saturation pressure ratio, [21].
adsorbed thicknesses given the saturation pressure ratio for any non-polar liquid on a smooth substrate in an evaporating as well as a non-evaporating environment. Near the saturation pressure ratio value of 1.0, the agreement among the data is the poorest, however, this constitutes the smallest experimentally measured temperature rise, and is subject to the most uncertainty.

The proposed variation of disjoining pressure of $1/h_o^3$ from Equation 2.19 can be examined by plotting $h_o$ versus $-ln(P/P_s)$ on a log-log scale. Assuming that the value of $h_r$ is constant for each individual experiment, Equation 5.3 may be rewritten as

$$-ln\left(\frac{P}{P_s}\right) = \frac{-h_r^3}{h_o^3}. \quad (5.4)$$

Taking the logarithm of both sides results in

$$log\left(-ln\left(\frac{P}{P_s}\right)\right) = -3log(h_o) + 3log(-h_r). \quad (5.5)$$

This relationship was fit to the experimental data and is shown in Figure 5.7. Examination of Figure 5.7 shows good agreement with the proposed $1/h_o^3$ relationship for the majority of the data. This results strongly supports the proposed disjoining pressure relationship, Equation 2.19. For the data points on either end of the graph, the largest experimental uncertainties exist creating the possibility of errors in these points.

Equation 5.5 was also plotted on Figure 5.7 for the case of the theoretical Hamaker constant $A_{12} = 1.0x10^{-19}J$ used to calculate the non-dimensional thickness, $h_r$. From Figure 5.7 it is apparent that while the slope of the relationship is well approximated by the data, the theoretical position of the line as calculated by the Hamaker constant equation, Equation 2.20, does not match the data well. This indicates that the Hamaker constant equation as presented does not match the experimental results. This equation is an approximation to the more complex theory, as given for example by Wayner [25]. It is not possible from these experimental results to determine if the difference between the
Figure 5.7: Adsorbed thickness vs. saturation pressure ratio, Equation 2.19.
experimental data and the theoretical calculation is due to the equation approximation or to physical factors, such as surface contamination, surface roughness, or liquid impurities. Calculating the intercept of the line through the experimental points gives a value for $A_{12} = -4.3 \times 10^{-19}$ J, approximately four times larger than the theoretical value. However, using the theoretical value of the Hamaker constant results in adsorbed thickness values of less than 50% lower than the measured values. This suggests that unless detailed liquid property data is available, using Equation 2.20 to calculate the Hamaker constant would be useful in practical engineering designs.

Assuming that the $1/h_0^3$ dependency for disjoining pressure is correct as suggested by theory, the Hamaker constants given in Equation 2.19 were calculated using the adsorbed thickness and saturation pressure ratios which were measured experimentally. The saturation pressure ratios were determined from the measured vapour temperature and substrate surface temperature. In the adsorbed liquid region, the surface temperature was assumed equal to the liquid-vapour surface temperature. The pressures were calculated from the manufacturer's data on vapour pressure. The vapour pressure relationship is given by

$$P_v = 10^{(7.6042 - 15/2)},$$

where $P_v$ is given in torr. The calculated values of the Hamaker constant were subject to large errors primarily due to the ellipsometer thickness measurements which are raised to the third power in the calculation. The best estimate of the random error which occurred in each ellipsometer measurement was $\pm 5 \text{Å}$ as previously discussed in Chapter 4. Errors due to temperature uncertainty were much less during each Hamaker constant calculation as the estimate of temperature uncertainty was less than 10%, and significantly less than this at the higher power inputs. Accounting for these errors, the calculated values of the Hamaker constant are given in Table 5.3. The calculation procedure is detailed
Table 5.3: Experimentally calculated Hamaker constants.

in Appendix F. Examining the values in Table 5.3 it is apparent that when the error estimates are taken into account, a strong case can be presented for the existence of a constant value of $A_{12}$. This was confirmed by the results presented graphically in Figure 5.7 where the data fit to the experimental 1/3 slope does not show any obvious trends. Although averaging over a series of experiments aids in eliminating the random error, significant uncertainty in the ellipsometer measurements makes any distinct pattern impossible to establish. The one apparent fact is that the experimentally calculated value of $A_{12}$ is approximately 5X larger than the theoretical value. Given the fact that the theoretical value was calculated from Equation 2.20, which is an approximation to the more detailed theoretical calculations, and surface contaminants and impurities could
affect the experimental results, the result indicates that the given equation is adequate in providing a value to use in evaporating situations.

5.5 Hydrodynamic Model

Determination of the effectiveness of the hydrodynamic model, Equation 2.32 requires a mathematical description of the liquid film thickness profiles which must be differentiated four times to obtain the evaporative mass flux from the liquid-vapour surface. In this experimental setup, there was an insufficient number of data points per profile for the use of a spline routine. Therefore a polynomial curve-fit of order 6 was chosen to fit the entire experimental profile. The polynomial approximation to the data points was very good except in regions close to the interline region where the resulting curve showed a large gradient. To circumvent this problem, the profile near the interline, in the disjoining pressure dominated region, was modelled with a separate curve. The results of the polynomial curve fit are shown in Figure 5.8.

Using the coefficients from the polynomial curve fit in an equation to give the film thickness as a function of the relative position, Equations 2.31 and 2.32 may be calculated to give the mass flow rate per unit length through the meniscus, \( \Gamma \), and the evaporative mass flux from the liquid-vapour surface, \( \dot{m}_e \). An indication of the forces which cause fluid motion in the meniscus is shown by the curvature, \( K \), of the liquid film surface. The curvature, approximated by Equation 2.29, is shown in Figure 5.9 for the polynomial curve fit. The Figure shows that the curvature generally increases from the liquid pool region until a maximum is reached at approximately the same x location from the 3 \( \mu \)m thickness position, \( x_o \). One curve, \( P=23 \) mW does not peak as much as expected in accordance with the other results and is a more even curvature profile. The reason for this individual behaviour is not certain. From Figure 5.9 the curve fit limitations at
Figure 5.8: Polynomial curves fit to full profiles.
either end of the data are immediately apparent. Without the ability to clamp the curve ends during the regression analysis, the end information was not sufficient to properly model the curves at these locations. This fact becomes more prominent as the profile equation is differentiated.

