STUDY OF THE THICKNESS
OF ADSORBED WATER LAYERS
BY ATOMIC FORCE MICROSCOPY

submission for the degree of Doctor of Philosophy

by

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SUMMARY

The effect of ambient humidity and adsorbed water can be of critical importance in the processing of fine powders in air. Adsorbed water layers can influence the adhesive properties of the powder and may lead to difficulties in processing and handling. It has been shown, in the current work, that in ambient conditions the interaction between two solid surfaces is dominated by the force arising from the presence of adsorbed water layers.

In the current work an atomic force microscopy technique has been developed to determine the separation distance at which two solid surfaces, *i.e.* the AFM cantilever tip and the sample surface, 'jump' into contact. From the separation distance the thickness of the adsorbed water layers on the cantilever tip and sample surface can be determined based on an analytical method originally developed by Forcada (1993), which considers the interacting forces which cause the 'jump' to contact.

The adsorbed layer thickness as a function of relative humidity, has been determined for silicon wafer, using the AFM technique. This localized adsorption isotherm has been compared with those published by other investigators, who have used different measurement techniques on large sample areas. The adsorption isotherm determined using the AFM technique reports adsorbed layer thicknesses that are significantly larger than those measured by other investigators.

Adsorption isotherms have been determined, using the AFM technique, for three forms of α-lactose monohydrate, which is widely used throughout the pharmaceutical industry. It was observed that each form of lactose gave a different level of water adsorption. Laboratory grown crystals exhibited the greatest levels of moisture adsorption, while commercially produced milled α-lactose displayed lower levels of water adsorption. Differences in surface roughness may possibly explain the variation. For rough samples the probe tip makes contact with surface asperities and therefore does not detect the presence of condensed water in the surface valleys. It is
also possible that surface contamination and process history may have influenced the levels of water adsorption but these are complex effects to quantify.

Water adsorption isotherms were measured on bulk samples of classified lactose, to attempt to validate the AFM technique, developed in the current study. It can be observed that the adsorbed layer thicknesses determined using AFM are significantly larger than those inferred from bulk measurements.

The AFM method provides layer thickness values which are approximately four times larger than what are believed to be the true values. This is seen for tests on silicon, aluminium and lactose surfaces. This discrepancy is thought to arise from the presence of the probe tip on the surface causing a local spatial inhomogeneity. The associated increase in surface potential will promote nucleation of water molecules, leading ultimately to capillary condensation.
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CONTENTS

SUMMARY i
ACKNOWLEDGEMENTS iv
CONTENTS v
NOMENCLATURE x

1 INTRODUCTION 1

2 LITERATURE REVIEW 7

2.1 Introduction 7

2.2 Adsorbed Water Layers 8

2.2.1 Introduction 8

2.2.2 Measurement Techniques 8

2.2.2.1 Early Methods 8

2.2.2.2 Ellipsometry 9

2.2.2.3 Other Methods 11

2.2.2.4 Vapour Pressure Control 11

2.2.2.5 Summary of Previous Experimental Investigations 12

2.2.3 Modelling 16

2.2.3.1 Introduction 16

2.2.3.2 DLVO Theory 16

2.2.3.3 Polarization Theory 20

2.2.3.4 BET Adsorption Theory 21

2.2.3.5 FHH Theory 24

2.3 Atomic Force Microscopy 26

2.3.1 Introduction 26

2.3.2 AFM Force Studies 27

2.3.2.1 Types of Force 27

2.3.2.2 Interpretation of AFM Force Curves 28

2.3.2.3 Spring Constant 31
2.3.3 Adsorbed Layer Thickness Measurement 33
2.4 Conclusions 36

3 ATOMIC FORCE MICROSCOPY 39
3.1 Introduction 39
3.2 AFM Nanoscope II 39
  3.2.1 Introduction 39
  3.2.2 Hardware 40
    3.2.2.1 Scanner Support 40
    3.2.2.2 Scanner 42
    3.2.2.3 Head 43
  3.2.3 Software 44
3.3 Cantilevers 45
3.4 Experimental Procedure 47
  3.4.1 Preparation 47
    3.4.1.1 Sample Mounting 47
    3.4.1.2 Optical Alignment 48
    3.4.1.3 Contact 48
  3.4.2 Imaging 48
  3.4.3 AFM Output Curves 50
3.5 Layer Thickness Measurements 52
  3.5.1 Interpretation of the AFM Output Curve 52
  3.5.2 Jump-on Region 54
  3.5.3 Van der Waals Contribution 55
  3.5.4 Calculation of Layer Thickness and Contact Gradients 59
  3.5.5 Sampling Rate 61
  3.5.6 Hydrophobic Tips 63
  3.5.7 Instability of Liquid Layers Prior to Contact 66
    3.5.7.1 Introduction 66
    3.5.7.2 Liquid Film Formation 66
    3.5.7.3 Perturbation of the Liquid Film 68
6.2 Silicon

6.2.1 Introduction

6.2.2 Silicon Wafer Experiment

6.2.2.1 Experimental Variables

6.2.2.2 Results for Silicon

6.2.2.3 Tip Wear

6.2.3 Silicon Adsorption Isotherm

6.2.3.1 Layer Thickness Data

6.2.3.2 Fitted Data

6.2.3.3 DLVO Theory Predictions

6.2.3.4 Comparison with Previous Investigators

6.2.4 Half Separation Distance

6.3 Lactose

6.3.1 Introduction

6.3.2 Experimental Results

6.3.3 Discussion

6.3.3.1 Introduction

6.3.3.2 Surface Topography

6.3.3.3 Contamination

6.3.3.4 Process History

6.4 Dynamic Vapour Sorption Experiments

6.4.1 Introduction

6.4.2 DVS Technique

6.4.3 Aluminium Experiments

6.4.3.1 DVS Experimental Results

6.4.3.2 AFM Experimental Results

6.4.3.3 Comparison of AFM and DVS adsorption isotherms

6.4.4 Classified Lactose Experiments

6.4.4.1 DVS Experimental Results

6.4.4.2 AFM Experimental Results

6.4.4.3 Comparison of AFM and DVS adsorption isotherms
NOMENCLATURE

A  Hamaker constant (J)
    Surface area (m²)

c  constant, BET model (-)

d  separation distance (m)

½d  half separation distance (m)

d_c  cantilever displacement (m)

d_def  cantilever deflection prior to jump to contact (m)

d_s  sample displacement (m)

d_{VDW}  van der Waals contribution to jump distance (m)

e  electronic charge (C)
    extent of local deformation (m)

è  amplitude of local deformation (m)

E  Young's modulus (N m⁻²)
    energy (J)

f  function (N m⁻³)

F  force (N)

G  specific excess free energy (J m⁻²)

G_0  contact region gradient (V nm⁻¹)

H  mean curvature (m)

k  Boltzmann constant (J K⁻¹)
    Cantilever spring constant (N m⁻¹)
    Wave number (m⁻¹)

k_c  Critical wave number (m⁻¹)

K  constant, FHH model (-)

K_1, K_2  constants, BET model (-)

K_1, K_3, K_4  constants, Polarization model (-)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_c$</td>
<td>Cantilever length (m)</td>
</tr>
<tr>
<td>$M$</td>
<td>change in mass of sample (kg)</td>
</tr>
<tr>
<td>$n$</td>
<td>refractive index (-)</td>
</tr>
<tr>
<td>$n_{ads}$</td>
<td>Number of molecules adsorbed (-)</td>
</tr>
<tr>
<td>$n_{ mono}$</td>
<td>Number of molecules in a monolayer (-)</td>
</tr>
<tr>
<td>$N$</td>
<td>constant, FHH model (-)</td>
</tr>
<tr>
<td></td>
<td>Number of points considered in the determination of surface roughness (-)</td>
</tr>
<tr>
<td>$p$</td>
<td>partial vapour pressure (Pa)</td>
</tr>
<tr>
<td>$P$</td>
<td>vapour pressure over a curved surface (Pa)</td>
</tr>
<tr>
<td>$p^o$</td>
<td>saturated vapour pressure of the liquid (Pa)</td>
</tr>
<tr>
<td>$p/p^o$</td>
<td>relative vapour pressure (-)</td>
</tr>
<tr>
<td>$Q_1$</td>
<td>heat of adsorption of the first molecular layer, BET model (J mol$^{-1}$)</td>
</tr>
<tr>
<td>$Q_v$</td>
<td>heat of condensation of liquid adsorbate, BET model (J mol$^{-1}$)</td>
</tr>
<tr>
<td>$r$</td>
<td>Cantilever tip radius (m)</td>
</tr>
<tr>
<td>$r_{ave}$</td>
<td>mean radius of curvature (m)</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant (J mol$^{-1}$ K$^{-1}$)</td>
</tr>
<tr>
<td>$R_{RMS}$</td>
<td>Average surface roughness (m)</td>
</tr>
<tr>
<td>$S_x$</td>
<td>AFM output curve horizontal scaling (nm division$^{-1}$)</td>
</tr>
<tr>
<td>$S_y$</td>
<td>AFM output curve vertical scaling (V division$^{-1}$)</td>
</tr>
<tr>
<td>$t$</td>
<td>layer thickness (m)</td>
</tr>
<tr>
<td>$t_c$</td>
<td>cantilever thickness (m)</td>
</tr>
<tr>
<td>$t_m$</td>
<td>monolayer layer thickness (m)</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>$u$</td>
<td>potential energy (J m$^{-3}$)</td>
</tr>
</tbody>
</table>
Nomenclature

\( U \)  Interaction energy (J m\(^{-3}\))

\( v_m \)  molecular volume (m\(^3\) molecule\(^{-1}\))

\( V_{ads} \)  volume of adsorbate (m\(^3\))

\( V_{mono} \)  volume of a monolayer of adsorbate (m\(^3\))

\( w_c \)  cantilever leg width (m)

\( x \)  \( p/p^0 \), BET model (-)

\( x, y \)  position of local perturbation

\( x_A, x_B \)  AFM output curve horizontal pixel coordinates

\( y_A, y_B \)  AFM output curve vertical pixel coordinates

\( z \)  valency (-)

\( z, \)  distance (m)

\( z_i \)  local height of surface at point \( i \) (m)

\( z_{ave} \)  average \( z \) value for surface (m)

\( \gamma \)  surface tension (N m\(^{-1}\))

\( \varepsilon \)  relative permittivity of the adsorbate, dielectric constant (-)

\( \varepsilon_0 \)  permittivity of free space (C\(^2\) J\(^{-1}\) m\(^{-1}\))

\( \kappa \)  inverse Debye length (m\(^{-1}\))

\( \Pi \)  disjoining pressure (N m\(^{-2}\))

\( \Pi_{EL} \)  electrostatic contribution to disjoining pressure (N m\(^{-2}\))

\( \Pi_S \)  structural contribution to disjoining pressure (N m\(^{-2}\))

\( \Pi_{VDW} \)  van der Waals contribution to disjoining pressure (N m\(^{-2}\))

\( \rho \)  density (kg m\(^{-3}\))

\( \rho_\infty \)  ionic concentration away from the surface (m\(^3\))

\( \sigma \)  standard deviation (-)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>( \nu )</td>
<td>molar volume ( (m^3 \text{ mol}^{-1}) )</td>
</tr>
<tr>
<td>( \nu_e )</td>
<td>main electronic adsorption frequency in UV range ( (s^{-1}) )</td>
</tr>
<tr>
<td>( \psi )</td>
<td>filling angle ( (^\circ) ) (defined in Figure 6.11)</td>
</tr>
<tr>
<td>( \psi_o )</td>
<td>electrostatic potential at the surface ( (V) )</td>
</tr>
<tr>
<td>( \psi_m )</td>
<td>electrostatic potential away from the surface ( (V) )</td>
</tr>
<tr>
<td>( \phi_o )</td>
<td>surface potential ( (J \text{ mol}^{-1}) )</td>
</tr>
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1. INTRODUCTION

The effect of ambient humidity and adsorbed water can be of critical importance in the processing of fine powders in air. Adsorbed water layers can influence the adhesive properties of the powder which may or may not be desirable and which may lead to difficulties in processing and handling. For example, cohesion between single particles is to be discouraged if the powder is required to flow, - conversely it is to be encouraged if an agglomerated product is required. Often an agglomerated powder product requires interparticle forces of sufficient magnitude to withstand processing, packaging and transport. However, once in the hands of the customer the product is required to break down into its single particle constituents very readily when subjected to some method of dispersal. The corollary of this is that a critical level of interparticle force is required that satisfies the two criteria.

The interparticle force, under ambient conditions can be attributed to three phenomena; van der Waals forces, electrostatic forces and forces due to the presence of adsorbed moisture. It is shown later in this dissertation, that of these phenomena, in an ambient environment, the force associated with the presence of adsorbed moisture will tend to dominate the overall interparticle interaction.

Traditionally water adsorption for powdered materials is measured on bulk samples. These measurements combine the effect of surface adsorption and capillary bridge formation. A method of decoupling the two phenomena is desirable for investigation of the relative quantities of water bound to the surface and present in capillary bridges. The decoupling of these phenomena will assist in the understanding of interparticle force mechanisms and the associated prediction of bulk behaviour. This dissertation reports on the development of such a method, in which the thickness of adsorbed moisture films can be determined at a single point on a particle surface.

Recently, there has been much activity in the field of distinct element analysis for the prediction of the behaviour of an assembly of particles from single particle properties.
These computer models require the specification of interaction laws for the particles. At present no account is made for the presence of adsorbed liquid layers in these models. The present work is therefore able to contribute to this modelling by providing values for the actual thickness of water adsorbed on individual particles.

The atomic force microscope (AFM) is a member of the family of scanning probe microscopes. It was originally designed for imaging sample surfaces but can be used to study the interaction between a probe tip and a sample surface. During sample imaging, a probe with a sharp tip, which is attached to a fine cantilever, is scanned across the surface of a sample. The deflection of the cantilever with changes in surface topography is recorded and an image of the surface formed. The AFM can also be used to study the interaction forces between the probe tip and the sample. However, although these forces have been studied by many previous investigators, accurate determination is difficult due to the inherent problems in the calculation of the spring constant value for the cantilever tip.

In the present study a method has been developed, from a technique originally proposed by Mate et al. (1989), by which the thickness of adsorbed water films can be determined on individual particles using atomic force microscopy (AFM). The use of atomic force microscopy allows the determination of adsorbed layer thickness values at a single point on an individual particle. It would be possible, in principle, to use the technique to study the distribution of water on a particle surface. Due to the small sample areas that are required for this technique (< 1 \( \mu \text{m}^2 \), whereas ellipsometry, for example, requires a surface area of \( \sim 1 \text{ cm}^2 \)), it is extremely flexible and almost any material can be analysed. Note that a typical probe tip has an effective contact area of approximately 175 \( \text{nm}^2 \).

The current work addresses several issues that were either unresolved, or not considered by Mate et al. i.e. the inclusion of the cantilever displacement in the calculation of layer thickness, the presence of a liquid layer on the AFM cantilever tip, and the instability of the liquid films as the tip and sample approach contact. In
the current work the thickness of the adsorbed moisture films has been determined as a function of relative humidity$^1$ giving adsorption isotherms at individual points on a sample surface.

Many investigators have previously measured and attempted to predict the thickness of adsorbed liquid layers, using a range of experimental techniques and predictive models. The most commonly used experimental technique, ellipsometry, cannot be applied to powder samples as it requires a relatively large and flat sample surface area. Gravimetric techniques are also commonly used to determine the amount of adsorbed water, particularly on powder samples, however they require bulk samples of powder and consequently cannot give information for adsorption at a single point on an individual particle. Of the predictive models conventionally used only one (DLVO model) is truly theoretical, whereas the other models (polarization theory, BET theory, and FHH theory) are semi-empirical in nature as their equation constants are commonly determined from experimental data. In the present study, an adsorption isotherm has been determined for silicon wafer, which is considered to be an ‘ideal’ reference material and has similar surface properties to the materials studied by some of the previous investigators (glass, quartz and silicon). Consequently it enables comparison with these other investigations and also with theoretical predictions of adsorbed layer thickness.

Lactose is widely used throughout the pharmaceutical industry as a diluent in powder tablets, capsules and inhalation products. It is also used in the food industry, for example in infant feed formulas as it is less sweet than sucrose. The most common forms in which it is used are either anhydrous α-lactose, or α-lactose monohydrate, with anhydrous β-lactose used to a lesser extent. To date, many studies have been carried out on the physical properties of lactose powders, with a view to optimizing tabletting performance. This type of study involves measurements on bulk powder samples, and therefore any fundamental information regarding the interactions

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$^1$ By definition, relative humidity, RH = p/p°.
between single particles and the role of adsorbed moisture is hidden by the complexity of the packing geometry.

In this study, adsorption isotherms have been determined for three types of α-lactose monohydrate; laboratory grown crystals, and commercially available milled lactose from two different source companies. The differences observed between the adsorption isotherms are discussed in terms of differences in surface roughness, contamination and process history.

Attempts have been made to validate the AFM technique for the determination of water adsorption isotherms, by comparison with the established gravimetric measurement technique of dynamic vapour sorption (DVS). These attempts have so far proved inconclusive and point the way for areas of future work.

In chapter 2, the literature is reviewed in two key areas: measurement and modelling of water adsorption isotherms, and the use of atomic force microscopy. The first section can be subdivided into an examination of the techniques used previously to measure adsorbed layer thicknesses and a review of the way in which the prediction models have been used by previous investigators. The models themselves are discussed in more detail in chapter 4. Significant differences in published experimental data of adsorbed water layer thickness are evident for experiments conducted under ostensibly similar conditions. These differences arise for studies of the adsorption of water on quartz, glass or silicon, which all have similar surface properties. The differences are discussed and possible sources of the discrepancies are proposed.

The second section of chapter 2 deals with the development of the atomic force microscope and details some previous studies, with particular reference to the interpretation of AFM output curves and the measurement of interaction forces. The work of Mate et al. (1989), in the determination of layer thicknesses using atomic force microscopy, is described and the differences they observe between AFM and
ellipsometric measurements are discussed. The main cause of the discrepancy is generally attributed to the instability of the liquid films on the tip and the sample as they approach contact. In this dissertation a theoretical approach is discussed that can be used to take account of this effect.

Chapter 3 is concerned with the atomic force microscope experimental setup and procedure. The AFM used in the present study is described and the procedures prior to and during experimentation are explained. The calculation procedure for determination of the adsorbed layer thickness, from the experimental data, is discussed together with details on the adjustment of the measured data to take account of both the presence of adsorbed water on the cantilever tip and the instability of the adsorbed liquid films as the tip and the sample come into contact. The measurement of adsorbed layer thickness as a function of relative humidity to obtain adsorption isotherms and the method of variation and control of relative humidity are explained.

The purpose of chapter 4 is to comment on the various methods of predicting adsorbed layer thickness. The use of the DLVO theory to predict the thickness of adsorbed layers is discussed, together with some of the parameters, such as solute ion concentration, which may affect the predicted values. The polarization theory is also discussed; although it has been dismissed from a theoretical viewpoint, it provides a useful method of fitting experimental data, particularly for the adsorption of water.

Experimental studies have been conducted on three materials; lactose, silicon wafer and aluminium foil. The relevance of each material together with material properties and a description of the sample preparation methods are discussed in chapter 5.

In chapter 6 experimental results are presented for adsorption isotherms obtained on the different sample materials; silicon wafer, aluminium foil, lactose crystals, granulac and classified lactose. Silicon was used as an ‘ideal’ reference material. The adsorption isotherm obtained is compared with the results of previous investigators and with theoretical predictions for layer thickness. The attempts made
to validate the AFM measurement technique are discussed. Milled $\alpha$-lactose monohydrate from two sources is studied together with 'ideal' laboratory grown $\alpha$-lactose monohydrate crystals. The observed differences in the adsorption isotherms are discussed with particular reference to the differences in surface roughness.

The conclusions that can be drawn from the current study and possible areas for future work are presented in chapter 7.
2. LITERATURE REVIEW

2.1 Introduction

As discussed in chapter 1, interparticle forces play an important role in powder processing and handling. The forces which hold particles together as they come into close contact are dependent on the physical process by which the particles interact and the physical characteristics of the individual particles. Rumpf (1958) categorized the interparticle forces as intermolecular attractive forces (van der Waals forces), electrostatic forces and liquid bridge modes (forces due to condensed liquid layers and liquid bridges).

In ambient atmospheric conditions, when water vapour will be present in the environment, the liquid bridge modes can dominate the interparticle force (see section 3.5.3). Israelachvili (1991) comments that the adhesive properties of many substances are sensitive to the presence of even trace amounts of vapours in the atmosphere. Visser (1976) notes that the adhesion of powders is dependent on the relative humidity. Tyrrell & Cleaver (1998) have experimentally assessed the role of relative humidity on the adhesive force. They find an anomaly, in both their experimental results and in the results of previous investigators, that the adhesive force may increase or decrease with increasing relative humidity. They consider that this anomalous behaviour is the result of two factors i) surface hydrophobicity (contact angle), and ii) the surface roughness or angularity in the contact region.

The magnitude of the force between particles, due to the presence of water, will partly be dependent on the amount of water present prior to contact \textit{i.e.} the thickness of the adsorbed water layer. The thickness of this layer is dependent on the atmospheric relative humidity, the temperature and the properties of the adsorbing material. The measurement of the thickness of adsorbed layers has been of great interest to a number of investigators, who have proposed a number of different measurement techniques. Investigators have also proposed a range of theoretical and semi-
empirical models in an attempt to predict layer thicknesses. The relevant techniques and models will be reviewed in detail in sections 2.2.2 and 2.2.3 respectively.

In the current work the thickness of adsorbed water layers is determined at a single point on a sample using an atomic force microscope. Initially, atomic force microscopy was developed purely as a method of imaging a sample surface (Binnig et al. 1986). However, it was discovered that manipulation of the force between the probe tip and the sample would improve the resolution of the images (Hutter and Bechhoefer 1993). From this, atomic force microscope techniques have been developed in order to study a range of phenomena which affect the interparticle force or give detailed information about the sample surface. One such technique was developed, by Mate et al. (1989) in order to determine the thickness of thin liquid films on a surface, reviewed in section 2.3.3. In the current work this technique has been extended to measure the thickness of water layers, adsorbed from the atmosphere, and to study the variation of layer thickness with humidity.

2.2 Adsorbed Water Layers
2.2.1 Introduction
The amount of water adsorbed on a single particle or surface will be of critical importance when it is brought into contact with another particle or surface. The thickness of these adsorbed water layers is dependent on the atmospheric relative humidity, temperature and the chemistry of the solid surface. In this study we are primarily concerned with the effect of humidity on the layer thickness at room temperature (range 20 - 27 °C). In the following sections various previous attempts at measuring the thickness of adsorbed water layers are discussed. Atomic force microscope measurements are discussed separately in section 2.3.3.

2.2.2 Measurement Techniques
2.2.2.1 Early Methods
The adsorption of water on to sample surfaces has been of interest for many years and has been studied using many different techniques. Frazer (1929) gives details of two previously used methods. The first, 'Langmuir's method' makes use of pressure-
volume measurements. The difference between a theoretical final pressure (calculated using Boyle’s law) and the experimental final pressure for a system where a gas or vapour is allowed to expand, from one chamber, into a second chamber, of known volume, containing an adsorbing material with a large surface area, is measured. The difference between the predicted and experimental pressures is attributed to adsorption on the large surface area. As Frazer comments this method can only be used at pressures far below saturation as the pressure difference decreases and becomes negligible as the pressure approaches saturation.

The second method Frazer mentions is that of ‘Frazer and Patrick’, which appears to be similar to the method of McHaffie and Lenher (1925). In this method a pressure-temperature curve is obtained for a vapour in a closed vessel containing the adsorbent material. Also plotted are the theoretical vapour pressure curve for water and the curve showing the effect of temperature on the pressure of a gas at constant volume (Charles Law). The difference between the experimental curve and the theoretical curves, particularly in the region where the theoretical curves interact, is attributed to the adsorption of the vapour on to the adsorbing material. Frazer comments that this method is limited in that it is restricted to the region close to saturation and it requires a large surface area of adsorbent material.

As Frazer (1929) remarks neither of these methods allow adsorption to be studied at all pressures and both require a large amount of the adsorbing material. In both these early methods the accuracy of the result is dependent on the accuracy of the measurements, which in some cases may be limited i.e. determination of adsorbate surface area.

### 2.2.2.2 Ellipsometry

Due to the inherent difficulties of the above methods Frazer (1929) employs an optical method based on Drude’s theory and previously used by Lord Rayleigh and others, more commonly referred to as ellipsometry. The ellipsometry technique relies on the elliptical polarization of linearly polarized light of a known orientation when it
is reflected at an oblique angle of incidence on a surface. The shape and orientation of the ellipse depend on the angle of incidence, the direction of the polarization of the incident light and also the reflection properties of the surface. If a sample has an adsorbed layer on the surface then the reflection properties will be different from a bare surface. By measuring the changes in the reflection properties it is possible, in principle, to determine the thickness of the adsorbed layer and the refractive index of that layer.

Over many years several investigators have studied the adsorption of water on to different surfaces using ellipsometry as the measuring technique. This literature review concentrates on those investigators studying glass, quartz and silicon, which all have similar surface properties in that they are all oxides of silicon. Most investigators, for example Frazer (1929), Derjaguin & Zorin (1957), Pashley & Kitchener (1979) and Gee et al. (1990), use ‘home-built’ equipment, whereas others, such as Hall (1970) use commercially available ellipsometers.

Using the technique of ellipsometry it is usually possible to determine both the thickness of a layer and the refractive index of the layer. However for thin films, less than 20 nanometers (nm) (Pashley & Kitchener 1979) it is not possible to determine both variables. Consequently in the calculation of the thickness of adsorbed water layers the refractive index of bulk water is normally applied. There has been great discussion among different investigators about the presence of ‘anomalous’ water in these adsorbed layers. The idea is that the water will be more structured in thin layers than it would be in bulk, and hence the refractive index of the layer will be different from that of the bulk. However no one, as yet, seems to have determined a method to measure this refractive index and consequently investigators tend to use the refractive index of bulk water. Gee et al. (1990) suggest that the water in the adsorbed layer will have a refractive index in the range 1.33 - 1.52 where 1.33 is the refractive index of bulk water. Hall (1970) also suggests that the refractive index of the layer will be larger than the bulk. If the refractive index for a thin film is larger than the value for the bulk material the values of layer thickness will be smaller and the difference may
be significant. However Beaglehole & Christenson (1992) suggest that the refractive index will be less than the bulk value, leading to increased film thicknesses. This apparent discrepancy may be due to the difference in magnitude of the layer thickness measured by the different investigators. Both Gee et al. (1990) and Hall (1970) report adsorbed layer thicknesses that are greater than monolayer thickness (~0.3 nm). Whereas Beaglehole and Christenson (1992) report submonolayer thicknesses. For example at a relative humidity of 60% Gee et al. measure a layer thickness of 1.15 nm (equivalent to ~3.8 monolayers) compared with 0.24 nm (~0.8 monolayers) measured by Beaglehole and Christenson.

2.2.2.3 Other Methods
Garbatski & Folman (1956) measure the change in capacitance as the vapour pressure is varied in a condenser comprising two plates of adsorbent material at a fixed separation. The capacitance measurements are then related theoretically to the adsorbed layer thickness. The method relies on the validity of the assumptions made in the derivation of the theory. The accuracy of this method is also limited by the sensitivity of the electrical system and the accuracy in the measurement of the plate separation.

Hagymassy et al. (1969) and Badmann et al. (1981) both use gravimetric techniques to determine the thickness of adsorbed liquid layers. Hagymassy et al. do not detail their experimental technique except to describe it as a ‘desiccator method’ and to refer to a paper by Kantro et al. (1961). Badmann et al. (1981) determine their adsorption isotherms gravimetrically by the use of an electronic microbalance. In this technique, the relative humidity is maintained at a given value and the uptake of water, at that humidity value, is determined by comparison of the mass of the sample at zero humidity and the mass at the experimental humidity. The gravimetric technique used in the current study (DVS) is discussed further in section 6.4.

2.2.2.4 Vapour Pressure Control
One of the critical parameters in the study of adsorption isotherms is accurate control and measurement of vapour pressure. The method used by Frazer (1929), and the
majority of subsequent investigators, is to enclose the sample in a sealed and insulated chamber which is evacuated to remove any ambient moisture, the addition of water vapour into the chamber is then carefully regulated. Exceptions to the use of this method are Garbatski & Folman (1956) and Pashley & Kitchener (1979) who expose their samples to solutions of accurately known vapour pressure. Garbatski & Folman use solutions of mannitol and potassium chloride to achieve vapour pressures greater than 0.86, while Pashley & Kitchener use various concentrations of sodium chloride solutions for vapour pressures greater than 0.9. Gee et al. (1990) primarily use the method of the addition of water vapour in their experiments but partially repeat the experiments of Pashley and Kitchener using salt solutions to control vapour pressure. They find good agreement between both sets of data and comment that both methods of vapour pressure control are equally valid. This is also noted by Bikerman (1970), who found that the presence of air neither hindered or promoted the adsorption of water by asbestos.

2.2.2.5 Summary of previous experimental investigations

The results of a few of the many investigators who have measured water adsorption as a function of vapour pressure are given in Table 2.1. The data derive from a range of different measurement techniques: ellipsometry, capacitance measurement and gravimetric techniques, and investigation of a number of different materials: glass, quartz and silicon.
<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>Material</th>
<th>Temp</th>
<th>Method</th>
<th>Vapour Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>McHaffie &amp; Lenher</td>
<td>1925</td>
<td>glass / vacuum</td>
<td>25</td>
<td>p-t curve</td>
<td></td>
</tr>
<tr>
<td>Frazer</td>
<td>1929</td>
<td>glass / vacuum</td>
<td></td>
<td>ellipsometry</td>
<td>0.27</td>
</tr>
<tr>
<td>Garbatski &amp; Folman</td>
<td>1956</td>
<td>glass / air</td>
<td>30</td>
<td>capacitance</td>
<td>2.7  5.8 10.9 20.4</td>
</tr>
<tr>
<td>Derjaguin &amp; Zorin</td>
<td>1957</td>
<td>glass / vacuum</td>
<td></td>
<td>ellipsometry</td>
<td>1.0  6.5</td>
</tr>
<tr>
<td>Hagymassy et al</td>
<td>1969</td>
<td>quartz / vacuum</td>
<td>25-30</td>
<td>gravimetric</td>
<td>0.47 0.53 0.60 0.70</td>
</tr>
<tr>
<td>Hall</td>
<td>1970</td>
<td>quartz / vacuum</td>
<td></td>
<td>ellipsometry</td>
<td></td>
</tr>
<tr>
<td>Pashley &amp; Kitchener</td>
<td>1979</td>
<td>quartz / air</td>
<td>25</td>
<td>ellipsometry</td>
<td>3.2  8.0 20.0 150</td>
</tr>
<tr>
<td>Badmann et al</td>
<td>1981</td>
<td>silicate / vacuum</td>
<td>20</td>
<td>gravimetric</td>
<td>0.29 0.41 0.52 0.66 0.99</td>
</tr>
<tr>
<td>Busscher et al</td>
<td>1986</td>
<td>glass / vacuum</td>
<td></td>
<td>ellipsometry</td>
<td>0.28 0.80 1.60</td>
</tr>
<tr>
<td>Gee et al</td>
<td>1990</td>
<td>quartz / vacuum</td>
<td></td>
<td>ellipsometry</td>
<td>1.15 1.20 1.49 2.64</td>
</tr>
<tr>
<td>Beaglehole &amp; Christenson</td>
<td>1992</td>
<td>silicon / vacuum</td>
<td>18.1</td>
<td>ellipsometry</td>
<td>0.08 0.15 0.24 0.36</td>
</tr>
</tbody>
</table>
As Gee et al. (1990) commented in their summary of the work of different investigators, no two sets of data are the same, which is initially surprising as glass, quartz and silicon (it readily forms an oxide layer) all have similar surface properties. Hall (1970) comments that the layers measured using conventional techniques are generally larger than those measured using optical methods, however this does not seem to be born out by the results presented here. The gravimetric techniques used by Hagymassy et al. (1969) and Badmann et al. (1981) give layer thickness measurements which are in the same range as those values measured by Busscher et al. (1968) and Gee et al. (1990) using ellipsometry. However, the results of Garbatski and Folman (1956), obtained using a capacitance method, are significantly higher than the values obtained by the other investigators summarized in Table 2.1.

Various reasons have been proposed for the variations in results of the different investigators. Surface contamination will have a large effect on the results. Gee et al. (1990) observed that the equilibrium film thickness was dependent on the preparation of the quartz. Interestingly Pashley & Kitchener (1979) report that if surface contamination was present thick films did not form and the film thickness fell rapidly. Gee et al. (1990) also observe that thinner films will form in the presence of contamination. However Beaglehole & Christenson (1992) suggest that if surface contamination is present thicker adsorbed layers would be observed.

Gee et al. (1990) followed the guidelines set down by Pashley & Kitchener (1979) for the preparation and handling of the quartz samples yet they measured markedly thinner adsorbed layers. Gee et al. discuss the possible factors that cause this variation and also the variations with other investigators’ studies. They conclude that the two most plausible explanations are that the surface of silica (glass) samples dissolve to a certain extent to form a ‘gel’ layer which will lead to the observation of thicker films. Secondly that the adsorption of water on quartz is dependent on the arrangement of the surface hydroxyl groups which can either enhance or destroy the hydrogen bonding network of water on the surface.
From a study of Table 2.1 it is noticeable that Beaglehole & Christenson (1992) report thicknesses that are lower than those of other investigators. This may be due to the use of silicon wafer as the substrate; although it will have an oxide layer on the surface leading to similar surface properties as the other sample materials. Beaglehole & Christenson have measured, ellipsometrically, the thickness of the oxide layer to be 3 nm in the absence of adsorbed gases. Also the presence of two films on the surface will necessitate more complex analysis of the ellipsometry results. It must also be noted that a water monolayer has a thickness of ~0.3 nm hence at the lower vapour pressures Beaglehole & Christenson are measuring submonolayer thickness and there is therefore a question of what this represents in physical terms. If, as their results suggest, the layer thickness is less than a monolayer in depth, they must be measuring incomplete layers, with regions of adsorbed water and regions of bare substrate. This suggests that the surface they are studying is non-wetting at low humidities.

It is interesting to compare the reported accuracies of the adsorbed layer thicknesses. Using ellipsometry Beaglehole and Christenson (1992) report an accuracy of ± 0.002 nm which is about 100 times greater than earlier investigators. Also using ellipsometry, Frazer (1929) reports an accuracy of less than 0.3 nm, Derjaguin & Zorin (1957) no more than ± 0.5 nm and Pashley & Kitchener (1979) approximately ± 0.2 nm. This increase in the accuracy of ellipsometry in 13 years is remarkable. It is also not always clear whether the reported errors are for the equipment (systematic) or take into account the reproducibility of the experiments (random).

For the non-optical techniques, Garbatski & Folman (1956) comment that the layer thicknesses cannot be measured with more than a few Ångstroms accuracy using their capacitance method.
2.2.3 Modelling

2.2.3.1 Introduction

Attempts have been made to predict the adsorbed layer thickness using a range of theoretical and semi-empirical models. The development and usefulness of these models are discussed in this section, while the theory of the models is discussed in greater detail in chapter 4.

The DLVO theory (section 2.2.3.2) is the only truly theoretical model discussed in this study. Whereas the polarization theory (section 2.2.3.3), the BET adsorption theory (section 2.2.3.4) and the FHH theory (section 2.2.3.5) are semi-empirical models where the constants within the equations are based in and can be calculated from theory but are more usually determined experimentally.

2.2.3.2 DLVO Theory

The DLVO theory (Derjaguin-Landau-Verwey-Overbeek) was developed separately by Derjaguin & Landau (1941) and Verwey and Overbeek (1948). It combines the contributions of the van der Waals force and the electrostatic double layer interaction to give an overall interaction. Although the DLVO theory was developed for colloid stability it is directly linked to predictions of liquid film thickness.