The calculated curvature of the above profiles are replotted in Figure 5.10 as a function of film thickness. The results show a definite trend of the maximum curvature to be located at a thinner portion of the film as the input power increased. Also, the value of the maximum curvature increased, indicating an greater evaporation rate, for increased power input. Due to the need to differentiate the polynomial curves twice to obtain the curvature, the effect of having a different curve fit to the data was examined using polynomial curves of order 4 through 9 and power law curve fits. The size and location of the maximum curvature did not vary appreciably with any of these other curve fits.

The evaporative mass flux described in Equation 2.32 was calculated using the polynomial curve fit and is shown in Figure 5.11. The mass flux is plotted against the liquid film thickness. The results show that very little mass flux occurs in the disjoining pressure dominated region, less than 1 $\mu$ m film thickness. The mass flux increased with increased power input as is expected. The result for $P=23$ mW follows the same result as the curvature graph with respect to its totally independent behaviour from the other experimental results. These mass flux results indicate that the majority of the evaporating mass is occurring in liquid film thicknesses on the order of microns, outside the zone of influence of the disjoining pressure.

A similar procedure to that previously described for calculating the evaporative mass flux for the full profile was used to calculate the flux for the disjoining pressure dominated region. One major difference was in the type of profile required to approximate the data in this region. Polynomial curve fits were not very accurate representations of the experimental data due to the sharp relative curvature in the data as the profile approaches
Figure 5.9: Profile curvatures at relative positions.
Figure 5.10: Profile curvatures as a function of film thickness.
Figure 5.11: Evaporative mass flux vs. film thickness for the full profile.
the interline. A more accurate representation was a power law curve fit of the form

\[ h = ax^b. \]  

(5.7)  

The fitted curves are shown in Figure 5.12. The Figure shows the effect of increased input power on the liquid film profile. The major differences between the power settings occur in the curvature of the profile below 1000 Å.

Using the power law profiles in the disjoining pressure region, the disjoining pressure versus the relative distance location is calculated with Equation 2.19. The resulting disjoining pressure curves are shown in Figure 5.13. The curves are plotted with the reference position of \( x_1 \) located at the liquid film thickness of 3500 Å, estimated to be the beginning of the disjoining pressure dominated region from the full profile plots. Examining Figure 5.13, this assumption appears valid as the calculated value of the disjoining pressure is below \( 1 \, N/m^2 \) at this thickness for all input power levels. The relative size of each disjoining pressure region along with the steepness of each profile in this region are evident from the graph.

Using the second derivative of the disjoining pressure equation and the curvature calculation in Equation 2.32, the evaporative mass flux in the disjoining pressure controlled region are shown in Figure 5.14. It is evident from the Figure that the evaporative mass flux increased with increasing input power with a large increase occurring between \( P=185 \, mW \) and the other power settings. However, the absolute value of the mass flux is negligible compared with the flux occurring in the film thicknesses greater than \( 1 \, \mu m \), as shown in Figure 5.11. Therefore, it appears that the disjoining pressure caused liquid flow in this region but the level of evaporation is very small compared to the region where the changes in curvature are responsible for fluid motion, at least 2 orders of magnitude in all cases.
Figure 5.12: Curve fit to profiles in the disjoining pressure region.
Chapter 5. Discussion of Results

Figure 5.13: Disjoining pressure profiles.
Figure 5.14: Evaporative mass flux in the disjoining pressure region.
5.6 Heat and Mass Transfer

The evaporative mass fluxes presented above allow the calculation of the interfacial heat transfer coefficient due to evaporation. Using Equation 2.33 the heat transfer coefficients are shown in Figure 5.15 for the full meniscus profiles. It is apparent from Figure 5.15 that there are very low values of $h_e$ in film thicknesses below 1.5 $\mu m$. For the input power levels between 23 and 185 mW, the heat transfer coefficients reach a maximum of between 500 and 1000 $W/m^2K$ at a thickness level of 3 $\mu m$. The heat transfer coefficients for the $P=4$ mW case indicate a much greater value. Because this result does not follow the others, it appears that the temperature difference measurement of 0.015 K for this case could be influencing the result significantly. However, the magnitude of possible error in the temperature measurement does not account for the increase in the heat transfer coefficient shown. Therefore, for very low power inputs, significant heat transfer coefficients are possible below 3 $\mu m$. For the input power settings above $P=23$ mW, possible large heat transfer coefficients may exist but at film thicknesses greater than 3 $\mu m$.

From Figure 5.15, the heat transfer coefficients in the disjoining pressure dominated region are shown to be very small. Figure 5.16 shows the calculated values of $h_e$ for the film thicknesses below 3500 Å. Again, the values for $P=4$ mW are the least accurate due to the small temperature difference to be measured at this level. The heat transfer coefficients in this area are very low, below 1.0 $W/m^2K$ for the power levels greater than $P=4$ mW. The values are very consistent throughout the range, without much variation. From these results, the available cooling due to evaporation in this region is negligible compared with that which was shown for film thicknesses above 1.5 $\mu m$.

Using the calculated evaporative mass fluxes for the full profiles, integrating from the
Figure 5.15: Heat transfer coefficient for the full profile.
Heat Transfer Coefficients vs. Film Thickness

Figure 5.16: Heat transfer coefficient in the disjoining pressure region.
Table 5.4: Experimental vs. calculated mass flow rates.

<table>
<thead>
<tr>
<th>Power (mW)</th>
<th>$\Gamma_e$ (measured) $\times 10^8$ kg/s</th>
<th>$\Gamma_c$ (calculated) $\times 10^8$ kg/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.6</td>
<td>0.14</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>0.13</td>
</tr>
<tr>
<td>23</td>
<td>14</td>
<td>0.021</td>
</tr>
<tr>
<td>59</td>
<td>19</td>
<td>0.35</td>
</tr>
<tr>
<td>114</td>
<td>27</td>
<td>0.60</td>
</tr>
<tr>
<td>185</td>
<td>39</td>
<td>2.6</td>
</tr>
</tbody>
</table>

interline to the reference position of 3 $\mu$m, Equation 2.31 (multiplied by the experimental width) gives the total mass evaporation in each input power setting. These values were compared with the experimentally measured values and are shown Table 5.4. It is immediately obvious from the results presented that the calculated mass flow rate into the region of the experiment is at least 1 order of magnitude less than the measured value. This indicates that another substantial driving force might exist in this area to account for the flow. However, examining the presented results closely indicates that the evaporative mass flux is increasing substantially in the region of the data that is on the outer limit of the current measurement capabilities. This region exists at approximately a thickness of between 2-3 $\mu$m. Therefore, when comparing the calculated mass flows with the actual measured values, it appears that the majority of the evaporative mass flux must occur outside the present measurable region to account for this substantial difference.

Theoretical prediction of the interfacial mass transfer involves the use of Equation 2.37.
Corrections to the pressure and temperature in this mass transfer model for the specific case of thin evaporating liquid films are given in Equations 2.38 and 2.39. Using the evaporative mass flux calculated with Equation 2.32, the evaporation coefficients in Equation 2.37 may be calculated and compared with the ideal theoretical value of 1.0. The calculated values of the evaporation coefficient, $\sigma_e$, are shown in Figure 5.17. It is apparent that the value of $\sigma_e$ is not constant over the range of the meniscus profile. In the region where the evaporative mass flux was significant, greater than 1.5 $\mu m$, the evaporation coefficient ranged between 0.001 and 0.0025 for input power levels above $P=4$ mW. Again, the result for $P=4$ mW is significantly different from the other results, reflecting the previous differences in all calculations involving the measured temperature difference. These values of $\sigma_e$ differ from the ideal value of 1.0 by almost 3 orders of magnitude but results similar to these have been reported [46]. The extremely small values of $\sigma_e$ shown in liquid thicknesses below 1.5 $\mu m$ are indicative of the very small amounts of evaporation occurring in this region. A more detailed graph of this region is shown in Figure 5.18. The values of the evaporation coefficient are reasonably constant in the disjoining pressure dominated region, but the overall values are 3 orders of magnitude less than those occurring in the thicker film region dominated by capillary forces (greater than 1.5 $\mu m$), and 6 orders of magnitude less than the theoretical values. The most obvious reason for this large discrepancy is in the use of Equation 2.37. The derivation was made for interfacial pressure and temperature differences on the order of molecular distances, whereas the current design attempts to use a form of this analysis on a macroscopic scale. The driving temperature and pressure differences in the experiment are those required for a practical design and the results reflect this desire. The evaporation coefficient when used in the present context must account for macroscopic effects such as non-condensables and temperature and pressure gradients, the effects of which are shown to be substantial and must be accounted for.
Figure 5.17: Evaporation coefficient for the full profile.
Figure 5.18: Evaporation coefficient in the disjoining pressure region.
There is a basis for expecting evaporation coefficients of this low a magnitude from the 3M corporation product manual [2]. When air is present, the FC-72 vapour is heavier than air and does not diffuse easily through air. Using the interfacial mass transfer equation, Equation 2.37, with the measured evaporation loss at room temperature [2], a calculated evaporation coefficient of approximately $1.0 \times 10^{-5}$ is obtained. This indicates an extremely large influence on the evaporation rate due to the presence of air, and this is verified by the present experimental results.

5.7 Experimental Accuracy

The previously listed results were all subject to the limitations of the current experimental setup and procedure. The most obvious type of error which occurred was random error (operator error or unanticipated exterior factors) and was easily controlled by repeating the experiments numerous times and evaluating the repeatability of the results and to average the results in order to eliminate the random errors. As mentioned, all the results were averaged over a minimum of six full experimental tests plus some partial tests which did not include thin film profile photographs. All the results obtained were consistent and repeatable. This was assumed to effectively reduce the random error component to a negligible value.

The other type of error was the accuracy limitations of the experimental equipment. The most significant error was in the profile region greater than $1 \mu m$ where the interference colour bands in the experimental photographs were not precisely defined by a mathematical expression. Due to this fact, the calculation of evaporative mass flows in this region using the change in curvature as representative of the flow rate had the possibility of large errors after having the resulting least squares curve fit differentiated four times. The change in curvature among the profiles shows the effect of increased power
input but definite conclusions about the actual numerical comparison of mass flow rates could not be drawn.

The remaining experimental measurements were all determined to be very accurate. The mass flow rate was measured with a maximum error of less than 3%. The surface temperature rise had a maximum error of less than 5%. The only other measured quantity was the adsorbed thickness. The ellipsometer measurements contained two sources of error, one of which was random and the other systematic. The random error involved the manual setting of the analyzer and compensator angles. Tests on this repeatability with samples of known thickness indicated an error of no more than 2% and usually lower. The other error involved the determination of the substrate index of refraction which would affect the absolute level of the ellipsometer reading. Cleaning of the silicon wafer was done before each test, however, after cleaning there was some variation in the refractive index determination, sufficient to cause an uncertainty of $18\AA \pm 5\AA$ in the $SiO_2$ thickness measurement. This error was systematic because the same refractive index measurement was used for each test case, thus resulting in no effect on the adsorbed thickness readings relative to each other. Therefore, the relative temperature effects on $A_{12}$ contain maximum possible errors of 10%.

5.8 Summary of Relevant Experimental Observations

During the course of this research, various interesting and not always explainable observations were made that have already been discussed and will be summarized here.

1. The most obvious experimental phenomena was the continued presence of the bubbles in the liquid between the extended meniscus and the liquid pool. Unlike previous researchers, the majority of the bubbles did not appear to be caused by dust particles and did not behave as reported in the literature. The opinion of
the author was that they are dissolved air bubbles which cannot remain dissolved as the film thins to less than approximately 1\(\mu m\) due to the changes in the film properties.

2. Another interesting result which has been reported in the literature numerous times but has yet to be satisfactorily recorded or analytically explained is the unsteady oscillatory behaviour of the interline as the evaporation rate is increased to a significant level. It appears as a dry-out and rewetting cycle which has a frequency unrelated to any time dependent process measured in the experiment.

These two observations require investigation separate from the current work because of the potential impact on the use of thin liquid film evaporative cooling.
Chapter 6

Conclusions

With reference to the original objectives of an increased understanding of the heat and mass transfer processes occurring in the contact line region, the following conclusions were drawn from this experimental work.