The thickness of an adsorbed water layer can be related theoretically to the vapour pressure of a system via the disjoining pressure. The disjoining pressure can be defined as the difference between the thermodynamic equilibrium state pressure applied to surfaces separated by a film and the pressure on the bulk phase with which the film is in equilibrium. The concept of disjoining pressure, $\Pi$, was first developed by Derjaguin & Shcherbakov (1969). They suggest it can be expressed as:-

$$\Pi = \frac{-kT}{v_m} \ln \left[ \frac{p}{p^o} \right] = -\left[ \frac{\partial G}{\partial t} \right]_T$$ (2.1)

where $p = \text{partial vapour pressure (Pa)}$

$p^o = \text{saturated vapour pressure of the liquid (Pa)}$
The definition of the disjoining pressure assumes that the liquid film is in contact and equilibrium with a bulk phase. This is not the case with an adsorbed film where equilibrium is achieved through vapour transfer (Gee et al. 1990).

The DLVO theory takes into account both contributions to the disjoining pressure from van der Waals interactions ($\Pi_{\text{VDW}}$) and from electrostatic interactions ($\Pi_{\text{EL}}$).

\[
\Pi = \Pi_{\text{VDW}} + \Pi_{\text{EL}} \tag{2.2}
\]

\[
\Pi = -\frac{A}{6\pi t^3} + \frac{\varepsilon \varepsilon_0}{2t^2} \left( \frac{\pi kT}{ze} \right)^2 \tag{2.3}
\]

where $t =$ layer thickness (m)

$A =$ Hamaker’s constant (J)

$\varepsilon =$ relative permittivity of the adsorbate (-)

$\varepsilon_0 =$ permittivity of free space (constant) (C$^2$ J$^{-1}$ m$^{-1}$)

$k =$ Boltzmann’s constant (J K$^{-1}$)

$T =$ temperature (K)

$z =$ valency (-)

$e =$ electronic charge (C)

As noticed by several investigators, Derjaguin and Churaev (1974), Pashley and Kitchener (1979) and Gee et al. (1990) the DLVO theory does not adequately predict the measured disjoining pressure.
Derjaguin and Churaev (1974) suggest the inclusion of an additional structural term, $\Pi_S$, to take account of any structuring in the water layer, which may be the cause of the discrepancy between experimentally measured and predicted values of the disjoining pressure. They suggest that this component may be positive or negative, but for the interaction of a hydrophilic substrate with a polar liquid, i.e. the adsorption of water on quartz or glass, it will be greater than zero and consequently will increase the disjoining pressure. Derjaguin and Churaev also comment that with the absence of theory for polar liquids the structural disjoining pressure component cannot be calculated. Hence $\Pi_S$ is usually calculated to be the discrepancy between the predictions of DLVO theory and experimental results.

Israelachvili (1991) remarks that the attractive interactions, between the solid surface and the liquid molecules and a geometric constraining effect, force the liquid molecules to order (structure) into quasi-discrete layers. However the effect is only observed at a few molecular diameters into the liquid and is not observed at liquid-vapour interfaces.

Pashley and Kitchener (1979) also discuss the difference between DLVO predictions and their experimental results. They find that away from saturation ($p/p_0 < 0.98$) there is no theoretical agreement between the predicted and experimental values. They also note that within the theory used by Langmuir, for the electrostatic interactions, there are two assumptions that are not valid in a thin film system. The first is that the quartz/water interface has a constant potential and consequently is independent of film thickness, and that the potential gradient at the air/water interface is zero. Pashley and Kitchener comment that as the hydrogen-ion concentration in a thin film will vary as the film thickness is varied, the surface charge is also expected to vary and consequently cannot be assumed to be constant. Pashley and Kitchener also suggest that the potential gradient at the air/water interface is unlikely to be zero as previous investigators, Usui & Sasaki (1978), have observed evidence for preferential adsorption of hydroxyl ions at this interface.
The second assumption is that the film is in contact with bulk electrolyte. This is not the case in this system and equilibrium is achieved through vapour transfer. This assumption is inherent to both the DLVO theory and the definition of the disjoining pressure.

Gee et al. (1990) again discuss the difference between DLVO theory and experimental results, both in terms of the values obtained and the general shape of the adsorption isotherms. Gee et al. continue the discussion of Pashley and Kitchener about the shortcomings of the DLVO theory due to its inherent assumptions in the electrostatic component. Gee (1987) has developed a more appropriate expression for $\Pi_{EL}$ taking into account the absence of a reservoir of bulk electrolyte and allowing for mass action in the system with particular attention to the amphoteric nature of the quartz surface. Gee et al. comment that these corrections do not produce a result much different from classical DLVO predictions.

Gee et al. also discuss the possible inclusion of a structural term to allow for a layer of oriented water molecules. They distinguish between the electrostatic and the entropic contributions of these oriented molecules. Gee (1987) has calculated the electrostatic contribution by the inclusion of interfacial dipole moments and although the layer thickness predictions are larger there is still an offset between theory and experiment. Gee et al. (1990) suggest that some other force or some peculiarity of the experimental system is responsible for the thick water films obtained. It is noted that the entropic component of the structural effect is not easily calculated and the calculation has not been attempted by Gee et al.

In summary, previous investigators have used the DLVO theory to predict the thickness of adsorbed water layers. The investigators have found that the predicted values are significantly lower than the values determined experimentally. The difference is accounted for by the inclusion of an additional structural term.
2.2.3.3 Polarization Theory

De Boer and Zwicker (1929) and later Bradley (1936) derived the polarization theory for adsorbed films. It is based on electrostatic forces between an ionic adsorbent and non-polar adsorbate molecules. The concepts of the theory were first introduced by Polanyi (1920, 1922). The theory was then further developed, seemingly independently by DeBoer and Zwicker (1929) and Bradley (1936). The details of the polarization theory are discussed in section 4.3.

An expression for adsorption was developed by both sets of investigators.

\[
\log \left( \frac{p^o}{p} \right) = K_1 K_2 + K_4
\]

(2.4)

where \( p^o/p \) = inverse of the relative vapour pressure (-)

t = thickness of the adsorbed film (m)

\( K_1, K_3, K_4 \) = constants (-)

The constants \( K_1, K_2 \) and \( K_4 \) can be calculated theoretically but the task is complex, refer to Bradley (1936) for more details. Bradley suggests that the constants can instead be found from experimental data.

Bradley (1936) found that his experimental data, for the adsorption of water on copper oxide, could be fitted using equation 2.4 except at high pressures, near saturation, where the theory is not valid as capillary condensation will occur.

Brunauer et al. (1938) critically discuss the polarization theory before going on to discuss their own adsorption theory (Section 2.2.3.4). They comment that the polarization of the second adsorbed layer by the first is too small to form the major portion of the binding energy between the two adsorbed layers for non-polar adsorbates and consequently the predicted adsorption is too low. However they do not exclude the possibility that the interaction of permanent dipoles may give the energies required. They conclude that the polarization theory will give interesting but
empirical relationships. Consequently, the polarization theory has been largely ignored.

Garbatski and Folman (1956) find that their isotherms for the adsorption of water, which has a permanent dipole, on glass fit equation 2.4 for the polarization theory of adsorption. They have empirically determined the constants using the method suggested by Bradley (1936). They comment that they have not attempted to deduce the constants from the properties of the adsorbent surface and adsorbate.

Badmann et al. (1981) use a two parameter variation of equation 2.4, where $K_4$ is set to zero, to fit their data of adsorption of water on calcium silicate samples. They observe a better fit of their experimental data using the polarization theory (equation 2.4) than when using the FHH theory (equation 2.9, section 2.2.3.5). Badmann et al. suggest that as water is a molecule with a permanent dipole moment then the polarization theory best represents the sigmoid shape of the isotherm.

In summary some previous investigators have severely criticized the polarization theory for the prediction of adsorption of non-polar molecules. However, several other investigators have found that the polarization model provides a good fit of experimental data for water adsorption. In the current study, the form of the equation of the polarization theory is used to fit experimental isotherm data to produce a single convenient empirical expression but the theory is not used to predict values of adsorbed layer thickness.

2.2.3.4 BET Adsorption Theory

In 1938 Brunauer, Emmett and Teller generalized Langmuir’s approach to multilayer adsorption producing what is now commonly known as the BET equation

$$\frac{V_{\text{ads}}}{V_{\text{mono}}} = \frac{n_{\text{ads}}}{n_{\text{mono}}} = \frac{cx}{(1-x)[1+(c-1)x]}$$ (2.5)
where

\[ c \approx \exp\left(\frac{Q_1 - Q_v}{RT}\right) \]  

2.6

where \( V_{\text{ads}} \) = volume of adsorbate (m\(^3\))

\( V_{\text{mono}} \) = volume of a monolayer of adsorbate (m\(^3\))

\( n_{\text{ads}} \) = number of molecules adsorbed (-)

\( n_{\text{mono}} \) = number of molecules in a monolayer (-)

\( x = \frac{p}{p_0} \) = relative vapour pressure (-)

\( Q_1 \) = heat of adsorption of the first layer (J mol\(^{-1}\))

\( Q_v \) = heat of condensation of the liquid adsorbate (J mol\(^{-1}\))

\( R \) = universal gas constant (J mol\(^{-1}\) K\(^{-1}\))

\( T \) = temperature (K)

A derivation of equation 2.5 is given in Adamson (1990) p 611. The basic assumptions are that the Langmuir equation applies to each layer and that the heat of adsorption for the first adsorbed layer has a special value, \( Q_1 \), whereas for subsequent layers the value is that of the heat of condensation of the liquid adsorbate, \( Q_v \). It is also assumed that evaporation and condensation can only occur from or on exposed surfaces, and that no lateral interaction occurs between molecules.

Although, it is possible to theoretically calculate the value of \( c \), in the majority of previous work \( c \) is treated as a constant and is used as a parameter to fit experimental data.

Brunauer et al. (1938) apply equation 2.5 to numerous experimental adsorption isotherms obtained by themselves and by other investigators. They study adsorption isotherms for various gases adsorbing on a range of materials which are mainly catalysts. They do not appear to have investigated water adsorption isotherms.

Pashley (1980) discusses the use of the BET model for multilayer adsorption near saturation and for thick adsorbed layers. He comments that if a suitable and large value of \( c \) is used, for a polar liquid on a polar surface, then the experimental data of
Pashley and Kitchener (1979) and Frazer (1929) is well fitted. He goes on to show that for any large value of \( c \) equation 2.5 can be approximated to:

\[
\ln \left( \frac{p}{p_b} \right) = \ln \left( 1 - \frac{0.3}{t} \right) \tag{2.7}
\]

where \( t = \) film thickness (nm)

monolayer thickness, \( t_m = 0.3 \) nm

Pashley (1980) suggests this form of the equation also gives a good fit with experimental data. However, it yields an upper limit to the thickness of adsorbed films that can predicted and for which experimental data can be fitted. In the current work, water adsorption on various surfaces has been considered for a range of relative humidity values between 10 % and 70 %. Using the limiting BET model, equation 2.7, this predicts maximum layer thicknesses between 0.333 nm and 1.0 nm. The majority of the film thicknesses measured by previous researchers and in the current work (detailed in chapter 6) are greater than these maximum values. Consequently, the BET theory does not appear to be an appropriate model for predicting the thickness of adsorbed water layers.

Pashley also discusses the possible effect of the presence of a contaminant salt on the sample surface. He suggests that the BET theory could be developed to a surface solute theory. The layer thickness would then be given by:

\[
\ln \left( \frac{p}{p_b} \right) = -\ln \left( 1 + \frac{K}{t} \right) \quad t > K \tag{2.8}
\]

where \( K = K_2/K_1 \)

\( K_1 \) = number of water molecules in the adsorbed film

\( K_2 \) = number of solute species in the film (\( K_2 \) is independent of film thickness)

Gee et al. (1990) also study the effect of surface solute theory. They show that the use of the surface solute theory does predict thicker adsorbed layers but they conclude...
that neither the BET model nor the hypothesis of a water-soluble impurity layer adequately account for the behaviour of water adsorption as seen in their own work.

On the strength of the observation of Gee *et al.* (1990) that the surface solute theory does not account for amount the of water adsorption seen in their own work, it has not been considered in the present work, which reports comparatively larger film thicknesses (section 6.2.3).

### 2.2.3.5 FHH Theory

The Frenkel-Halsey-Hill theory looks at multilayer adsorption with the assumption that the principal interaction between the solid and the adsorbate is dispersive in nature, and consequently the surface potential for a plane surface should decrease with the inverse cube of the distance.

The general approach was outlined by Frenkel (1946) and was elaborated on by Halsey (1948), Hill (1952) and McMillan and Teller (1951).

Badmann *et al.* (1981) give the FHH equation as:

\[
\ln \left( \frac{p}{p^0} \right) = \frac{K}{V_{ads}/V_{mono}}^N
\]

where \( p/p^0 \) = relative vapour pressure

\( K = \text{constant (s)} \)

\( N = \text{constant (s)} \)

\( V_{ads} = \text{volume adsorbed (m}^3\) \)

\( V_{mono} = \text{monolayer volume (m}^3\) \)

The 'constant' \( K \) can be expressed theoretically as:-

\[
K = \frac{\phi_0}{t_m^{NRT}}
\]

where \( \phi_0 = \text{surface potential (J mol}^{-1}\) \)
t_m = monolayer thickness (m)
R = universal gas constant (J mol\(^{-1}\) K\(^{-1}\))
T = temperature (K)

The constants in the FHH theory, in common with the constants in the polarization theory and in the BET theory, are not usually calculated theoretically but are used as parameters in the fitting of experimental data.

From equation 2.9, the thickness of an adsorbed layer can be determined. \(\frac{V_{\text{adv}}}{V_{\text{mono}}}\) represents the number of monolayers that have been adsorbed. Therefore, the adsorbed layer thickness can be calculated to be the number of monolayers multiplied by the thickness of a monolayer.

Badmann et al. (1981) discuss the relevance of the constant N. They suggest that N can be used as a guide to the strength of the interaction between the adsorbate and the solid. If N is large then short-range specific forces are acting, whereas if N is small then the forces are of the long-range dispersion type. They also add that N = 3 corresponds to van der Waals dispersion forces. Adamson (1990) comments that in Halsey's tabulation of N values for various systems (Halsey 1948) values between 2 and 3 are fairly common.

Badmann et al. (1980) did not obtain a good fit between their experimental data for water adsorption on calcium silicates and the FHH model. Pashley (1980) also discusses the FHH theory commenting that it gives similar results to BET theory.

In the current study, attempts have been made to fit data for water adsorption on silicon wafer using the FHH model. However, the optimum value of N for the experimental data was 7.9 which is outside the expected range and this indicates that the FHH theory does not provide a suitable model for use in the current study.
2.3 *Atomic Force Microscopy*

2.3.1 Introduction

The atomic force microscope (AFM) is a member of the family of scanning probe microscopes, in which a small probe is moved across the sample surface in close proximity or in contact. A three-dimensional relief of the surface is obtained from local interactions between the probe and the sample. The first member of this family was the scanning tunnelling microscope, which was developed in 1981 by Binnig and Rohrer (1982) and earned them a Nobel Prize in 1986. The atomic force microscope was developed in 1986 by Binnig, Quate and Gerber (1986).

The AFM operates by scanning the sample surface using a sharp tip attached to a flexible cantilever stylus. The forces acting between the sample surface and the tip cause minute deflections of the cantilever. These deflections are detected by an optical laser system and are used to produce a topographic map of the surface.

Studies have shown that by manipulating the forces acting between the tip and the sample it is possible to increase the imaging resolution without damaging the sample. It is also possible to study directly the forces between the tip and the sample in order to investigate interactions for different materials in various media. It has been noticed that the forces acting in air are significantly larger than those observed under liquids (Weisenhorn *et al.* 1989). The difference is generally attributed to capillary interactions from adsorbed water layers on both the tip and the sample. Burnham *et al.* (1993) illustrate the typical shape of an AFM output curve observed when a liquid layer is present. Little, as yet, has been reported on the measurement of these adsorbed water layers using atomic force microscopy. However Mate *et al.* (1989) have developed a technique to measure the thickness of thin polymer films. There are a number of shortcomings inherent in their technique which are addressed in this present work. This method forms the basis of the experimental technique developed in the present work, and is discussed in detail in section 2.3.3.
2.3.2 AFM Force Studies

2.3.2.1 Types of Force

Some of the earliest reported force measurement work using the AFM was done in order to gain greater understanding of the forces between sample and cantilever tip, so that they could be minimized. This would increase imaging resolution and reduce the potential sample surface damage allowing softer samples to be imaged. Hutter and Bechhoefer (1993) consider the interpretation of the force curves and comment that interpretation can be complex as there may be several forces acting simultaneously. In a later paper, (Hutter and Bechhoefer 1994), they describe the different forces which act in different media. In a vacuum they suggest van der Waals and electrostatic forces will be present, in humid air condensed water may lead to capillary forces and in a liquid medium electrostatic double-layer forces may arise from the dissociation of tip and sample ions into solution. Weisenhorn et al. (1989) studied the forces acting between a silicon nitride tip and a mica surface. They noted that there was a much greater level of hysteresis between the jump-on forces and the adhesive (pull-off) forces in air, compared with the same system in water. They suggest that this is due to attractive surface tension forces. Hence the reported minimum force in air ($10^{-7}$ N) is two magnitudes larger than in water ($10^{-9}$ N).

The majority of the AFM investigations into force interactions, to date, have either been carried out in a vacuum or within a liquid medium, as the presence of adsorbed liquid on the sample surface and the formation of capillary bonds can significantly affect the force interaction and make the subsequent interpretation more complex. One of the few published studies conducted in air was performed by Sugawara et al. (1993) who examined the effect of humidity on the adhesive force. They noted a tendency for the adhesive force to increase with an increase in humidity and suggested that this observation was not in agreement with the classical theory for capillary adhesion between a sphere and a flat plate, as summarized by Israelachvili (1991). However this classical theory only applies for a fully saturated vapour and therefore it is not surprising that poor agreement was found.
Interestingly, several AFM force studies conducted in liquid media show a general agreement with the DLVO theory. Ducker *et al.* (1991) consider the interaction between a silica sphere and a planar silica surface in a sodium chloride solution. They note that their results are in broad agreement with those predicted from the DLVO theory, however the roughness of the substrate complicates the analysis of the forces. Li *et al.* (1993) also find the results of their investigations into the effect of electrolyte strength on the force between two spheres to be in general agreement with DLVO theory. They found that the long range forces (non-contact region) show a systematic dependence on electrolyte concentration whereas the adhesive forces show no such trend.