1. The concept of a disjoining pressure in thin liquid films (typically less than 1 micron), originally developed to describe \textit{equilibrium} thin films (non-evaporating), appears to be applicable to \textit{non-equilibrium} films also, based upon experimental results. The support for this conclusion comes from:

(a) Measured values of adsorbed liquid film thickness for an evaporating, non-polar, extended meniscus on a silicon substrate compared favourably with the results of data for a non-evaporating experiment, Figure 5.6. For non-polar liquids on a smooth substrate under either static or evaporating conditions, when the adsorbed thickness is non-dimensionalized by the reference thickness given by Equation 5.1,

\[ h_r^3 = \left( \frac{A_{12}}{6\pi} \right) \left( \frac{M}{RT_c \rho_l} \right), \]  

(6.1)

the non-dimensional thickness becomes a unique function of the saturation pressure ratio.

132
(b) The inverse cubic relationship, proposed for equilibrium thin film conditions, between the disjoining pressure and the adsorbed thickness Equation 2.19,

$$\frac{\mathcal{R}T \rho_t}{M} \ln \frac{P}{P_s} = A_{12} \frac{1}{6\pi h_0^3}.$$  \hspace{1cm} (6.2)

was shown (Figure 5.7) to also hold for the case of a non-polar liquid on a smooth substrate in an evaporating environment.

2. Despite the strong support for using the disjoining pressure concept in evaporating thin films, the Hamaker constant, $A_{12}$, inferred from averaging experimental measurements of a non-polar evaporating liquid on a silicon substrate was 4-5 times higher than predicted by the theoretical equation of Israelachvili [26], Equation 2.20

$$A_{12} = (\sqrt{A_{22}} - \sqrt{A_{11}})(\sqrt{A_{00}} - \sqrt{A_{11}}),$$  \hspace{1cm} (6.3)

However, the adsorbed thickness predicted by this equation was within 50% of the measured value and therefore could be useful in an engineering design calculation. More detailed property data are needed for evaluating the Hamaker constant using more complex Hamaker constant equations.

3. While the overall concept of disjoining pressure seems to be valid as noted in conclusion 1, above, hydrodynamic and heat transfer models using disjoining pressure to predict the mass flow in a thin film as well as evaporating mass flux from the liquid surface and the total heat transfer rate require further study. No firm conclusions can be drawn regarding the hydrodynamic and heat transfer model validity owing to the poor comparison between predicted and measured values, as cited below:

(a) The hydrodynamic model based on thin film lubrication theory, Equation 2.32

$$\dot{m}_e = -\frac{d\Gamma}{dx} = -\frac{\sigma}{3\nu} \left( h^3 \frac{d^4 h}{dx^4} + 3h^2 \frac{d h}{dx} \frac{d^3 h}{dx^3} \right) - \frac{A_{12}}{6\pi \nu} \left( \frac{1}{h} \frac{d h}{dx} - \frac{1}{h^2} \left( \frac{d h}{dx} \right)^2 \right),$$  \hspace{1cm} (6.4)
which uses the disjoining pressure and changes in curvature as driving forces for liquid into the evaporating region, predicts overall evaporating mass flow rates at least one order of magnitude less than measured results.

(b) The evaporation coefficient in interfacial mass transfer theory, as presented in Equation 2.37

$$\dot{m}_e = \left( \frac{2\sigma_e}{2 - \sigma_e} \right) \sqrt{\frac{M}{2\pi R}} \left[ \frac{P_{lv}}{T_{lv}^{\frac{3}{2}}} - \frac{P_v}{T_v^{\frac{3}{2}}} \right], \quad (6.5)$$

was calculated to be approximately $1.0\times10^{-6}$ (see Figure 5.15) in the disjoining pressure dominated region of an evaporating non-polar liquid when the reference conditions for mass transfer are taken to be the macroscopic temperature and pressure. This is significantly less than previously published values.
Chapter 7

Future Work

The current experimental design has been shown to be very useful in examining the disjoining pressure controlled region of a thin film. However, additional experimental information that would lead to analytical predictions which verify overall measurements of mass evaporation and heat transfer in this region requires some specialized adjustments to the present design.

1. First, and most important is the heater design. The concept is quite viable but a lower electrical resistance would be beneficial so an electrical controller, such as a constant temperature hot wire anemometer, could be used. Also, a thinner heater, in the range of 20 – 30μm, is required to restrict the heater surface to the disjoining pressure region exclusively plus allow some freedom of heater movement within this region. These two requirements indicate a need for much higher boron deposition rates or complimentary ion implantation. If this technology is insufficient, a different method such as etching and vapour depositing a pure metal would be necessary. Ideally, the substrate would also be of a higher thermal insulation than silicon to restrict the heat flow to the heater-liquid interface. One additional criterion would be the addition of more robust electrical lead connections to the heater to prevent resistance change with movement. A good path for future investigators would be convenient access to a microelectronic fabrication location and also access to a precision machining centre. These two are required to easily construct a range of devices based on ideas drawn from the current work.
2. One item that could be incorporated into the present design that would significantly enhance these results would be the incorporation of a more detailed profiling mechanism which incorporated all the features which create a very detailed profile. First, remove the scanning stage from inside the chamber and fix the chamber position while moving the ellipsometer past the meniscus region. This will eliminate all the vibration which disturbs the meniscus profile in the current design. Second, have a two light system in the interferometer, one a fluorescent light for accurate fringe details below 3000 Å, and another monochromatic light for exact fringe details as the meniscus thickens. Third, incorporate a more powerful microscope and a digitized image similar to that described in Wayner's works (i.e. [38]).

3. Elimination of the air inside the experimental chamber and repeating the experimental conditions described here would satisfy the question as to the origin of the bubbles.

4. Another modification to the present experimental design which would be extremely useful would be the automating of the ellipsometer so that measurements could be taken on the order of 1 second while scanning the meniscus.