### 2.3.2.2 Interpretation of AFM Force Curves

Generally AFM force data found in literature are presented in the form of force vs. separation curves (force curves) which are derived from cantilever diode voltage vs. piezo displacement curves (AFM output curves). The AFM output curves presented in this dissertation were obtained using a commercial AFM, a Nanoscope II manufactured by Digital Instruments.

In principle a great deal of information can be obtained from the AFM output curves, such as the thickness of an adsorbed liquid layer, the nature of the forces acting in the non-contact region, and the magnitudes of the jump-on forces and the adhesive forces (pull-off). Figure 2.1 shows a typical force curve in schematic form. Figure 2.2 gives an example of an AFM output curve; this curve was obtained using a Nanoscope II for the interaction between a lactose particle and a silicon nitride cantilever tip in ambient humidity.
The long-range attractive region extends over several tens of nanometers (Hutter and Bechhoefer 1993) and (Pollock 1994). Burnham et al. (1993) and Pollock (1994) discuss various possible force types and their potential prevalence in this region. The force mechanisms discussed include; magnetic, capacitance, van der Waals, discrete electronic charges, capillary, surface layers of dielectric materials, fixed permanent dipoles and work function anisotropies or patch charges. In the current work the long-range attractive region is not often observed due to the high spring constant of the ‘stiff’ cantilevers used in the determination of adsorbed layer thickness.
A cantilever instability as the tip jumps into contact may or may not be observed depending upon the cantilever spring constant, the tip and substrate materials and the nature of the intervening medium. The magnitude and source of the attractive forces causing the mechanical instability will depend on the nature of the intervening media. In air the dominant force will be the formation of a liquid capillary as the tip initially comes into contact with the adsorbed liquid layer. However the initial instability is likely to arise prior to this contact, and is the result of van der Waals and electrostatic interactions.

As the tip advances further through an adsorbed layer, a point is reached when solid-solid contact is made between the tip and the sample materials. Burnham et al. (1993) propose that this contact is defined as the position on the curve at which the repulsive component can first be detected. Li et al. (1993) suggest that the contact point can more easily be described if there is an obvious jump into contact as the point at which the rapid downward displacement of the cantilever changes into an upward displacement as seen on the AFM output curves.

Once the cantilever and tip are in contact the relationship between the piezo displacement and the cantilever diode response will be linear, assuming a rigid substrate. Hence this region on the AFM output curve can be used to calibrate the cantilever deflection in terms of distance and consequently can be used to calculate the force or layer thickness. However as noted by Li et al. (1993) and Ducker et al. (1991) if the substrate is compliant then there will be an under estimate in the force. Both parties therefore suggest independently calibrating the cantilever deflection using a rigid substrate, such as steel or silicon.

The adhesive force (pull-off) has been reported in literature far more widely than the jump-on force. This is undoubtedly because it represents the surface forces between the tip and the sample in contact, is simpler to measure and easier to visualize. Generally it is possible to observe significant hysteresis between the jump-on and pull-off forces in the force distance curves, with the pull-off force being greater than
the jump-on force. The major cause of the hysteresis, when operating in air, is generally attributed to capillary forces. Although another possible reason for the irreversibility of the process is plastic deformation at the solid-solid contact site and the associated energy dissipation. Senden et al. (1994) suggests that in a gaseous environment the pull-off force due to the formation of a capillary bridge between tip and sample is dependent only upon the surface tension of the condensed liquid and the radius of contact. Hence the contact area between the two surfaces is of great relevance to the adhesive force. Burnham et al. (1993) comment that the adhesive force will vary with the maximum load applied which in turn will affect the contact area via a relationship as proposed in JKR theory (Johnson, Kendall and Roberts 1971).

2.3.2.3 Spring Constant

“One of the major criticisms of the use of the AFM for force measurement is the error of the magnitude of the forces which arise from uncertainty in the cantilever spring constant”

Senden and Ducker (1994)

The spring constant, k is used to calculate the force, F from the cantilever deflection, \( d_c \):

\[
F = kd_c \tag{2.11}
\]

Consequently any error in the spring constant will be related directly into an error in the measured force. Hence the spring constant must be determined by direct measurement or be calculated for each individual cantilever. It has been shown that a V-shaped cantilever can be well approximated by two rectangular beam cantilevers, Albrecht et al. (1990) and Cleveland et al. (1993). Hence:

\[
k = \frac{Et^3w_c}{2l_e^3} \tag{2.12}
\]
where \( t_c = \) cantilever thickness (m), \( w_c = \) leg width (m), \( l_c = \) length (m) & \( E = \) Young's modulus (N m\(^{-2}\)).

From this expression it should be possible to calculate the spring constant, however as noted by Senden and Ducker (1994), the cantilever thickness and Young's modulus are not known accurately.

Table 2.2 - Values of Young's modulus for silicon nitride.

<table>
<thead>
<tr>
<th>Source</th>
<th>( E \times 10^{11} ) N/m(^2)</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sarid &amp; Elings (1991)</td>
<td>1.5</td>
<td>AFM</td>
</tr>
<tr>
<td>Kawai et al. (1992)</td>
<td>2.94</td>
<td>AFM</td>
</tr>
<tr>
<td>Hutter &amp; Bechhoefer (1994)</td>
<td>1.5</td>
<td>AFM &quot;typical value&quot; for Si(_3)N(_4)</td>
</tr>
<tr>
<td>Vlassak &amp; Nix (1992)</td>
<td>2.2</td>
<td>non-AFM Si(_3)N(_4) film</td>
</tr>
<tr>
<td>Lefevre et al. (1991)</td>
<td>3.5</td>
<td>non-AFM Si(_3)N(_4) thin window</td>
</tr>
<tr>
<td>Grow &amp; Levy (1994)</td>
<td>0.75 - 0.95</td>
<td>non-AFM Si(_3)N(_4) film at high temps.</td>
</tr>
</tbody>
</table>

In order to obtain high force resolution the cantilevers are typically very thin (<1 \( \mu \)m) and there is considerable variation in this value. Any error in the thickness value is critical as it is cubed in equation 2.12. The most common material of construction for AFM cantilevers is silicon nitride (although silicon cantilevers are also widely used) for which the Young's modulus must be known. Young's modulus may vary because of the formation of nonstoichiometric silicon nitride and due to anisotropic growth of the film (Senden and Ducker 1994). Table 2.2 shows the diversity of Young's modulus values for silicon nitride that are quoted in literature, both for AFM and non-AFM applications.
Various methods have been proposed to measure spring constants. The calibration criterion is that a known force leads to a measurable deflection. Cleveland et al. (1993) propose a method whereby the spring constant is calculated from a change in resonant frequency between a cantilever unloaded and loaded with a tungsten sphere. However they report a large scatter in the results due to errors in measuring the tungsten sphere diameters (average diameter 20 μm).

Li et al. (1993) have measured spring constants by pushing a cantilever against a glass fibre and monitoring the relative deflection under an optical microscope. The glass fibres were precalibrated by measuring their deflection when loaded with known weights.

Senden and Ducker (1994) detail a static measurement technique where the deflection due to gravity of an end loaded cantilever was measured. A small mass was added to the end of a cantilever and the deflection recorded in terms of the output voltage, using an AFM. The cantilever (and AFM head) was then placed upside down and once again the deflection recorded. The difference in the output readings was found to be twice the deflection due to gravity. Then the cantilever deflection was calibrated from voltage units to distance units, in the usual AFM manner, by measuring the cantilever deflection when moving in contact with a rigid substrate.

Due to a lack of a method for the determination of spring constant in this work any forces quoted have been calculated using the nominal spring constant as provided by the manufacturer. If force values are to be compared the same cantilever has been used so that any systematic error from this source is eliminated.

2.3.3 Adsorbed Layer Thickness Measurement

Mate et al. (1989) propose that the atomic force microscope can be used to measure the thickness of films on a surface. They suggest that the distance the sample moves after the tip contacts the surface of the liquid until it contacts the solid surface of the substrate should be a measure of the thickness of the liquid film (liquid layer
thickness = ds, Figure 2.3). However, this analysis fails to take into account the simultaneous deflection of the cantilever. In the current work the distance moved by the cantilever is accounted for in the determination of the film thickness, given by ds + dc, as shown in Figure 2.3.

Mate et al. (1989) test their hypothesis by comparing the layer thickness measured using AFM with that measured by ellipsometry. They study the thickness of a polymer liquid (perfluoro-poly propylene oxide) on a smooth silicon wafer. They find that as the ellipsometry thickness of the film increases the thickness measured by AFM also increases. AFM, however, tends to measure a thicker film than that measured by ellipsometry and the offset between the sets of data increases as the film thickness increases. It is interesting to note that this deviation would have been still greater if Mate et al. had accounted for the cantilever deflection in their analysis.

Mate et al. suggest that the offset may be due to the liquid polymer coating the tip on the first contact with the film and consequently giving larger values of film thickness. In the current work where the thickness of an absorbed water layer is being measured, the adsorbed water on the cantilever tip must also be taken into account. Mate et al. also suggest there may be a layer of adsorbates on the tip from the ambient air. This is likely to be an adsorbed water layer which will be present on both the tip and possibly on the polymer film. Mate et al. present no record of the ambient conditions
under which they carry out their experiments so it is not possible to make an estimate of the thickness of adsorbed water layers.

Mate et al. comment that the ability of ellipsometry to measure film thickness is well established and the ellipsometric film thicknesses are accurate to ± 0.1 nm. Yet they themselves comment that for very thin films (<20 nm) it is not possible to determine both the film thickness and the refractive index of the layer, hence the refractive index is assumed to be the bulk value. This may cause an error in the film thicknesses measured by the ellipsometer.

Grigg et al. (1992) studied the difference in the attractive force between an AFM output curve obtained in air and one obtained under water, where capillary forces will not be present. They comment that in air, van der Waals forces may pull the surface of the film towards the probe and initiate a liquid bridge prematurely. They also comment that it is difficult to determine this effect analytically. They suggest that a simple interaction energy argument, using pairwise summation of the van der Waals energy between macro particles predicts a negligible effect (Israelachvili 1991). Yet a similar effect has been seen for solid surfaces using molecular dynamic simulation (Landman 1990), where the molecules comprising the solid surface were shown to be attracted towards a probe prior to jumping into contact.

Forcada et al. (1991) also attribute the difference between the AFM and ellipsometry measurements obtained by Mate et al. (1989) to the swelling of the liquid surface towards the AFM cantilever tip and the film instability causing the premature jump to contact. They develop a method, based on the interactions of the liquid film with a cantilever tip, to predict the minimum tip/sample separation below which the bulge is no longer stable and the surface tension of the liquid and the adhesion of the film to the substrate cannot keep the liquid from jumping into contact with the tip. This method appears to over predict the layer thickness, however the presence of a liquid layer on the cantilever tip has not been considered.
In a later paper, Forcada (1993) considers instability and premature liquid bridge formation for a system of two interacting liquid films. In this paper, he develops an expression to relate the separation distance at which the instability occurs, to the physical properties of the liquid, \textit{i.e.} the activity and Hamaker constant. From the theory used in the development of this expression it is possible to derive a relationship, based on van der Waals interactions, between the thickness of the adsorbed liquid layer and the separation distance at which the jump to contact occurs. In the current work, this relationship is developed to take account of the present geometry, approximated as a sphere (the tip) approaching a flat surface (the sample), as opposed to the interaction between two planar surfaces as studied by Forcada (1993). The formation of the instability and premature jump to contact are discussed in greater detail in section 3.5.7.

\textbf{2.4 Conclusions}

In this chapter the literature has been reviewed in two key areas; measurement and modelling of water adsorption isotherms, and the use of atomic force microscopy.

Several techniques, for the measurement of water adsorption isotherms have been identified and their relative merits discussed. It has been noted that there is little agreement between the results of previous investigators for materials which display similar surface properties.

Ellipsometry is the most commonly used technique and is the method that is generally considered to give the most reliable results. However, evidence has been uncovered that points to inherent errors in the measurement of thin films using ellipsometry. For thin films (thickness < 20 nm) it is not possible to determine both the layer thickness and the refractive index, consequently the refractive index of the film is taken to be that of the bulk material and it can be concluded that the resulting layer thicknesses are therefore approximate.
The literature reveals that attempts have been made previously to predict layer thickness using a range of theoretical models. Of the models discussed in this study the DLVO theory is the only truly theoretical model. Previous investigators have used the DLVO theory to predict the thickness of adsorbed water layers. The investigators have found that the predicted values are significantly lower than the values determined experimentally. The difference is generally accounted for by the inclusion of an additional structural term.

Some previous investigators have severely criticized the polarization theory for the prediction of adsorption of non-polar molecules. However, several other investigators have found that the polarization model provides a good fit of experimental data for water adsorption. In the current study, the form of the equation of the polarization theory is used to fit experimental isotherm data to produce a single convenient empirical expression but the theory is not used to predict values of adsorbed layer thickness.

Previous investigators have found that the BET model can be used to fit experimental data for adsorption of a polar liquid on a polar surface. It is shown, in the current work, that the form of the model equation where the model constant $c$ becomes infinitely large gives an upper limit to the predicted thickness of adsorbed layers. These maximum values are below the experimentally measured values for adsorbed water thickness (for all the systems considered in this study) and consequently the BET model cannot be used to fit the experimental data of the current study.

The FHH model has been used to fit some of the experimental data of the current study. Previous investigators suggest that the value of the constant $N$ should be in the range 2-3, however the value obtain in the present work is 7.9, which is outside the expected range. This indicates that the FHH theory does not provide a suitable model for use in the current study.
The development and use of atomic force microscopy for force studies has been reviewed. It has been noted that the majority of force studies have been performed in a vacuum or under liquid to avoid the more complex interactions which occur in air due to the presence of adsorbed liquid on the sample surface and the formation of capillary bonds.

Also the problems associated with the accurate determination of the cantilever spring constant have been discussed. Inaccuracy in the determination of the spring constant leads directly to uncertainty of the accuracy of measured force values.

The more recent use of AFM for the measurement of film thickness, by Mate et al. and their comparison between AFM and ellipsometry measurements have been discussed. They notice an offset between the two sets of results, with the AFM providing the larger values. Forcada et al. (1991) attribute the difference between the ellipsometry and AFM measurement to the swelling of the liquid surface towards the AFM cantilever tip and the film instability causing a premature jump to contact.

Forcada et al. (1991) and Forcada (1993) attempt to model the system to provide an expression relating the separation distance at which the jump to contact occurs to the physical properties of the liquid. In the current work the layer thickness measurement method of Mate et al. has been extended to account for the cantilever displacement, and the theoretical approach of Forcada (1993) has been developed and is discussed in greater depth in Chapter 3.
3. ATOMIC FORCE MICROSCOPY

3.1 Introduction
The atomic force microscope (AFM) has been developed primarily for imaging however it can also be utilized to study the force interactions between a cantilever tip and a sample surface. In imaging mode a sharp tip attached to a flexible cantilever stylus is used to scan the sample surface. The forces acting between the sample surface and the tip cause minute deflections of the cantilever. These deflections are detected by an optical laser system and are processed to produce a topographic map of the surface. In the conventional mode for force measurement the cantilever is moved solely in the vertical direction and the tip comes in and out of contact with both the sample surface and any water layer that may be present. An AFM output curve is obtained which records the relative movements of the cantilever and the sample. This output curve constitutes the raw data from which the thickness of the adsorbed water layer is inferred.

3.2 AFM Nanoscope II
3.2.1 Introduction
The atomic force microscope used in the current work is a Nanoscope II from Digital Instruments\(^1\). In this particular design the cantilever is held in a rigid position and the sample is moved relative to the tip. The microscope hardware is made up of three components: the scanner support, the scanner and the head, which are linked via a control unit to a computer. The computer is used to control the microscope during operation. The different elements of the AFM are described in the following sections. Figure 3.1 is a schematic diagram of the Nanoscope II atomic force microscope. Figure 3.2 is a photograph of the Nanoscope II system used for the current investigations, showing the microscope hardware within the humidity chamber and the computer control system. Figure 3.3 is a photograph illustrating the three components of the microscope hardware.

\(^1\) Digital Instruments, 520 East Montecito Street, Santa Barbara, California. 93103
3.2.2 Hardware

3.2.2.1 Scanner Support

The scanner support, as the name suggests, provides rigid support for the scanner and the head. It also contains the automated approach electronics and stepper motor. Figure 3.4 illustrates the scanner support.
Figure 3.3 - Nanoscope II hardware.

- head
- scanner
- scanner support

Figure 3.4 - Scanner support.

- stepper motor control
3.2.2.2 Scanner

The scanner provides three-dimensional motion to the sample, which is necessary for both imaging and force work. The single tube, piezoelectric scanner is mounted in a cylindrical housing, also containing three adjustment screws. Two of the screws provide coarse adjustment and the third screw is driven by the stepper motor in the scanner support for automatic engagement of the cantilever to the sample. Mounted on top of the scanning tube is a magnetic cap on which samples mounted to steel disks are placed.

The Nanoscope II comes with different scanners. In this study two different scanners have been used. The D scanner which has a 12 μm horizontal scan range and a vertical range of 2.5 μm, and the J scanner with a horizontal scan range of 125 μm and a vertical range of 5 μm. The D and J scanners are shown in the photograph in Figure 3.5.

Figure 3.5 - AFM scanners.
3.2.2.3 Head

Resting over the sample on the tripod formed by the adjustment screws is the laser head. This unit contains the removable cantilever mount, laser, laser power supply, focussing and steering optics and the photodetector. The laser head is shown in Figure 3.6 together with a schematic of the head in Figure 3.7. The head allows adjustment of the position of the laser diode and the photodetector. These positioners are used to align the optics after a cantilever has been installed. Alignment of the optics prior to experimentation is discussed in section 3.4.1.2.

Figure 3.6 - Nanoscope II laser head.

Figure 3.7 - Nanoscope II laser head.
The laser diode (5 mW max. output at 670 nm) emits a beam which is reflected from a cantilever held in the cantilever mount, to the surface of the photodiode detector via a mirror. Any deflection in the cantilever, caused by surface forces, causes the reflected beam to move across the surface of the detector. This deflection manifests itself as differences in light intensity falling on separate segments of the photodiode.

Figure 3.8 - Position of cantilever in cantilever mount.

The cantilevers are fabricated attached to a substrate. These substrates are placed into a slot in the cantilever mount and are held in position, to ensure the correct positioning of the cantilever, using a fine wire clip (Figure 3.8). The cantilever mount, which is removable, is held in the laser head by a holding arm. Two cantilever mounts are available. The mount used in the majority of experiments in this study is made of metal and its shape allows convenient viewing of the cantilever during alignment. The other is made of glass and can be sealed against the scanner with an O-ring to allow imaging under liquid.

3.2.3 Software

The Nanoscope II operation is controlled using a standard PC linked via a control unit to the microscope hardware. The microscope is controlled using commercial software (Nanoscope II version 2.5.1) and operates using a series of command menus. The software allows the microscope to be used for sample imaging or to obtain AFM
output curves, and also performs statistical analysis, such as measures of roughness, in addition to controlling the image export. The system uses two monitors, the first to display the command menus and the second to display the microscope images.

3.3 Cantilevers
AFM cantilevers can be obtained in two basic configurations; V-shaped and single beam, as shown in Figure 3.9. For both configurations the cantilever is attached to a substrate which allows the tip to be held in the cantilever mount. At the end of the cantilever is the tip, used for imaging or for interaction with surface forces when in force mode. In this study the cantilevers are single beam springs that are relatively stiff. The average spring constant of these cantilevers was 4 N/m which is significantly larger than the spring constant of the conventional tips used for imaging (k = 0.06 - 0.58 N/m). The advantage of ‘stiff’ cantilevers is that the ‘pull-off’ of the tip from the sample and the liquid layer requires less retraction of the sample (adhesion force = spring constant x separation of the tip and sample as the liquid neck breaks). Consequently the horizontal (sample movement) scaling can be minimized and it is possible to gain more detail of the ‘jump-on’ region. Also the use of a stiff tip reduces extent of the mechanical instability during the jump to contact, increasing the accuracy of the film thickness measurements.

Pointprobe silicon ‘force modulation’ cantilevers, supplied by L.O.T.-Oriel Ltd. have been used in this study. A summary of the cantilever characteristics is shown in Table 3.1. The cantilevers are made from monolithic material to avoid any strain due to change in temperature and are doped to dissipate static charge on insulating samples.

2 L.O.T.-Oriel Ltd., 1 Mole Business Park, Leatherhead, Surrey, KT22 7AU.
Figure 3.9 - Single beam and V-shaped cantilever configurations.

Table 3.1 - Summary of cantilever characteristics.

<table>
<thead>
<tr>
<th></th>
<th>Force Modulation</th>
<th>Conventional Imaging</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cantilever Material</td>
<td>silicon</td>
<td>silicon nitride</td>
</tr>
<tr>
<td>Substrate Material</td>
<td>silicon</td>
<td>glass</td>
</tr>
<tr>
<td>Nominal Spring Constants</td>
<td>1-5 N/m</td>
<td>0.58, 0.32, 0.12, 0.06 N/m</td>
</tr>
<tr>
<td>Resonant Frequency</td>
<td>60-100 kHz</td>
<td>77, 77, 19, 19 kHz</td>
</tr>
<tr>
<td>Nominal Tip Radius</td>
<td>5-10 nm</td>
<td>20-60 nm</td>
</tr>
<tr>
<td>Cantilever Length</td>
<td>225 μm</td>
<td>100 &amp; 200 μm</td>
</tr>
<tr>
<td>Configuration</td>
<td>single beam</td>
<td>V-shaped</td>
</tr>
<tr>
<td>Reflective Coating</td>
<td>uncoated</td>
<td>gold</td>
</tr>
<tr>
<td>Tip Half Angle</td>
<td>17° side, 25° front, 10° back</td>
<td>35°</td>
</tr>
<tr>
<td>Tip Shape</td>
<td>triangular pyramidal</td>
<td>square pyramidal</td>
</tr>
</tbody>
</table>

For imaging, ‘conventional’ soft cantilevers have been used. These ‘conventional’ imaging cantilevers are supplied in groups of four tips having different spring
constants depending on the length of the cantilever and the width of the cantilever legs (see Table 3.2). The softer cantilevers allow greater resolution during imaging. These cantilevers are made of silicon nitride mounted on a glass substrate. The cantilever characteristics are summarized in Table 3.1. In the current study, the 200 μm cantilever with narrow legs has been used for imaging as it has the lowest spring constant.

Table 3.2 - Nominal Spring constants for the V-shaped cantilevers.

<table>
<thead>
<tr>
<th>Cantilever Length</th>
<th>Spring Constant (N/m) (narrow legs &lt; 20 μm)</th>
<th>Spring Constant (N/m) (wide legs &gt; 20 μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 μm</td>
<td>0.38</td>
<td>0.58</td>
</tr>
<tr>
<td>200 μm</td>
<td>0.06</td>
<td>0.12</td>
</tr>
</tbody>
</table>

3.4 Experimental Procedure

3.4.1 Preparation

3.4.1.1 Sample Mounting

All samples must be fixed to steel mounting disks for attachment to the magnetic cap on the end of the scanner. Silicon wafer and aluminium foil samples are mounted by sticking a small piece of the sample material to the disk using double-sided sticky tape. The sample must not protrude over the sample disk (diameter 15 mm) otherwise it may interfere with the movement of the scanner or be knocked during scanning. Single lactose crystals were glued to pieces of acetate film using nail polish. The acetate was then attached to the metal disk using a piece of double sided sticky tape. The crystals were mounted in this way so that the sample could be centred on the disk and any excess acetate could easily be trimmed. The milled lactose powder was mounted by scattering a small amount of the powder over a drop of nail polish on a piece of acetate film. Any excess unstuck particles were removed by a puff of air. The acetate was then mounted on to the steel disks. Again this method was used so that the sample could be centred on the disk and a well distributed region of lactose could be selected so that it was possible to identify and scan the surface of individual particles.
3.4.1.2 Optical Alignment

Before the AFM can be used for imaging or force work, the optics must be correctly aligned. Firstly the laser beam must be positioned so that the beam is reflected from the very end of the cantilever, in order to record the maximum cantilever deflection. The mirror must then be adjusted so that the maximum signal is read by the photodiode, to give the greatest sensitivity in the readings. Finally the photodiode is adjusted to give an offset value of approximately -2 V so that as the sample and tip move into contact the voltage can rise to the set-point value of zero at contact.

3.4.1.3 Contact

Once the microscope optics have been correctly aligned the tip and sample can be brought into contact. It is possible to view the cantilever using a travelling microscope placed in front of the AFM. The AFM head is lowered manually using the two coarse adjustment screws and the motorized fine adjust screw until the tip and sample are close but not touching (~0.1 mm). A bright red spot can be seen on the tip of the cantilever, from the laser beam, and a reflected spot can also be seen on the sample surface. When the sample and tip are close there will only be a slight gap between the two red dots. The head should be kept as level as possible. The tip and sample can now be brought into contact using the computer 'engage' command.

If the tip and the sample touch only one red dot will be visible and the photodiode voltage will be zero. Bringing the tip and the sample into contact manually risks damage to the cantilever.

3.4.2 Imaging

Once the tip and the sample are in contact the AFM will start to image the sample surface and the image can be observed on the 'image' monitor. Meanwhile the AFM menu will be available on the 'menu' monitor. The AFM menu allows adjustment of the imaging parameters in order to obtain a good image. The size of the scan area and the centre position of the scan can be adjusted, as can the vertical range of the scan. The scan area is always square and consequently the area is defined by a single
parameter (e.g. 5000 nm represents a square having sides of 5000 nm in length). The scan rate and number of data points per scan line and scan lines per image can also be controlled. Correct setting of the proportional and integral gain can reduce the amount of noise in an image.

While obtaining the images for the current work, a mid-range value of scan area has generally been used (~5000 nm). Smaller imaging areas do not always give a good representation of the sample surface, particularly if the sample has an irregular surface. Large imaging areas can also cause problems. If a sample is very flat, as in the case of aluminium foil and silicon wafer, a large area image may give the impression of being curved due to the azimuthal movement of the piezo crystal. However, if a sample is particularly rough or is small in area (lactose particles) a large area image may cause the vertical scan range to go off scale (i.e. falling off the edge of a particle) and it may prove difficult to obtain a stable image.

The resolution of an image can be improved by several means. The first is to optimize the vertical scan range. If the vertical scan range is large, surface detail may be unobservable, however if the range is small the Nanoscope II image will not display the extreme points. For example a high peak on a surface may appear to have a plateau instead of coming to a point (Figure 3.10). The vertical range can, however, be adjusted later while the images are being prepared for export.

Figure 3.10 - Imaging error caused by small vertical range.
If an image has a large amount of noise this can often be reduced by increasing the feedback gain however if this is set too high artifacts will appear in the image. Increasing the number of samples and reducing the scan rate can also improve the image.

Due to the set up of the Nanoscope II once contact has been made, the sample must be imaged before force mode can be initiated. If a large scan area is being used it may not be possible to predict where in the sample area the AFM output curves are being taken. Consequently in this study an image of the surface is obtained (≈5000 nm) and then a suitable area for force curves is selected and the scan area is reduced to cover just this small area (≈200 nm). This enables AFM output curves to be obtained in specific areas. The regions of a sample normally selected for curve measurement tend to be reasonably flat and away from any sudden changes in the surface topography, to reduce the risk of multiple tip contacts or other artifacts arising from surface topography.

3.4.3 *AFM Output Curves*

In conventional force mode the sample is moved solely in the vertical direction and the tip comes in and out of contact with both the sample surface and any water layer that may be present. AFM output curves record the relative movements of the cantilever and the sample.

In some sources, such as the Nanoscope II manual the output curves are termed 'force' curves. They are not true force curves, as it is the movement of the cantilever and the sample that is recorded, not the force. AFM output curves can, however, be transformed into force/displacement curves if the spring constant of the cantilever is known.

Once force mode has been engaged the 'force cal' menu is displayed on the 'menu' monitor and the AFM output curve on the 'image' monitor.
The AFM output curve consists of two sections. The first is the approach curve which shows the displacement of the cantilever before it is affected by surface forces, then undergoing a ‘jump’ as it is attracted to the sample and finally the movement of the tip and sample once they are in contact. The withdrawal curve shows the opposite motion; the tip and sample moving in contact, then the ‘pull-off’ as the tip leaves the sample surface and finally the tip returning to its rest initial position. The relative movements of the tip and the sample in the output curve are discussed in section 3.5.1. and are illustrated in Figure 3.13.

The ‘force cal’ menu allows the optimisation of the force curves for the desired purpose. In the current study it is the approach curve that is of interest so this is the region that is focussed upon. In force mode the Nanoscope II continually moves the sample into and out of contact with the tip. The distance the sample moves, known as ‘S scan’, and the frequency of the ‘in-out’ cycle, sampling rate, can be controlled. The effect of the sampling rate is discussed in section 3.5.4. The ‘S scan’ distance is reduced as much as possible to improve the level of detail of the jump region and reduce error in the layer thickness measurements, however the total distance must still be large enough to allow the tip to pull free of the liquid layer on withdrawal (Figure 3.11).

The graph range can also be adjusted to maximize the region of interest on the force curve and again reduce the error in the layer thickness measurements, (Figure 3.12). The set point may also need adjusting to bring the force curve on to scale.

Once the desired AFM output curve can be seen it is captured electronically, and manipulated through software to provide the required data for further analysis.

When using the Nanoscope II in force mode the tip and sample move continually into and out of contact. It is not possible to obtain an AFM output curve for a single contact.
3.5 Layer Thickness Measurements

3.5.1 Interpretation of the AFM output curve

An AFM output curve records the relative movements of the cantilever and the sample (Figure 3.13). From this output curve the thickness of the adsorbed water layer can be determined. The water layer thickness can be inferred from the sum of the distances moved by the tip and the sample from the point at which rapid
Atomic Force Microscopy

cantilever displacement is initiated (point A, Figure 3.13), to the point of solid contact (point B, Figure 3.13). The region A-B is known as the ‘jump-on’ region. Once the tip has made contact with the solid sample surface the tip and sample move together. This is known as the contact region. As the tip is withdrawn from the surface there is a point C at which the tip loses contact with the sample but is still held within the liquid layer. As the tip and sample are further separated a liquid neck will form. Finally the liquid neck will break (point D) and the cantilever will return to its initial position. The region C-D is known as the ‘pull-off’ region.

Figure 3.13 - Schematic of an AFM output curve.

The AFM output curve illustrated in Figure 3.13 illustrates the relative movements of the cantilever and sample, for a stiff silicon cantilever. If a ‘softer’ conventional imaging cantilever is used the AFM output curves obtained will have a slightly different form, where it is not possible to view the entire pull-off region as it is beyond the maximum range of the graph. The use of a stiff cantilever allows the piezo crystal scaling to be minimized and it is possible to gain a more detailed view of the ‘jump-on’ region, as discussed in section 3.3. In this work, it is only the jump-on section of the approach curve that is studied.
3.5.2 Jump-on Region

The force mechanisms acting between the cantilever, the sample and their respective adsorbed water layers during the jump-on region are complex. The solid sample surface will be moved through a distance \( d_s \) by the action of the piezoelectric crystal and the cantilever tip will travel a distance \( d_c \) in this 'jump-on' region under the influence of attractive forces arising from a number of sources or mechanisms. The sum of the distances moved by the cantilever tip and the sample through the jump-on region, which can be determined from an AFM output curve, is known as the tip-sample separation distance, \( d \).

In the present system, i.e. a cantilever tip, with an adsorbed water layer, approaching a sample surface with an adsorbed water layer in ambient air, the likely contributing forces which cause the cantilever movement are van der Waals, electrostatic and capillary forces, arising from the presence of adsorbed liquid layers.

As the tip and sample approach each other the cantilever tip may first be attracted towards the sample, prior to the onset of the 'jump', by van der Waals forces, leading to a deflection of the cantilever, \( d_{\text{def}} \) (I, Figure 3.14). The adsorbed liquid layers on the tip and sample may also be attracted to each other and 'bulge' towards each other - this phenomenon is discussed in greater detail in section 3.5.7. As the tip and sample continue to approach, the surfaces initially jump into contact, due to mechanical instability, through a distance \( d_{\text{VDW}} \), under the influence of van der Waals forces (II, Figure 3.14). Once the two liquid surfaces are in contact a capillary effect will pull the tip and sample into solid contact through the thickness of the combined adsorbed layers, \( 2t \) (III, Figure 3.14). Consequently the separation distance, \( d \), is made up of the adsorbed layer thicknesses, \( 2t \), plus a combined contribution from van der Waals interactions causing a cantilever deflection, \( d_{\text{VDW}} + d_{\text{def}} \). The contribution of the van der Waals interactions to the jump distance must be quantified and if necessary taken into account during the calculation of the adsorbed layer thickness from the separation distance.
3.5.3 *Van der Waals Contribution*

An experiment was carried out to compare the separation distance measured in air with that measured in a liquid medium. The purpose of this experiment was to eliminate the effect of the adsorbed water layers *i.e.* the capillary forces in order to quantify the magnitude of the contribution to the separation distance by van der Waals and electrostatic interactions. In air the jump distance is expected to be dominated by the adsorbed layer thickness, when using stiff cantilevers. In a liquid medium there is no air/liquid interface to give rise to capillary forces and consequently the jump distance can be attributed to the effect of van der Waals and electrostatic forces. The contribution from electrostatic charge is likely to be small, as the majority of the electrostatic forces will be dissipated by the presence of the water and by the doping within the cantilever tip. There may however be a negative contribution from the electric double layer effect, which is caused by the dissociation of surface ions leading to an atmosphere of counterions close to the surface and a negatively charged surface. As two negatively charged surfaces approach contact, *i.e.* the cantilever tip and the sample, the surfaces will repel one another.
Force curves were obtained for a silicon tip interacting with a silicon wafer sample in the two media. The first medium was air, with an ambient relative humidity of 41%, where water is assumed to be adsorbed on both the tip and the sample. Force curves were also measured in the AFM fluid cell containing water as the liquid medium. Prior to the experiment the cantilever tip were cleaned as described in section 6.2.3.4. Comparison of the displacement of the cantilever, \( d_c \), in the ‘jump-on’ region (between points A and B in Figure 3.13) in both media provides a measure of the contribution of van der Waals forces to the separation distance, \( d_{V_{DW}} + d_{d_{def}} \). The same cantilever and silicon sample were used throughout the experiment to preclude systematic errors. The results are shown below in Table 3.3.

Table 3.3 - Comparison of the cantilever displacement measured in air and in water.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Cantilever Displacement, ( d_c )</th>
<th>Standard Deviation</th>
<th>No. of Curves</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIR</td>
<td>7.43 nm</td>
<td>0.22</td>
<td>5</td>
</tr>
<tr>
<td>WATER</td>
<td>0.66 nm</td>
<td>0.37</td>
<td>20</td>
</tr>
</tbody>
</table>

It can be seen that the cantilever displacement in air is significantly larger than that under water. Assuming that the distance \( d_c \) in water represents the total van der Waals attraction in air \( (i.e. d_{V_{DW}} + d_{d_{def}}) \) then in air the van der Waals force contribution is approximately 9% of the cantilever displacement. This is equivalent to 8% of the total separation distance \( (i.e. d_c + d_s) \). In the current study this contribution to the separation distance has not been considered in the calculation of layer thickness from separation distance.