5. One last recommendation for further work in this area is the combining of the resistance of the heater with that of the probe so the change in the respective resistances is measured immediately, automating the temperature difference measurement.
Appendix A

Physical Description of the Stokes Parameters

Describing the X–Y components of a transverse electric wave propagating in the Z–direction of an X–Y–Z co-ordinate system as

\[ E_x = E_{xo} \cos(\omega t - \frac{2\pi z}{\lambda} + \delta_x) \]
\[ E_y = E_{yo} \cos(\omega t - \frac{2\pi z}{\lambda} + \delta_y) \]  \hspace{1cm} (A.1)

Choosing an arbitrary transverse plane as \( z = 0 \), the components become

\[ E_x = E_{xo} \cos(\omega t + \delta_x) \]
\[ E_y = E_{yo} \cos(\omega t + \delta_y) \]  \hspace{1cm} (A.2)

Suppressing the time variance and representing the electric vector in phasor notation, (the Jones vector)

\[ \mathbf{E}_{x,y} = \begin{bmatrix} E_{xo} e^{i\delta_x} \\ E_{yo} e^{i\delta_y} \end{bmatrix} \]  \hspace{1cm} (A.3)

Examining the Stokes’ parameter definitions to determine the physical meaning of the definitions, the four parameters are

\[ S_0 = E_{xo}^2 + E_{yo}^2 \]
\[ S_1 = E_{xo}^2 - E_{yo}^2 \]
\[ S_2 = 2E_{xo}E_{yo} \cos(\delta_y - \delta_x) \]
\[ S_3 = 2E_{xo}E_{yo} \sin(\delta_y - \delta_x) \]  \hspace{1cm} (A.4)
Appendix A. Physical Description of the Stokes Parameters

A.1 The First Stokes' Parameter, $S_0$

The intensity of an electromagnetic wave is proportional to the amplitude of the wave.

\[
I = S_0 = |E_0|^2 = |E_{x0}|^2 + |E_{y0}|^2
\]  

(A.5)

Therefore, $S_0$ is the total intensity of the wave.

A.2 The Second Stokes' Parameter, $S_1$

The intensity of a component is also proportional to the amplitude of the component wave.

\[
S_1 = |E_{x0}|^2 - |E_{y0}|^2
\]  

(A.6)

Therefore, $S_1$ is the X-axis intensity minus the Y-axis intensity.

A.3 The Third Stokes' Parameter, $S_2$

The phasor components for an axis notation of $-\frac{1}{4}\pi$ from the previous X-Y position is given by using an axis rotation is given by using an axis rotation matrix.

\[
\begin{align*}
E'_{x,y} &= \begin{bmatrix} E_{-1/4\pi} \\ E_{1/4\pi} \end{bmatrix} = R(-1/4\pi) \begin{bmatrix} E_x \\ E_y \end{bmatrix} \\
&= \begin{bmatrix} \cos(-1/4\pi) & \sin(-1/4\pi) \\ -\sin(-1/4\pi) & \cos(-1/4\pi) \end{bmatrix} \begin{bmatrix} E_x \\ E_y \end{bmatrix} \\
&= \frac{1}{\sqrt{2}} \begin{bmatrix} E_x - E_y \\ E_x + E_y \end{bmatrix}
\end{align*}
\]  

(A.7)
The intensity of a component beam given in phasor notation is \( I = |E_a|^2 = E^*E \). Using this definition for the rotated axes,

\[
I_{1/4\pi} - I_{-1/4\pi} = \frac{1}{2} (E_x + E_y)^* (E_x + E_y) - \frac{1}{2} (E_x - E_y)^* (E_x - E_y)
\]

\[
= \frac{1}{2} (E_{xo} e^{-i\delta_x} + E_{yo} e^{-i\delta_y}) (E_{xo} e^{i\delta_x} + E_{yo} e^{i\delta_y})
\]

\[
- \frac{1}{2} (E_{xo} e^{-i\delta_x} - E_{yo} e^{-i\delta_y}) (E_{xo} e^{i\delta_x} - E_{yo} e^{i\delta_y})
\]

\[
= E_{xo} E_{yo} e^{-i(\delta_x - \delta_y)} + E_{xo} E_{yo} e^{i(\delta_y - \delta_x)}
\]

\[
= 2E_{xo} E_{yo} \cos(\delta_y - \delta_x)
\]

(A.8)

Therefore, \( S_2 \) is the difference between the \( 1/4\pi \) – axis intensity (measured counterclockwise from X-axis) and the \( -1/4\pi \) – axis intensity.

A.4 The Fourth Stokes' Parameter, \( S_3 \)

The phasor components for left and right circular polarizations involves transforming the component phasors as

\[
E_{l,r} = \begin{bmatrix} E_1 \\ E_r \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ -1 & -i \end{bmatrix} \begin{bmatrix} E_x \\ E_y \end{bmatrix}
\]

\[
= \frac{1}{\sqrt{2}} \begin{bmatrix} E_x + iE_y \\ E_x - iE_y \end{bmatrix}
\]

(A.9)

The intensity of a component beam given in phasor notation is \( I = |E_a|^2 = E^*E \). Using this definition for the left and right polarizations,

\[
I_r - I_l = \frac{1}{2} (E_x - iE_y)^* (E_x - iE_y) - \frac{1}{2} (E_x + iE_y)^* (E_x + iE_y)
\]

\[
= \frac{1}{2} (E_{xo} e^{-i\delta_x} + iE_{yo} e^{-i\delta_y}) (E_{xo} e^{i\delta_x} - iE_{yo} e^{i\delta_y})
\]

\[
- \frac{1}{2} (E_{xo} e^{-i\delta_x} - iE_{yo} e^{-i\delta_y}) (E_{xo} e^{i\delta_x} + iE_{yo} e^{i\delta_y})
\]
Therefore, $S_3$ is the difference between right circular polarization intensity and left circular polarization intensity.
Appendix B

Stokes Parameter Description Using Ellipse Parameters

The concise Jones vector representation of a polarized monochromatic wave is given by

\[ \mathbf{E} = \begin{bmatrix} E_x \\ E_y \end{bmatrix} = \begin{bmatrix} E_{x0} e^{i\delta_x} \\ E_{y0} e^{i\delta_y} \end{bmatrix} \quad (B.1) \]

In general, the above Cartesian components describe an ellipse in the transverse plane. A more convenient elliptical description is shown in Figure 3.3. The unknowns of azimuth, \( \theta \), and ratio of minor to major axis, \( \tan |\epsilon| \), are related to the Cartesian components by Azzam and Bashara [56].

\[ \mathbf{E} = \begin{bmatrix} E_x \\ E_y \end{bmatrix} = A e^{i\theta} \begin{bmatrix} \cos \theta \cos \epsilon - i \sin \theta \sin \epsilon \\ \sin \theta \cos \epsilon + i \cos \theta \sin \theta \end{bmatrix} \quad (B.2) \]

To relate the ellipse parameters of \( \theta \) and \( \epsilon \) to the Stokes parameters, we start with the Stokes parameter definitions in Cartesian terms,

\[
\begin{align*}
S_0 &= E_{x0}^2 + E_{y0}^2 \\
S_1 &= E_{x0}^2 - E_{y0}^2 \\
S_2 &= 2E_{x0}E_{y0}\cos(\delta_y - \delta_x) \\
S_3 &= 2E_{x0}E_{y0}\sin(\delta_y - \delta_x) 
\end{align*} \quad (B.3)
\]

Using the expanded forms of the Stokes parameters given in Appendix A, the following transformations are shown.

\[
S_0 = E_{x0}^2 + E_{y0}^2 = \mathbf{E}_x^\dagger \mathbf{E}_x + \mathbf{E}_y^\dagger \mathbf{E}_y
\]

141
\[ S_1 = E_{x_0}^2 - E_{y_0}^2 = E_x^* E_x - E_y^* E_y \]

\[
= [Ae^{i\theta}(\cos \theta \cos \epsilon - i \sin \theta \sin \epsilon)]^* [Ae^{i\theta}(\cos \theta \cos \epsilon - i \sin \theta \sin \epsilon)] \\
+ [Ae^{-i\theta}(\sin \theta \cos \epsilon + i \cos \theta \sin \epsilon)]^* [Ae^{i\theta}(\sin \theta \cos \epsilon + i \cos \theta \sin \epsilon)] \\
= [Ae^{-i\theta}(\cos \theta \cos \epsilon + i \sin \theta \sin \epsilon)] [Ae^{i\theta}(\cos \theta \cos \epsilon - i \sin \theta \sin \epsilon)] \\
+ [Ae^{-i\theta}(\sin \theta \cos \epsilon - i \cos \theta \sin \epsilon)] [Ae^{i\theta}(\sin \theta \cos \epsilon + i \cos \theta \sin \epsilon)] \\
= A^2(\cos^2 \theta \cos^2 \epsilon + \sin^2 \theta \sin^2 \epsilon) + A^2(\sin^2 \theta \cos^2 \epsilon + \cos^2 \theta \sin^2 \epsilon) \\
= A^2 \quad \text{(B.4)}
\]
Appendix B. Stokes Parameter Description Using Ellipse Parameters

\[ S_3 = 2E_{z_0}E_{y_0} \sin(\delta_y - \delta_x) \]
\[ = \frac{1}{2}(E_x - IE_y)(E_x - IE_y) - \frac{1}{2}(E_x + IE_y)(E_x + IE_y) \]
\[ = \frac{1}{2} \left[ A e^{i\theta} \left[ \cos \theta \cos \epsilon + \cos \theta \sin \epsilon - i(\sin \theta \sin \epsilon + \sin \theta \cos \epsilon) \right] \right] \]
\[ = \times \left[ A e^{-i\theta} \left[ \cos \theta \cos \epsilon + \cos \theta \sin \epsilon + i(\sin \theta \sin \epsilon + \sin \theta \cos \epsilon) \right] \right] \]
\[ = -\frac{1}{2} \left[ A e^{i\theta} \left[ \cos \theta \cos \epsilon - \cos \theta \sin \epsilon + i(\sin \theta \cos \epsilon - \sin \theta \sin \epsilon) \right] \right] \]
\[ = \times \left[ A e^{-i\theta} \left[ \cos \theta \cos \epsilon - \cos \theta \sin \epsilon - i(\sin \theta \cos \epsilon - \sin \theta \sin \epsilon) \right] \right] \]
\[ = 2A^2 \left[ \cos^2 \theta \cos \epsilon \sin \epsilon + \sin^2 \theta \sin \epsilon \cos \epsilon \right] \]
\[ = A^2 \sin 2\epsilon \]  

Therefore, the Stokes parameters in terms of the elliptical parameters \( A, \theta, \epsilon \) are

\[ S_0 = A^2 \]
\[ S_1 = A^2 \cos 2\epsilon \cos 2\theta \]
\[ S_2 = A^2 \cos 2\epsilon \sin 2\theta \]
\[ S_3 = A^2 \sin 2\epsilon \]  

(B.8)
Appendix C

Complex Polarization Ratio Determination

The Cartesian X and Y components written in phasor notation may be related to ellipse description parameters \( \theta \), (azimuth), \( \tan |\epsilon| \), (ratio minor to major axis), \( A \), (overall amplitude), \( \phi \), (overall phase), by Hauge et al. [55] as

\[
\begin{align*}
E &= \begin{bmatrix} E_x \\ E_y \end{bmatrix} = \begin{bmatrix} E_{x0}e^{i\phi} \\ E_{y0}e^{i\phi} \end{bmatrix} \\
&= Ae^{i\phi} \begin{bmatrix} \cos \theta \cos \epsilon - i \sin \theta \sin \epsilon \\ \sin \theta \cos \epsilon + i \cos \theta \sin \epsilon \end{bmatrix}
\end{align*}
\]  
(C.1)

The complex polarization ratio defined by Azzam and Bashara [56] is

\[
\psi = \frac{E_y}{E_x} = \tan \alpha e^{i\delta}
\]  
(C.2)

Equating equations C.1 and C.2,

\[
\tan \alpha e^{i\delta} = \frac{\sin \theta \cos \epsilon + i \sin \epsilon \cos \theta}{\cos \theta \sin \epsilon - i \sin \epsilon \sin \theta}
\]  
(C.3)