The larger standard deviation of the data in water compared with the values obtained in air can be attributed to the introduction of the O-ring in the AFM fluid cell, required for sealing. This will introduce a source of noise into the system as it constitutes a mechanical link between the tip and the sample.
The van der Waals contribution to the cantilever displacement can also be calculated theoretically. Tabor & Winterton (1969) proposed that the ‘jump-on’ occurs due to a mechanical instability when the rate of change of attractive force with separation exceeds the spring constant. If the attractive force is assumed to be purely due to a non-retarded van der Waals interaction, for a cantilever tip, approximated as a sphere coming into contact with a planar sample, the force is given by:

\[ F = \frac{A r}{6d_{VDW}^3} \]  

(3.1)

where \( A \) = Hamaker's constant (J)  
\( r \) = radius of the cantilever tip (m)  
\( d_{VDW} \) = tip/sample separation (m)

The force on the cantilever is given by:

\[ F = kd_{defl} \]  

(3.2)

where \( k \) = spring constant (N m\(^{-1}\))  
\( d_{defl} \) = cantilever deflection (m)

The cantilever instability occurs when the rate of change of attractive force exceeds the spring constant.

\[ \frac{d(kd_{defl})}{dd_{defl}} < \frac{d}{dd_{VDW}} \left( \frac{A r}{6d_{VDW}^3} \right) \]  

(3.3)

Since \( dd_{defl} = -dd_{VDW} \), then the jump occurs when:

\[ \frac{A}{3d_{VDW}^3} = \frac{k}{r} \]  

(3.4)

The separation distance, \( d_{VDW} \), of the tip and the surface at the point of the instability can be calculated from equation 3.4. Also the deflection of the cantilever prior to the
instability, $d_{\text{defl}}$, can be calculated. This deflection can be shown to be equal to exactly half the distance travelled through the instability, as shown below:

At the point at which the jump to contact occurs the force acting on the cantilever tip (equation 3.2) and van der Waals forces acting on the tip (equation 3.1) are equal, consequently equations 3.1 and 3.2 can be combined to give:

\[
\frac{Ar}{6d_{\text{VDW}}^2} = kd_{\text{defl}}
\]  

(3.5)

Also equation 3.4 can be rearranged to give:

\[
k = \frac{Ar}{3d_{\text{VDW}}^3}
\]

(3.6)

Combining equations 3.5 and 3.6 gives

\[
\frac{Ar}{6d_{\text{VDW}}^2} = \frac{Ar}{3d_{\text{VDW}}^3}d_{\text{defl}}
\]

\[
\Rightarrow d_{\text{defl}} = \frac{1}{2}d_{\text{VDW}}
\]

(3.7)

The Hamaker constant for the system has been calculated using Lifshitz theory (Appendix 1) and is $0.67 \times 10^{-20}$ J. The system considered is a silicon/silicon interaction with water as the intervening medium. This system is valid for both interactions in water and in air, where there are adsorbed water layers (see Appendix 1).

Using the above value for the Hamaker constant, together with a spring constant of 4.3 N/m (the nominal value for the cantilever provided by the manufacturer) and an assumed tip radius of 75 nm (section 6.2.2.3), the separation at which the 'jump-on' region starts can be calculated. The nominal tip radius of a new tip is quoted by the manufacturer as being 5-10 nm, however SEM images of AFM cantilevers which have been used for layer thickness measurements show some degradation of the tips due to wear, leading to an increased tip radius (Figures 6.3 and 6.4).
At the point of the instability, the tip/sample separation, \( d_{\text{VDW}} \), calculated from equation 3.4 is 0.34 nm and the cantilever deflection, \( d_{\text{defl}} \), calculated from equation 3.7, is 0.17 nm. Leading to a theoretically calculated cantilever displacement of 0.51 nm.

Table 3.4 - Comparison of experimental and theoretical cantilever displacements - in water.

<table>
<thead>
<tr>
<th></th>
<th>Cantilever Displacement, ( d_c )</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>0.66 nm</td>
<td>0.22</td>
</tr>
<tr>
<td>Theoretical</td>
<td>0.51 nm</td>
<td>n/a</td>
</tr>
</tbody>
</table>

It can be seen that the two values for the cantilever displacement are similar as the theoretical value is within the standard deviation of the experimental value. However, in the theoretical calculation of cantilever displacement it has been assumed that the force acting between the tip and the sample can be attributed solely to van der Waals interactions, whereas there may be other force mechanisms acting which may increase or decrease the force measurement.

3.5.4 *Calculation of Layer Thickness and Contact Gradients*

As discussed in section 3.5.1 the tip sample separation distance, \( d \), from which the adsorbed layer thickness can be calculated, is taken to be the sum of the distances moved by the tip and the sample from the point at which the tip first touches the water layer to the point of solid contact (Figure 3.13), \( d = d_c + d_s \).

Separation distance data are obtained from AFM output curves. The x-y pixel coordinates for the points A and B (Figure 3.13) are recorded together with the horizontal and vertical scalings (\( S_x \) nm/division & \( S_y \) V/division). The AFM output curve records the movement of the sample in nm and the displacement of the cantilever in volts. It is known that there are 20 pixels per division.
The sample movement is calculated as follows:

\[ d_s = \frac{|x_B - x_A|}{20} S_x \]  

(3.8)

where \( d_s \) = displacement of the sample (nm)
\( x_A, x_B \) = x co-ordinates of points A and B respectively
\( S_x \) = horizontal scaling (nm/division)

The cantilever movement is calculated in a similar manner but an additional term is added to convert from output voltage to distance.

\[ d_c = \frac{|y_B - y_A|}{20} S_y \frac{1}{G_c} \]  

(3.9)

where \( d_c \) = displacement of the cantilever (nm)
\( y_A, y_B \) = y co-ordinates of points A and B respectively
\( S_y \) = horizontal scaling (V/division)
\( G_c \) = contact region gradient (V/nm)

The contact region gradient, \( G_c \), essentially calibrates the cantilever deflection, as in this region the cantilever tip and the sample are in contact and so any displacement of the sample, through a piezo movement, should lead to an identical displacement of the cantilever tip. However, if the sample material is more compliant than the probe tip then the tip may cause a deformation of the sample. If this occurs the cantilever deflection is not accurately calibrated and will lead to an underestimate of the cantilever contribution to the layer thickness measurement. This effect has been noted by Li et al. (1993) and Ducker et al. (1991). Both parties therefore suggest independently calibrating the cantilever deflection using a rigid substrate, such as steel or silicon.

In the current work, the contact gradient has been measured prior to each experiment against a silicon substrate. These values have then been used in the calculation of separation distance. Typical contact gradient values range from 0.067 to 0.143 V/nm.
Atomic Force Microscopy

The large range of contact gradient values has been attributed to non-linearities in the expansion and contraction of the piezo electric crystal. This is discussed in detail in section 6.2.3.4.

3.5.5 Sampling Rate

In force mode, the Nanoscope II continually moves the tip in and out of contact with the sample. Each approach and withdrawal is one cycle. The number of cycles per second is known as the sampling rate. Alternatively it can be thought of as the ‘on-screen’ refresh rate. The Nanoscope II allows variation of the sampling rate between 0.01 and 25 Hz.

An experiment was performed to investigate the effect of the scanning rate on the separation distance. The separation distance was measured, on a silicon sample, for a range of sampling rates at two relative humidities. For each sampling rate the value of the separation distance is an average of 5 measured values. The results are shown in Figure 3.14 and Figure 3.15. The values of separation distance, given in the two figures, are as measured using the AFM and calculated as described in section 3.5.3.

It can be seen that above a sampling rate of about 2.5 Hz the separation distance increases markedly although the relative humidity and hence the actual separation distance should not have changed. It can also be noted that at the higher scan rates there is more scatter in the data reflected by the larger error bars.

The increase in the separation distances at higher scan rates is thought to be due to the formation of a region of increased adsorbed layer thickness. As the tip is withdrawn from a sample surface a liquid neck is formed. When this neck breaks the liquid will flow back to a stable equilibrium position. However if the sampling rate is high, the tip may re-engage with the liquid surface before it has reached its equilibrium position. Consequently a larger separation distance will be measured than is actually present; this is illustrated in Figure 3.17.
Figure 3.15 - Variation of separation distance with sampling rate at 52% RH.

Figure 3.16 - Variation of separation distance with sampling rate at 66% RH.
In the current work a sampling rate of 1 Hz has therefore been used to avoid this potential error in separation distance measurement.

3.5.6 Hydrophobic Tips

Water will adsorb on to both the sample surface and the cantilever surface in ambient conditions. The separation distance determined using this AFM technique will contain contributions from both the water layer on the sample and the water layer on the tip.

Attempts were made to simplify the system by the elimination of any water present on the tip by rendering the AFM cantilever tips hydrophobic. Silane compounds (R-Si), such as dimethyldichlorosilane (C₂H₅Cl₂Si), which are known to have hydrophobic properties and can be obtained commercially for ‘water-proofing’ glassware, have been used to render both silicon wafer samples and AFM cantilever tips hydrophobic.

In order to coat a silicon sample, or tip, a fresh layer of the native surface layer must be available to the silane compound. The original native oxide layer must be stripped from the surface and a fresh layer formed. In the current study, the oxide layer was removed by soaking the tips in a basic peroxide solution (10 minutes in 2M NH₄OH + 1.5M H₂O₂). The new oxide layer was formed using an acidic peroxide solution (10 minutes in 1.5M HCl +1.5M H₂O₂). After each stage the tips were rinsed in distilled...
water. The tips were then carefully dried and immersed in a 2% solution of dimethyldichlorosilane (C₂H₆Cl₂Si) in octamethyldicyclosiloxane for 20 minutes. Any excess silane solution was removed by an ethanol rinse. This is an adaptation of the method described by Wàlivara et al. (1995).

Figure 3.18 - Silane coated AFM cantilever tip.

Figure 3.19 - Uncoated AFM cantilever tip.
It was found that the silane coated tips gave unreliable and unreproducible experimental data. The coated tips did not always give smaller values of separation distance than the uncoated ‘hydrophilic’ tips. SEM examination of the tips found that the silane coating was incomplete and appeared to have formed a web-like structure. Figure 3.17 and Figure 3.18 illustrate the difference in appearance of a silane coated and an uncoated tip.

Another method of rendering the silicon probes hydrophobic, by carbon sputtering\(^3\), was also attempted. However, contact angle measurements of a silicon/water sample, prepared and carbon coated in the same manner and at the same time as the cantilever tips, revealed that the coating was no more hydrophobic than the initial silicon sample. The contact angle results are shown below in Table 3.5.

<table>
<thead>
<tr>
<th>Silicon Sample</th>
<th>Contact Angle °</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Advancing</td>
<td>Receding</td>
<td>Average</td>
</tr>
<tr>
<td>Uncoated</td>
<td>85.1</td>
<td>55.7</td>
<td>70.4</td>
</tr>
<tr>
<td>Carbon Coated</td>
<td>77.0</td>
<td>66.0</td>
<td>71.5</td>
</tr>
</tbody>
</table>

An alternative approach to eliminating the water layer on the tip is to assume that if the tip and the sample are made of the same material, water adsorption will occur equally and at any given humidity the adsorbed layers will be of equal thickness. Hence, the layer thickness measured experimentally will be twice the thickness of the water layer on the tip, if the tip and the sample are made of the same material. This approach was used here to obtain a standard adsorption isotherm for silicon probe tips. The moisture adsorbed on the probe can then be accounted for when working with other samples. The procedure for this analysis is discussed in the following section.

\(^3\) kindly performed by the Department of Materials Science and Engineering, University of Surrey.
3.5.7 Instability of Liquid Layers Prior to Contact

3.5.7.1 Introduction

As discussed in section 2.2.2.5, it has been found, by previous investigators, that the thickness of the adsorbed layer measured using atomic force microscopy is greater than that measured using the more conventional technique of ellipsometry. The difference has been attributed to van der Waals forces pulling the surface of the film on the sample towards the film on the probe and \textit{visa versa}, and consequently initiating a liquid bridge at greater separation distances than would be expected. Hence, the AFM detects the separation of the two surfaces when this instability occurs, \textit{i.e.} the separation distance, which is greater than the sum of the adsorbed layers.

Forcada (1993), while relating the separation distance at which the instability occurs to the activity of the liquid, provides a methodology by which the thickness of an adsorbed liquid layer can be determined from this separation distance. The distance at which the instability occurs can be considered to be the separation distance as measured using atomic force microscopy, where the other contributions to the measured distance as discussed in section 3.5.3 are not considered. Forcada uses a sequential approach to the determination of the adsorbed layer thicknesses from the separation distance at which the instability occurs. First the formation of the liquid film is considered followed by the development of the instability.

3.5.7.2 Liquid film formation

Forcada (1993) considers a system of two liquid films adsorbed on two identical solid surfaces, facing each other across a gap, as illustrated in Figure 3.20. The interaction energy for a point on the surface of the liquid with the system, $U_{\text{total}} \text{ (J m}^{-3}\text{)}$, is given by equation 3.10, where the meaning of the terms is illustrated in Figure 3.21.
Figure 3.20 - System of two planar surfaces.

Figure 3.21 - System interactions.

\[ U_{\text{total}} = -U_{ILS}(t) + U_{ULS}(d-2t) - U_{ILS}(d-t) \]  
where \( t = \text{film thickness (m)} \)

\( d = \text{solid/solid separation (m)} \)

The interaction energy can be expressed in terms of the sum of the potential energies for the interaction:

\[ U_{ABC} = u_{AC}(z) + u_{BB}(z) - u_{AB}(z) - u_{BC}(z) \]
where $u_{AB}(z) = u_{BA}(z)$ (J m\(^{-3}\)) represents the potential energy for the interaction of a unit volume of A with a semi-infinite volume of B at a distance $z$, and A, B & C may be liquid (L), solid (S) or intervening medium (I).

The necessary condition for the existence of a condensed spreading film of liquid L of thickness $t$ on a solid S immersed in medium I is $U_{ILS} > 0$.

3.5.7.3 Perturbation of the liquid film

Once the films have been formed, Forcada (1993) suggests their surfaces may be unstable to small perturbations. The local thickness of the film at a position $(x,y)$ on the surface will be $t + e(x,y)$, where $t$ is the average film thickness and $e$ is the extent of the local deformation, as illustrated in Figure 3.20. The deformations do not affect the average layer thickness (i.e. no liquid is added to the film). The change in the total energy of the system from the unperturbed state to the state in which one film has been perturbed, with a perturbation $e$, is given by Forcada (1993) as:

$$E[e] - E[0] = \gamma_{LI} \int dx \int dy \left[ \left( \frac{\partial e}{\partial x} \right)^2 + \left( \frac{\partial e}{\partial y} \right)^2 \right] - 1 \right]$$

$$+ \int dx \int dy \left[ \int_{d-2t}^{d-2t-e} dz U_{LIL}(z) - \int_{d-t-e}^{d-t-e} dz U_{ILS}(z) + \int_{t+e}^{t+e} dz U_{ILS}(z) \right]$$

(3.12)

where $\gamma_{LI} =$ surface tension at the liquid/intervening medium interface (N m\(^{-1}\)).

For a small perturbation of the form:

$$e = \hat{e} \cos(kx)$$

(3.13)

where $\hat{e} =$ amplitude of the perturbation (m)

$k =$ wave number (m\(^{-1}\))

$x =$ position of the perturbation (m)

and $e \ll t$ (film thickness (m))

$e \ll d$ (solid/solid separation distance (m))
the change in energy per unit area is given by:
\[ \Delta e = \varepsilon^2 (\gamma_{LL} k^2 - f)/4 \]  (3.14)

where
\[ f = U'_{LL}(d - 2t) - U'_{LS}(d - t) - U'_{LS}(t) \]  (3.15)

and
\[ U'_{ABC} = \frac{dU_{ABC}}{dz} \]  (3.16)

The system will become unstable and the perturbation will grow (i.e. formation of a liquid bridge) if \( \Delta e \) is negative. The rate of growth of the perturbation is controlled by the viscosity of the liquid film. The system will only become unstable if the value of the function \( f \) is positive and the wave number, \( k \), of the perturbation is smaller than \( k_c \), where \( k_c \) is the critical value of \( k \) that gives \( \Delta e = 0 \). From equation 3.14, it can be seen that when \( \Delta e = 0 \), the critical wave number \( k_c \) is given by:

\[ k_c = \sqrt{\frac{f}{\gamma_{LL}}} \]  (3.17)

A critical separation distance can be calculated below which instabilities start to be possible. This critical distance corresponds to the solid/solid separation distance, \( d \), that reduces the function \( f \) to zero. This critical value sets an upper bound to the jump to contact distance. Actual distances will be smaller because the finite size of the real system will define a minimum wave number \( k_c \).

3.5.7.4 Van der Waals interactions

Forcada (1993) assumes that all the forces in the system can be attributed to be non-retarded van der Waals interactions and consequently for a unit volume of A interacting with a semi-infinite volume of B, at a distance \( z \), the basic interaction is of the form:
Israelachvili (1991) comments that at distances beyond about 5 nm the assumption of non-retarded interactions is not strictly valid. Both in the current work and in the work of Forcada (1993) the separation distance may, at times, be larger than this value. However as there is no simple equation for the van der Waals force at all separations, which takes into account both the region of non-retarded and the region of retarded interactions, then the simple expression for non-retarded interactions is most appropriate.

An expression for the function \( f \), (equation 3.15), can be obtained by substituting equation 3.18 into equation 3.11 and differentiating:

\[
\begin{align*}
\frac{\gamma_{LS}}{2\pi} + \frac{A_{LL}}{2\pi} \left( \frac{1}{t^4} - \frac{1}{(d-t)^4} \right)
\end{align*}
\]  

(3.19)

3.5.7.5 Determination of layer thickness - similar solid surfaces

In the present study, experimental data, measured using the AFM technique, give the solid/solid separation at the point at which the instability occurs, \( i.e. \) the separation distance. The actual thickness of the layer adsorbed on the sample surface can be determined by setting the value of the function \( f \) to zero in equation 3.19, substituting the experimental values of the separation distance, \( d \), and solving for the layer thickness, \( t \). This will give the minimum layer thickness that can cause an instability at a given separation. As discussed in section 3.5.7.3 the actual layer thickness will be larger than this minimum value, due to the presence of a finite value of the critical wave number, \( k_c \). Consequently equation 3.19 should be solved by setting the function \( f \) equal to the value of \( \gamma_{LL}k_c^2 \) (equation 3.15). However, for a system of water adsorbed on silicon surfaces the solution of the adsorbed layer thickness is insensitive even to large changes in the value of \( k_c \), as illustrated in Table 3.6 where the change in the adsorbed layer thickness is only observable in the ninth decimal place.
Consequently in the current work, values of the adsorbed layer thickness have been determined when the critical wave number $k_c$ is considered to be zero.

Table 3.6 - Variation of adsorbed layer thickness with $k_c$.

<table>
<thead>
<tr>
<th>$k_c$ m</th>
<th>$\gamma_l k_c^2$</th>
<th>Separation distance (nm)</th>
<th>Adsorbed layer thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>4</td>
<td>1.663648401</td>
</tr>
<tr>
<td>3700</td>
<td>$1 \times 10^9$</td>
<td>4</td>
<td>1.663648402</td>
</tr>
</tbody>
</table>

3.5.7.6 Dissimilar solid surfaces

The theory of Forcada (1993) only considers systems comprising two identical sample surfaces. Therefore, of the systems studied using atomic force microscopy, with stiff silicon cantilevers, this theory is only applicable to the measurement of adsorbed water layers on silicon samples.

In the previous sections because the system was symmetrical, the choice of liquid layer from which to consider the overall interaction was immaterial, as was the layer in which the perturbation was introduced. Now, although the theory of section 3.5.7.2 can be used to develop an interaction expression (equation 3.20) for a system, which comprises two different solid materials, $S_1$ and $S_2$, and which due to their different surface properties will adsorb water layers of different thicknesses, $t_1$ and $t_2$, (Figure 3.22), it will not be valid due to the lack of inherent system symmetry.

Figure 3.22 - System Interactions.

$$0 - U_{LS_1}(t_1) - U_{LS_2}(t_1) - U_{UL}(d-t_1-t_2) + U_{UL}(d-t_1-t_2) - U_{LS_2}(d-t_2)$$

System interactions
The total interaction energy for the asymmetrical system in Figure 3.22 can be written as:

$$U_{\text{total}} = -U_{\text{ILS}}(t_1) + U_{\text{ILS}}(d - t_1 - t_2) - U_{\text{ILS}}(d - t_2)$$ (3.20)

The problem of the lack of symmetry in equation 3.20 is illustrated in Figure 3.23.

Figure 3.23 - Non symmetrical system.

Here, the adsorbed layer thickness on the lactose sample determined when the interaction is considered from the water layer above the lactose sample is different to the thickness determined when the interaction is considered from the water layer above the silicon sample. Consequently, it can be seen that the theory of Forcada (1993) cannot simply be extended to take account of the two solid surfaces being of different materials and an alternative approach to the problem must be sought.

3.5.7.7 Determination of layer thickness - dissimilar solid surfaces

In the previous section it was shown that the theory of Forcada (1993) cannot be easily adapted to take account of the two solid surfaces being of different materials. However for the current work an approach has been developed which allows the calculation of the thickness of an adsorbed water layer from experimental data, for a material surface which is different from that of the AFM cantilever tip (i.e. not
This approach comprises three steps and is described in general terms of the adsorption of water on two different samples S₁ and S₂.

First, the thickness of the adsorbed water layer, \( t_{S1} \), on the surface S₁ must be determined from experimental data. If it is assumed that water adsorbs equally on identical materials, Figure 3.24 (a), then the adsorbed layer thickness on surface S₁ can be determined, using equation 3.19, from the experimentally determined separation distance, \( d_{S1} \), for the interaction between two S₁ surfaces. The half separation distance, \( \frac{1}{2}d_{S1} \), is also determined from the experimental data. It is taken to be half of the experimental separation distance Figure 3.24 (b).

Second, the separation distance \( d_{\text{total}} \) for a system with two different solid materials, surfaces S₁ and S₂, is determined experimentally. This separation distance can be considered to be the sum of the half separation distance for surface S₁, \( \frac{1}{2}d_{S1} \), and the half separation distance for surface S₂, \( \frac{1}{2}d_{S2} \), Figure 3.24 (c). Once the separation distance, \( d_{\text{total}} \), is known the half separation distance for surface S₂ can be calculated, Figure 3.24 (d), as the half separation distance for surface S₁ has been determined previously.

Finally, a theoretical separation distance, \( d_{S2} \), for the interaction of two S₂ surfaces can be calculated by doubling the half separation value, \( \frac{1}{2}d_{S2} \), Figure 3.24 (e), and
The relative humidities used in the current study have been limited to the range 10-70%. With the current equipment it was not possible to achieve lower humidities. Humidities greater than 80% were thought to pose a risk to the instrument, and hence a ‘safe’ maximum limit of 70-75% RH was used.
hence the thickness of the adsorbed water layer on the surface $S_2$, $t_{S2}$, can be
determined from equation 3.19.

This method provides a fairly simplistic approach to the calculation of adsorbed layer
thickness for the interaction of two different materials. It is unlikely that the distance
at which the two surfaces jump into contact can be considered as two discrete regions
as there will always be an interaction, of some form and magnitude, across the
separation distance. However, as will be shown later, in chapter 6, the difference
between the separation distance, measured by the AFM, and the adsorbed layer
thickness for a silicon/silicon interaction i.e. two identical materials, is significant. It
would be remiss not to attempt to determine, albeit approximately, the thicknesses of
adsorbed water layers from experimental data for the interaction between two
different surfaces, as the difference in values could also be expected to be significant.

3.6 Adsorption Isotherms

3.6.1 Introduction

Adsorption isotherms can be obtained for a single point on a sample surface by
measuring the thickness of the adsorbed water layer as the relative humidity is varied.
It is also possible to obtain a more general adsorption isotherm for a sample by
averaging several single point isotherms.

3.6.2 Humidity control

In the current study, adsorption isotherms are obtained by measuring the adsorbed
layer thickness in a closed chamber as the relative humidity is varied. The humidity
is either ramped up or down and measurements are recorded at the required humidity
values. The humidity is increased from atmospheric using an open container of
distilled water to increase the vapour pressure within the enclosed chamber. To
decrease the humidity, silica gel is used to remove water vapour from the enclosed
environment.

* see facing page
The humidity chamber encloses only the AFM hardware, as seen in Figure 3.1. Air is circulated around the chamber using a small electric fan. The relative humidity is measured using a humidity probe\(^4\).

An experiment has been performed to ensure that the layer thickness, at a given relative humidity, obtained using this dynamic technique can be considered to be the equilibrium value. A silicon sample, for which a dynamic adsorption isotherm had previously been obtained, (see section 6.2), was placed in the humidity chamber together with a saturated solution of potassium acetate (CH\(_3\)COOK) which would maintain the relative humidity. After 6 hours the relative humidity had been reduced to a constant equilibrium value of 33%. The chamber remained at this humidity for a further 23 hours to ensure the adsorbed water layer on the sample had reached equilibrium. At this time, 29 hours after the start of the experiment, adsorbed layer thickness measurements were taken. The results shown in Table 3.7 give the equilibrium adsorbed layer thickness, measured after prolonged exposure to a constant relative humidity and the adsorbed layer thickness measured in a dynamic experiment. The layer thickness values presented here have been adjusted to take the instability of the liquid film prior to contact into account according to the methodology in section 3.5.7.

Table 3.7 - Dynamic vs. equilibrium layer thicknesses.

<table>
<thead>
<tr>
<th>Layer Thickness Measurement (nm)</th>
<th>Standard Deviation</th>
<th>Number of points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynamic humidity</td>
<td>2.28</td>
<td>0.11</td>
</tr>
<tr>
<td>Equilibrium humidity</td>
<td>2.31</td>
<td>0.24</td>
</tr>
</tbody>
</table>

It can be seen that the two values for layer thickness are almost identical, falling within one standard deviation of each other. These results indicate that the equilibrium thickness of the layer appears to be established effectively instantaneously.

\(^4\) Vaisala HM31 supplied by RS, PO Box 99, Corby, Northants.
Prior to equilibrium, it is expected that the rate of water adsorption will be different to the rate of desorption and consequently the values of the dynamically measured layer thickness should differ depending if they are obtained during adsorption or desorption. Of the data points measured for the average dynamic layer thickness value, given in Table 3.7, two were obtained during moisture uptake (adsorption) and the remaining three during desorption. From the data it is impossible to draw any firm conclusions about the differences in rate between adsorption and desorption.

3.7 Conclusions
An atomic force microscope technique has been developed to determine the thickness of the adsorbed water layer, from the AFM output curve as a function of relative humidity. A separation distance, \( d \), is determined to be the sum of the distances moved by the cantilever tip and the sample during the ‘jump-on’ region, from the point at which a rapid cantilever displacement is initiated to the point of solid contact.

It has been found that the van der Waals interactions, determined under water where there are no adsorbed layers, contribute approximately 8% of the total separation distance measured in air. In the current study this contribution has not been considered in the calculation of layer thickness from separation distance.

The van der Waals contributions to the cantilever displacement has been determined theoretically and it has been found that the theoretical value lies within the same range as the experimentally determined values.

In the current study the contact gradient has been determined using a rigid silicon sample, to eliminate possible indentation effects, however a large range of contact gradient values have been recorded. This range of values is attributed to non-linearities in the expansion and contraction of the piezo crystal which is discussed in greater detail in chapter 6.
It has been shown that at AFM sampling rates greater than 2.5 Hz an increased separation distance is observed (at constant humidity). The increase in separation distance is attributed to the formation of a region of increased adsorbed layer thickness. This occurs when the liquid neck, formed as the cantilever tip is withdrawn from the sample surface, breaks and the liquid which was contained within the neck does not have time to return to a stable equilibrium position before the tip re-engages the liquid layer. In the current study a sampling rate of 1 Hz was used for all experimental measurements.

In order to simplify the contributions to the separation distance attempts were made to eliminate the presence of adsorbed water on the cantilever tips by rendering them hydrophobic. Neither of the two methods tried, silane coating and carbon sputtering, gave reliable results.

Forcada (1993), while relating the separation distance to the activity of the adsorbed liquid, provided a method by which the thickness of the adsorbed layers, on identical surfaces, can be determined from the separation distance. In the present study, systems have been studied in which the cantilever tip and sample are made of different materials. It has been shown that the theoretical approach of Forcada cannot simply be extended to include non-symmetrical systems (i.e. where the cantilever tip and sample are made of different materials). Consequently, a three step process has been proposed for the calculation of layer thickness for a two component system. First, the half separation distance associated with the cantilever tip is determined from experimental data for the tip interacting with a surface of the same material, i.e. a silicon sample. Second, the separation distance for a two component system is determined experimentally. This distance is assumed to be the sum of the half separation distance for the cantilever tip and the half separation distance for the sample. Consequently, the half separation distance for the sample can be calculated. Finally, a theoretical separation distance is determined for the sample material, equal to twice the half separation distance, and from this the adsorbed water layer on the sample surface can be determined.
Adsorption isotherms can be obtained for a single point on a sample surface by measuring the thickness of the adsorbed water layer, using an atomic force microscope and subsequent analysis, as the relative humidity of the surrounding environment is varied. It is also possible to obtain a more general adsorption isotherm for a sample material by averaging several single point isotherms.

It has been demonstrated that the layer thickness values determined using this dynamic method are comparable to values measured after prolonged exposure (23 hours) to a constant relative humidity and consequently it can be concluded that the equilibrium thickness of the layer appears to be established effectively instantaneously.
4. MODELLING

4.1 Introduction

The purpose of this chapter is to comment in greater detail on the various methods of predicting adsorbed layer thickness, and to discuss their various merits.

As mentioned in chapter 2, the DLVO theory is the only model which predicts the adsorbed layer thickness, from a purely theoretical basis, rather than relying on any empiricism. The polarization theory, which has been dismissed from a theoretical viewpoint for this specific application, is however useful as a method fitting experimental data, particularly for the adsorption of water.

4.2 DLVO Theory

As discussed in section 2.2.3.2 the DLVO theory was developed separately by Derjaguin & Landau (1941) and Verwey & Overbeek (1948) for colloid stability although it has subsequently been applied to many different systems.

The DLVO theory can be used to relate the thickness of an adsorbed water layer to the vapour pressure of a system via the disjoining pressure, $\Pi$. A definition of disjoining pressure is given in section 2.2.3.2. For a thin film the disjoining pressure $\Pi$ can be related to the vapour pressure of the film by:

$$
\Pi = \frac{-kT}{v_m} \ln \left[ \frac{p}{p^0} \right]
$$

(4.1)

where

- $p$ = partial vapour pressure (Pa)
- $p^0$ = saturated vapour pressure of the liquid (Pa)
- $T$ = temperature (K)
- $k$ = Boltzmann’s constant (J K$^{-1}$)
- $v_m$ = molecular volume of the liquid ($m^3$ molecule$^{-1}$)
The DLVO theory takes into account contributions to the disjoining pressure from van der Waals interactions ($\Pi_{VDW}$) and from electrostatic interactions ($\Pi_{EL}$). These contributions are assumed to be additive as follows (Derjaguin and Churaev 1974):

$$\Pi = \Pi_{VDW} + \Pi_{EL}$$

(4.2)

These contributions can be expressed as:

$$\Pi = \frac{-A}{6\pi t^3} + \frac{8\varepsilon_0}{2t^2} \left( \frac{\pi kT}{ze} \right)^2$$

(4.3)

where $t =$ layer thickness (m)

- $A =$ Hamaker’s constant (J)
- $\varepsilon =$ relative permittivity of the adsorbate (-)
- $\varepsilon_0 =$ permittivity of free space (constant) ($C^2 J^{-1} m^{-1}$)
- $k =$ Boltzmann’s constant (J K$^{-1}$)
- $T =$ temperature (K)
- $z =$ valency (-)
- $e =$ electronic charge (C)

The van der Waals contribution is based on a simple non-retarded van der Waals interaction between two planar surfaces, (Pashley and Kitchener 1979), i.e. the surface of the solid sample and the surface of the liquid film. On a spherical particle, where particle radius is large compared with the thickness of the adsorbed layer, both surfaces will have a degree of curvature however they will still be parallel and can be considered to be planar surfaces. However, if the particle radius is similar in magnitude to the layer thickness the system becomes more complex; the curved surface will have an increased energy state and hence an increased partial vapour pressure as described by the Kelvin equation; additionally there will be a significant discrepancy between the surface area of the particle and the surface area of the adsorbed layer.
Modelling

The van der Waals interaction used in the disjoining pressure expression is based on the assumption of additivity, whereby it is assumed that the interaction between a molecule on one surface with a molecule on a second surface is not affected by the surrounding molecules within a bulk structure.

The assumption of additivity inherent in $\Pi_{VDW}$ can be overcome by the calculation of the Hamaker constant from Lifshitz theory (appendix 1), where the atomic structure is ignored and the interaction between large bodies, now treated as continuous media, are derived in terms of bulk properties namely, the optical characteristics of the material with respect to the whole electromagnetic spectrum.

As mentioned in section 3.5.7.4 Israelachvili (1991) comments that beyond about 5 nm the assumption of non-retarded interactions is not strictly valid. However, as there is no simple equation for the van der Waals interaction at all separations, which takes into account both the region of non-retarded and the region of retarded interactions, then the simple expression for non-retarded interactions is most appropriate.

The expression for the electrostatic contribution $\Pi_{EL}$ in equation 4.3, is determined from the electrostatic double layer theory, in which it is assumed there are no solute ions in solution, (Pashley and Kitchener 1979). The theory can be extended to take the presence of solute ions in solution into consideration, (Israelachvili 1991). The electrostatic contribution then becomes:

$$\Pi_{EL} = 2kT\rho_{m} \left[ \cosh \left( \frac{e\psi_{m}}{kT} \right) - 1 \right]$$ \hspace{1cm} (4.4)

where $\psi_{m} = \frac{2kT}{e} \log \left[ \frac{1 + \gamma e^{-xt}}{1 - \gamma e^{-xt}} \right]$ \hspace{1cm} (4.5)
and \[ \kappa = \left( \sum_{i} \frac{\rho_{si} e^2 z_i}{\epsilon_0 kT} \right)^{\frac{1}{2}} \] (4.6)

and \[ \gamma = \tanh \left( \frac{e\psi_0}{4kT} \right) \] (4.7)

where \( t \) = film thickness (m)
\( e \) = electronic charge (C)
\( k \) = Boltzmann’s constant (J K\(^{-1}\))
\( T \) = temperature (K)
\( z_i \) = valency of species i (-)
\( \varepsilon \) = relative permittivity of the adsorbate (-)
\( \varepsilon_0 \) = permittivity of free space (C\(^2\) J\(^{-1}\) m\(^{-1}\))
\( \kappa \) = inverse Debye length (m\(^{-1}\))
\( \rho_{in} \) = ionic concentration away from the surface (m\(^{3}\))
\( \rho_{si} \) = ionic concentration away from the surface of species i (m\(^{3}\))
\( \psi_0 \) = electrostatic potential at the surface (V)
\( \psi_m \) = electrostatic potential away from the surface (V)

Derivations of the electrostatic contributions to the spreading pressure, with and without the presence of solute ions can be found in Israelachvili (1991) chapter 12, p 213.

Equation 4.4 can be incorporated into equation 4.2 for the prediction of layer thickness, when the adsorbed layer contains solute ions. A low concentration of solute ions may arise from airborne or surface contamination, however, a more significant effect will be the dissolution of the sample surface. In the current work, of the materials studied, only lactose is considered to be soluble to any extent. The equilibrium solubility of \( \alpha \)-lactose monohydrate is given by Whittier (1944) to be 16.9 g/100 g water at 15 °C and 21.6 g/100 g water at 25 °C. This corresponds to equilibrium concentrations of 0.49 M and 0.63 M respectively. A ‘pure’ liquid, such
Modelling

as water will always contain some solute ions, from molecular dissociation, in the case of water the solute concentration is $10^{-7}$ M, (Israelachvili 1991). The solute concentrations for water and dissolved lactose have been taken as the limits of the concentration for the adsorbents and adsorbates used in the current work.