Expanding both sides of equation C.3

\[
\tan \alpha (\cos \delta + i \sin \delta) = \frac{\sin \theta \cos \theta \cos^2 \epsilon - \sin^2 \epsilon \cos \theta \sin \theta}{\cos^2 \theta \cos^2 \epsilon + \sin^2 \epsilon \sin^2 \theta} + \frac{\cos^2 \theta \sin \epsilon \cos \epsilon + \sin^2 \epsilon \cos \epsilon \sin \epsilon}{\cos^2 \theta \cos^2 \epsilon + \sin^2 \epsilon \sin^2 \theta}
\]  
(C.4)

Therefore, equating the real and imaginary components of equation C.4

\[
\begin{align*}
\tan \alpha \cos \delta &= \frac{\sin \theta \cos \theta \cos^2 \epsilon - \sin^2 \epsilon \cos \theta \sin \theta}{\cos^2 \theta \cos^2 \epsilon + \sin^2 \epsilon \sin^2 \theta} \\
\tan \alpha \sin \delta &= \frac{\cos^2 \theta \sin \epsilon \cos \epsilon + \sin^2 \epsilon \cos \epsilon \sin \epsilon}{\cos^2 \theta \cos^2 \epsilon + \sin^2 \epsilon \sin^2 \theta}
\end{align*}
\]  
(C.5) (C.6)
Solving equation C.6 for $\delta$,

$$\tan \delta = \frac{\cos^2 \theta \sin \epsilon \cos \epsilon + \sin^2 \theta \cos \epsilon \sin \epsilon}{\sin \theta \cos \theta \cos^2 \epsilon - \sin^2 \epsilon \cos \theta \sin \theta}$$

$$= \frac{\cos \epsilon \sin \epsilon}{\sin \theta \cos \theta (\cos^2 \epsilon - \sin^2 \epsilon)}$$

$$= \frac{1}{2 \sin 2\epsilon}$$

$$= \frac{1}{2 \sin 2\theta \cos 2\epsilon}$$

$$= \tan 2\epsilon \sin 2\theta$$

(C.7)

Solving equation C.6 for $\alpha$,

$$\tan^2 \alpha = \tan^2 \alpha \cos^2 \delta + \tan^2 \alpha \sin^2 \delta$$

$$= \left[ \frac{\sin \theta \cos \theta \cos^2 \epsilon - \sin^2 \epsilon \cos \theta \sin \theta}{\cos^2 \theta \cos^2 \epsilon + \sin^2 \epsilon \sin^2 \theta} \right]^2$$

$$+ \left[ \frac{\cos^2 \theta \sin \epsilon \cos \epsilon + \sin^2 \theta \cos \epsilon \sin \epsilon}{\cos^2 \theta \cos^2 \epsilon + \sin^2 \epsilon \sin^2 \theta} \right]^2$$

$$= \frac{\cos^2 \epsilon \sin^2 \theta + \cos^2 \theta \sin^2 \epsilon}{\cos^2 \theta \cos^2 \epsilon + \sin^2 \epsilon \sin^2 \theta}$$

(C.8)

But,

$$\cos 2\alpha = \frac{1 - \tan^2 \alpha}{1 + \tan^2 \alpha}$$

$$= \cos^2 \epsilon \cos^2 \theta + \sin^2 \epsilon \sin^2 \theta - \cos^2 \epsilon \sin^2 \theta - \cos^2 \theta \sin^2 \epsilon$$

$$= (\cos^2 \epsilon - \sin^2 \theta)(\cos^2 \epsilon - \sin^2 \epsilon)$$

$$= \cos 2\theta \cos 2\epsilon$$

(C.9)

Summarizing, the complex polarization parameters are

$$\tan \delta = \frac{\tan 2\epsilon}{\sin 2\theta}$$

(C.10)

$$\cos 2\alpha = \cos 2\theta \cos 2\epsilon$$

(C.11)
Appendix D

Description of Light Intensity at the Photodiode

In order to calculate the change in polarization state due to the sample, the Stokes parameters before and after the sample must be known. Before the sample, the light beam is linearly polarized without any other devices present to affect the polarization. However, after the sample the Stokes parameters must be calculated from intensity measurements at the detector. Converting the intensity measurements to Stokes parameters is not sufficient because the Stokes parameters at the detector must be related to the Stokes parameters immediately following the sample. Using Mueller matrices to describe the effects of the compensator and analyzer (see Hauge [68] and Clarke and Granger [54]) the Stokes vectors may be related. The analyzer is assumed to be perfect, (high extinction ratio) while the compensator cannot be quantified as easily. Providing the exact ratio of the fast axis to slow axis of the compensator may be measured, a complex representation of the compensator may be given as

\[ \rho_c = \tan \psi_c e^{-i\delta_c} = T_c e^{-i\delta_c} \]  \hspace{1cm} (D.1)

(for a perfect quarter-wave retarder \( T_c = 1, \psi_c = 45^\circ, \delta_c = 90^\circ \))
Using the Mueller matrices, the Stokes vectors are related by

\[
\begin{bmatrix}
S'_0 \\
S'_1 \\
S'_2 \\
S'_3
\end{bmatrix} = \frac{1}{2} \begin{bmatrix}
1 & 1 & 0 & 0 \\
1 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{bmatrix} \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & \cos 2(A - C) & \sin 2(A - C) & 0 \\
0 & -\sin 2(A - C) & \cos 2(A - C) & 0 \\
0 & 0 & 0 & 1
\end{bmatrix}
\]

**STOKES ANALYZER DETECTOR**

**CONVERSION OF STOKES TO ANALYZER F.O.R.**

\[
\begin{bmatrix}
1 & \cos 2\psi_c & 0 & 0 \\
\cos 2\psi_c & 1 & 0 & 0 \\
0 & 0 & \sin 2\psi_c \cos \delta_c & \sin 2\psi_c \sin \delta_c \\
0 & 0 & -\sin 2\psi_c \sin \delta_c & \sin 2\psi_c \cos \delta_c
\end{bmatrix}
\]

**RETARDER**

\[
\begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & \cos 2C & \sin 2C & 0 \\
0 & -\sin 2C & \cos 2C & 0 \\
0 & 0 & 0 & 1
\end{bmatrix}
\]

\[
\begin{bmatrix}
S_0 \\
S_1 \\
S_2 \\
S_3
\end{bmatrix}
\]

\[(D.2)\]

**CONVERSION OF STOKES STOKES TO ANALYZER F.O.R. SAMPLE EXIT**

Therefore, the intensity at the detector is given by equation 3.11

\[
2S'_0 = S_0 \left[ \cos 2\psi_c \cos (2C - 2A) + 1 \right] \\
+ S_1 \left[ \cos 2C \cos (2C - 2A) + \cos 2C \cos 2\psi_c \right] \\
+ \sin 2C \sin (2C - 2A) \sin 2\psi_c \cos \delta_c \\
+ S_2 \left[ \sin 2C \cos (2C - 2A) + \cos 2\psi_c \sin 2C \right] \\
- \cos 2C \sin (2C - 2A) \sin 2\psi_c \cos \delta_c
\]
\[ + S_3 [ - \sin 2\psi_c \sin \delta_c \sin (2\alpha - 2\Delta) ] \]
Appendix E

Determination of Compensator Imperfections

The compensator imperfections written in the ratio of fast axis to slow axis,

\[ \rho_c = \tan \psi_c e^{-i\delta_c} \]  \hspace{1cm} (E.1)

must be determined to accurately calculate the Stokes parameters.

If the polarizer axis is set along the X-axis (\(P = 0^\circ\)), the Stokes vector before the sample is given by

\[ S'_{\lambda} = S_1 \]  \hspace{1cm} (E.2)

Therefore, \(S'_{2} = 0, S'_{3} = 0,\) and \(S'_{0} = S''_{1}\) in this configuration.

From equation 3.11, the intensity readings for the three compensator-analyzer combinations \((C, A) = (0^\circ, 0^\circ), (45^\circ, 0^\circ), (90^\circ, 0^\circ)\) are

\[ 2I(0, 0) = S_0[\cos 2\psi_c + 1] + S_1[\cos 2\psi_c + 1] \]  \hspace{1cm} (E.3)

\[ 2I(45, 0) = S_0 + S_1[\sin 2\psi_c \cos \delta_c] + S_2[\cos 2\psi_c] + S_3[\sin 2\psi_c \sin \delta_c] \]  \hspace{1cm} (E.4)

\[ 2I(90, 0) = S_0[- \cos 2\psi_c + 1] + S_1[1 - \cos 2\psi_c] \]  \hspace{1cm} (E.5)
Solving for $\psi_c$ and $\delta_c$,

$$\cos 2\psi_c = \frac{2I(0,0) - 2I(90,0)}{2I(0,0) + 2I(90,0)} \quad (E.6)$$

and

$$\frac{1 - \sin 2\psi_c \cos \delta_c}{1 + \frac{S_0}{S_1}} - 2S_2[\cos 2\psi_c] - 2S_3[-\sin 2\psi_c \sin \delta_c] = \frac{2I(0,0) - 4I(45,0) + 2I(90,0)}{2I(0,0) + 2I(90,0)} \quad (E.7)$$

For a system without a sample the Stokes parameters before and after the sample are identical (ie $S = S''$) and using the results from the $P = 0^\circ$ configuration $\delta_c$ may be evaluated by

$$\frac{1 - \sin 2\psi_c \cos \delta_c}{2} = \frac{I(0,0) - 2I(45,0) + I(90,0)}{I(0,0) + I(90,0)} \quad (E.8)$$
Appendix F

Estimate of Hamaker Constant Calculation Errors

The estimate of the error arising in the Hamaker constant calculations presented in Table 5.3 was made using estimated values of the uncertainty in the experimental measurements reported in Chapter 4. The Hamaker constant was calculated from the experimental results by rearranging Equation 2.19 to give

\[ A_{12} = 6\pi h_0^3 \left( \frac{R T_v \rho_l}{M} \right) ln \left( \frac{P}{P_s} \right). \]  

(F.1)

Assuming that the vapour temperature, \( T_v \), and the liquid density, \( \rho_l \), were not subject to any experimental uncertainty (density varies negligibly over the entire range of temperatures considered), all the experimental uncertainty was concentrated in two areas, the pressure ratio, \( P/P_s \), and the adsorbed thickness, \( h_0^3 \). The pressure ratio is determined by manufacturer's data given the liquid temperature, as given in Equation 5.6.

\[ P = 10^{(7.6042 - \frac{T_v}{295})}. \]  

(F.2)

Rearranging Equation F.2 into exponential form the ratio \( P/P_s \) may be written as

\[ \frac{P}{P_s} = e^{\frac{3597}{T_s} - \frac{3597}{T}}. \]  

(F.3)

Substituting Equation F.3 into Equation F.1, \( A_{12} \) is given as

\[ A_{12} = (6\pi)(3597) \left( \frac{R T_v \rho_l}{M} \right) \left( \frac{1}{T_s} - \frac{1}{T} \right) h_0^3. \]  

(F.4)

Combining all the constant values into one term, \( \kappa \), Equation F.4 may be written as

\[ A_{12} = \kappa \left( \frac{1}{T_s} - \frac{1}{T} \right) h_0^3. \]  

(F.5)

151
Appendix F. Estimate of Hamaker Constant Calculation Errors

The error associated with the experimental temperature measurement occurs in the difference between the temperatures, \( T - T_s \), not in the absolute value of either temperature. Therefore, the absolute values may be assumed constant for the purposes of error analysis. Equation F.5 may be rearranged as

\[
A_{12} = \mathcal{K}(T - T_s)h_0^3. \tag{F.6}
\]

The percentage uncertainty of the calculated value \( A_{12} \) due to the present experimental errors may be expressed as

\[
\frac{dA_{12}}{A_{12}} = \frac{\partial A_{12}}{\partial(T - T_s)} \frac{d(T - T_s)}{(T - T_s)} + \frac{\partial A_{12}}{\partial h_0} \frac{dh_0}{h_0^3}, \tag{F.7}
\]

or

\[
\frac{dA_{12}}{A_{12}} = \frac{d(T - T_s)}{(T - T_s)} + \frac{3dh_0}{h_0}. \tag{F.8}
\]

Using the error estimates from Chapter 4, the uncertainty in the Hamaker constant calculations may be made using Equation F.8.
Bibliography