The adsorbed layer thickness is related to the relative vapour pressure via the disjoining pressure by solution of equations 4.1 and 4.3. The disjoining pressure is calculated from a given value of adsorbed layer thickness using equation 4.3 and from this the relative vapour pressure can be determined using equation 4.1. In the current study the following input parameters have been used for the solution of equations 4.3 and 4.1: relative permittivity of the adsorbate (water), $\varepsilon = 78.5$, temperature, $T = 298$ K, valency, $z = 1$, molecular volume of the liquid, $v_m = 2.99 \times 10^{-29}$ m$^3$/molecule, and the Hamaker constant is dependent on the adsorbing surface but values for lactose, silicon and aluminium are given in appendix 1.

Figure 4.1 illustrates the adsorbed layer thicknesses predicted using the DLVO theory for water adsorption on a lactose surface, over the range of humidity values of interest in this study. It can be seen that the inclusion of electrolyte ions in the calculation, i.e. the use of equation 4.4, increases the prediction of layer thickness but the value of the ionic concentration does not play a major role. The difference between the values of the layer thickness calculated with no solute present (equation 4.3) and the values calculated with solute present (replacing the electrostatic contribution in equation 4.3 with equation 4.4) is no more than 0.1 nm. This is a significant difference in absolute terms, however both predicted curves show significantly lower values than the experimentally determined values presented in chapter 6.
Note, in Figure 4.1, 10^{-7} M represents a solute concentration of 10^{-7} M; the concentration of ‘pure’ water, and 0.5 M the approximate equilibrium concentration of dissolved lactose at 20 °C. These values have been taken to be the limits of solute concentration for the current study.

As discussed in section 2.2.3.2 several researchers have suggested the inclusion of an additional term in equation 4.2 to account for any structuring in the water layer. The inclusion of this term was first proposed by Derjaguin and Churaev (1974). Structuring is believed to arise from the attractive interactions between the solid surface and the liquid molecules and a geometric constraining effect which together force the liquid molecules to order into quasi-discrete layers, (Israelachvili 1991). Current theory is unable to predict the magnitude of this term; it is usually calculated to be the discrepancy between the predictions of the DLVO theory and experimental results.

4.3 Polarization Theory
Polarization theory was first proposed in 1929 by de Boer and Zwikker (1929). It suggests that the adsorption of non-polar molecules can be explained by assuming that
a polar adsorbent surface induces dipoles in the first adsorbed layer and that these in turn induce dipoles in the next layer, and so on (Adamson 1990 p 622). Bradley (1936) suggests that the first layer is built up according to Langmuir’s concept of unimolecular films and that the subsequent layers are not directly affected by the solid.

The polarization model can be expressed as:

\[ \log\left(\frac{p^o}{p}\right) = K_1 K_3^t + K_4 \]  

where \( p^o/p \) = inverse of the relative vapour pressure (-)  
\( t = \) thickness of the adsorbed film (m)  
\( K_1, K_3, K_4 = \) constants (-)

As discussed in section 2.2.3.3 the validity of the polarization model as a predictive theory is doubtful. However, the form of the resulting equation, (4.8), can be used successfully to fit experimental adsorption isotherm data (Bradley 1936, Garbatski & Folman 1956 and Badmann et al. 1981). In the current study, the ‘theory’ is used to fit experimental data for adsorption of water on a silicon sample, section 6.2.3.2, and provides an empirical expression for the adsorbed layer thickness as a function of humidity.

The constants are calculated from the experimental data in the manner suggested by Bradley. The value of \( K_4 \) is varied, by trial and error, so that \( \log[\log(p^o/p)-K_4] \) gives a linear plot with film thickness, \( t \). \( K_3 \) and \( K_1 \) can then be determined from the slope of the straight line and the intercept with the vertical axis. If equation 4.8 is being used to fit experimental data it is not critical to which base the log is taken. Bradley (1936) uses \( \log_{10} \), whereas the majority of the other investigators use natural logarithms. In the current work natural logarithms are used.
Equation 4.8 can be rearranged so that the adsorbed layer thickness, \( t \), can be expressed in terms of the relative humidity, \( p/p^o \).

\[
t = \frac{\ln \left( -\ln \left( \frac{p}{p^o} \right) - K_4 \right) - \ln K_1}{K_3}
\]

(4.9)

### 4.4 Conclusions

The DLVO theory can be used to predict the thickness of adsorbed water layers as a function of relative humidity via the use of the disjoining pressure. The disjoining pressure is considered to be made up of two components: a van der Waals interaction, and an electrostatic interaction. The electrostatic contribution is discussed for a system containing solute ions in the liquid layer and for a system without solute ions in the liquid layer. The difference in the magnitude of the predicted adsorbed layer thicknesses between the two systems is no more than 0.1 nm. This is significant in absolute terms but less so when compared with experimental data.

The validity of the polarization model as a predictive theory is doubtful, however it has been used successfully by previous investigators to fit experimental adsorption isotherm data (Bradley 1936, Garbatski & Folman 1956 and Badmann et al. 1981). In the current study, the form of the equation of the polarization theory has been used, in chapter 6, to fit experimental data to produce a single convenient empirical expression, but the theory has not been used to predict values of adsorbed layer thickness.
5. SAMPLE MATERIALS

5.1 Introduction
Experimental studies have been conducted on three materials; lactose, silicon wafer and aluminium foil. The relevance of each material together with material properties and a description of the sample preparation methods are discussed in the subsequent sections.

5.2 Lactose
5.2.1 Introduction
Lactose (milk sugar), is a disaccharide which appears naturally in the milk of all animals. Chemically, it consists of one galactose unit and one glucose unit. Lactose exists in two isomeric forms, α-lactose and β-lactose and can be either crystalline or amorphous. Crystalline α-lactose occurs in the monohydrate (C_{12}H_{22}O_{11}.H_{2}O) and the anhydrous forms (C_{12}H_{22}O_{11}), whereas β-lactose exists only in the anhydrous form, (C_{12}H_{22}O_{11}). Pure amorphous lactose is not commercially available. As a solid lactose appears in a white crystalline form. It is odourless and slightly sweet-tasting; α-lactose is approximately 15 % as sweet as sucrose. The structural formula of α and β lactose is shown in Figure 5.1.

Figure 5.1 - Structural formula for lactose.
Crude α-lactose monohydrate is produced from casein or cheese whey by evaporation and crystallization. For the production of pharmaceutical grade lactose, the crude product is purified by recrystallization. Depending on the temperature of crystallization, different types of lactose can be obtained; below 93.5 °C, lactose precipitates as α-lactose monohydrate, and above this temperature as anhydrous β-lactose.

It is however, expected that there will be a small proportion of β-lactose within the α-lactose monohydrate crystals, leading to inhomogeneity across the crystal surface (Ghadiri 1996). Small quantities of other impurities, such as phosphates, can also be expected within α-lactose monohydrate. It is known that within a crystalline structure these impurities tend to be found at the surface of the material.

Within the pharmaceutical industry milled lactose is used as a diluent for active drug ingredients, to provide accurate dosage and to enable easier handling and processing of the product. The importance of lactose to the pharmaceutical industry is discussed in greater depth in chapter 1. Because of its importance within the pharmaceutical and food industries, the properties of lactose are of great interest. For this reason lactose has been chosen to be the primary material studied in the current work.

Industrially, the form of lactose most commonly used is milled α-lactose monohydrate. In this study two sources of milled α-lactose monohydrate are studied together with ‘ideal’ laboratory grown crystals of α-lactose monohydrate.

5.2.2 Granulac 200
Granulac 200 is milled α-lactose monohydrate manufactured by Meggle GmbH. The mean particle size is 16 μm. Granulac has a tapped density of 0.66 g/cm³ and a nominal free water content of 5.1 % by weight. An SEM image of this material is referred to in the current work as granulac.
shown below in Figure 5.2. The wide size distribution of this material and the small mean particle size can be observed.

Figure 5.2 - Granulac.

Figure 5.3 - SEM image: Granulac particle.
Large particles, with an approximate diameter of 65 µm, have been selected for AFM experiments due to the difficulty in aligning the AFM cantilever tip to small particles. A typical particle used for adsorbed layer thickness measurement experiments is shown in Figure 5.3. It can be seen that the particle is relatively 'clean' as there is little debris on the surface. This level of surface debris is typical of large granulac particles, see Figure 6.17.

5.2.3 'Classified Lactose'

The second form of commercial lactose is milled and classified α-lactose monohydrate\(^2\) manufactured by DMV International. It has a mean particle size of 60 µm, a tapped density of 0.83 g/cm\(^3\) and a nominal free water content of 5.2 % by weight. An SEM image of this material is shown in Figure 5.4. It can been seen that the size distribution is comparatively narrow which is to be expected as the material has been classified.

A typical classified particle, as used in AFM experiments, is shown in Figure 5.5. It can be seen that there is a large amount of debris on the particle surface; this is common to classified lactose particles, see also Figure 6.22 which shows an AFM image of the same material.

The amount of surface debris observed on the classified particles is greater than that observed on the Granulac particles; compare Figure 5.3 and Figure 5.5.

\(^2\) referred to in the current work as classified.
5.2.4 Laboratory Crystals

The α-lactose monohydrate crystals are used in an attempt to provide a reference case for water adsorption on an 'ideal' α-lactose surface. Whereas adsorption on the industrially relevant lactose particles is likely to be influenced by, for example, the surface roughness and process history, the lactose crystals provide a 'flat' surface.
where the history of the crystal is known. An SEM image of a lactose crystal is shown in Figure 5.6.

The crystals were grown from solution by evaporation at the University of Strathclyde and have an approximate size of 500 µm. The final shape of the α-lactose monohydrate crystals is dependent upon the conditions under which they are grown. This is discussed in detail by Herrington (1934). The most common form, and that which is considered to be fully developed is illustrated in Figure 5.7. It can be seen that the lactose crystal shown in Figure 5.6 is this shape but is chipped at the tip. The face on which AFM experiments have been performed is shaded in Figure 5.7 and is the uppermost face in Figure 5.6, the 100 face. This face has been selected for experimentation as it provides a large flat area on which to land the tip and can be easily mounted so that the face is parallel to the sample disk i.e. it is not sloping.

Figure 5.6 - Lactose crystal.
5.2.5 Sample Preparation
Rhône-Poulenc Rorer supplied approximately 1 kg of each of the milled lactose samples, granulac and classified. The powder samples were stored in closed glass powder bottles, in ambient conditions, away from the light. Prior to sample mounting, a smaller sample, of a few grams, was acquired from the bulk. A few grains of this powder were then picked up using a small spatula and mounted on to an AFM mounting disk, via an acetate film, as described in section 3.4.1.1. Both the granulac and the classified lactose powders were mounted in the same manner.

The lactose crystals were stored in a petri dish in ambient conditions and away from light. The mounting of the lactose crystals is also described in section 3.4.1.1.

Once the samples had been mounted they were stored, in a closed petri dish to prevent gross contamination from airborne particulates.

5.3 Silicon Wafer
Silicon wafer has been selected as a sample material primarily because the AFM cantilevers and tips are manufactured from the same material and consequently it can be used to determine the adsorption isotherm for the cantilever tip, section 6.2.3. It is also used routinely in AFM work as a reference material with which to calibrate the cantilever movement, as discussed in section 3.5.4.
Silicon wafer will have a native oxide on the surface, SiO$_2$, with a thickness of a few nanometers. Mate et al. (1989) suggest the native oxide on their silicon samples has a thickness of approximately 1.5 nm. Other investigators suggest values for the thickness of the native silicon oxide layer in the range 0.5-2.5 nm; Chemelli et al. (1993) 0.5 nm, Tomizuka & Ayame (1995) 0.57 nm, Montreo et al. (1993) 1 nm, Sekar et al. (1995) 1.5 nm, and Kobayashi (1995) 2.5 nm. The silicon tip will also have a thin oxide layer on the surface, making the tip and the sample comparable materials.

Silicon wafer is also relatively flat as illustrated in Figure 5.8, an AFM image of a silicon wafer sample. Due to its planar nature silicon wafer has been used previously by at least one investigator (Beaglehole & Christenson 1992) to study the thickness of adsorbed water layers using an ellipsometric technique. However, unless the thickness of the oxide layer is accurately known, ellipsometry will prove difficult due to the presence of two thin films; water and the oxide layer. Beaglehole and Christenson (1992) strip the native oxide from the silicon surface using an HF etch and then create a well-formed thin oxide layer using HNO$_3$. They have measured the resulting oxide layer using ellipsometry, in the absence of adsorbed vapour, and find the layer to have a thickness of approximately 3 nm.

Figure 5.8 - AFM image of silicon wafer
Sample Materials

Silicon wafer samples were provided by the Department of Materials Science and Engineering at the University of Surrey. Samples, approximately 1 cm x 1 cm, were cut from a larger piece of wafer using a diamond scribe. It must be noted that different crystal faces of silicon may exhibit different properties. In the current work the crystal face of the silicon wafer was unknown.

Prior to experimentation the samples were soaked in propan-2-ol for 20 minutes to remove any surface grease. They were then carefully dried and mounted for experimentation in the manner described in section 3.4.1.1.

5.4 Aluminium Foil

Aluminium foil has been selected as the sample material used for the validation of the experimental technique. The experimental validation, which is discussed in section 6.4, compares values for adsorbed layer thickness, at given humidities, measured using the AFM technique and using the more established technique of dynamic vapour sorption (DVS). DVS requires a large amount of sample surface area in order to maximize the water adsorption and hence the observable change in mass. However there is a limit to the mass and size of the sample that can be used. Aluminium foil provides a large surface area whilst being a relatively lightweight material, (density 269.8 kg/m$^3$ compared with 713.3 kg/m$^3$ for zinc and 1932.0 kg/m$^3$ for gold). Another advantage of aluminium is that it has a stable surface oxide layer and consequently is not expected to undergo any physical or chemical changes during the adsorption and desorption of water vapour.

Aluminium foil was bought from Goodfellow$^3$, in sheets 50 mm x 50 mm with a thickness of 0.0125 mm. The aluminium foil, for AFM experimentation, was cut into small squares, approximately 1 cm x 1 cm, and mounted in the manner described in section 3.4.1.1.

$^3$ Goodfellow Cambridge Ltd., Cambridge. CB4 4DJ
5.5 Conclusions

Experimental sample materials have been introduced, the relevance of each material together with material properties and a description of the sample preparation methods have been discussed.

The material of principal interest in the current study is $\alpha$-lactose monohydrate, due to its importance within the pharmaceutical industry. The two forms of milled $\alpha$-lactose monohydrate powder used in the current study, granulac and classified, have been shown to have significantly different particle surface topographies, with the classified lactose particles displaying a greater level of surface debris than the granulac particles. The laboratory grown $\alpha$-lactose monohydrate crystals can be seen to have little surface structure and consequently can be used as a 'flat' lactose reference sample.

Silicon wafer has been studied as it allows the determination of the thickness of adsorbed water layer on the AFM cantilever tips, as these are also manufactured from silicon. The presence and thickness of native silicon oxide layers on both the cantilever tip and the silicon wafer sample have been discussed.

Attempts to validate the AFM measurement technique have been made using dynamic vapour sorption, (DVS). Aluminium foil has been selected as the sample material for this technique, reasons for this choice have been discussed.
6. EXPERIMENTAL RESULTS AND DISCUSSION

6.1 Introduction
In this section experimental results are presented for adsorption isotherms obtained on the different sample materials; silicon wafer, aluminium foil, lactose crystals, granulac and classified lactose particles.

Silicon was used as an ‘ideal’ material. The adsorption isotherm obtained has been compared with the results of previous investigators and with theoretical predictions for layer thickness. The ‘half separation distance’ values, (discussed in section 3.5.7), for the silicon isotherm have been used to adjust the adsorption isotherms of the other materials in order to take account of both the instability of the liquid film as the tip and sample approach contact and the presence of an adsorbed liquid layer on the cantilever tip. The silicon experiments and results are discussed in detail in section 6.2.

As discussed in chapter 1, lactose is widely used in, and is of great importance to the pharmaceutical industry. Milled α-lactose monohydrate from two sources has been studied together with ‘ideal’ laboratory grown α-lactose monohydrate crystals. The observed differences in the adsorption isotherms are discussed in section 6.3.

Attempts have been made to validate the AFM measurement technique by comparing results from a gravimetric technique known as dynamic vapour sorption (DVS). The results of this investigation are discussed in section 6.4.

6.2 Silicon
6.2.1 Introduction
The data obtained from the AFM experiments on silicon wafer samples are used for two purposes. First, in this study silicon wafer is considered to be an ‘ideal’ sample as it is relatively flat, (Figure 6.1), and it has a stable surface oxide layer. The possible presence of a surface ‘gel’ layer is discussed later, in section 6.2.3.4.
Adsorption isotherms for silicon/silicon oxide have been published by several other investigators. The results of the current work are compared both with these previous isotherms and also with theoretical predictions of the layer thickness. Secondly, because the AFM cantilevers used in the current work are manufactured from silicon the silicon 'half separation distance' is needed for the calculation of adsorbed layer thicknesses on other materials. The silicon isotherm experiments also test how several variables, such as temperature, cantilever spring constant and wear on the tip, affect the isotherm results for this AFM technique.

Figure 6.1 - AFM image of a silicon surface.

6.2.2 Silicon Wafer Experiment
6.2.2.1 Experimental Variables
Experimental data from twelve adsorption isotherms have been obtained. Two silicon wafer samples (a & b) and a range of cantilevers with varying spring constants (-4-50 N/m) were used. The experiments were carried out at ambient temperature over a number of weeks, thus the isotherms were obtained at a range of different temperatures (21-27 °C). Over the course of each experiment there was some variation in ambient temperature, typically two or three degrees. The temperature
values given in Table 6.1 are the average of the initial and final temperatures. A summary of the experimental variables is given in Table 6.1.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Relative Humidity Range (%)</th>
<th>Temperature (°C)</th>
<th>Spring Constant (N/m)</th>
<th>Silicon Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41-71</td>
<td>24</td>
<td>49</td>
<td>a</td>
</tr>
<tr>
<td>2</td>
<td>33-69</td>
<td>25</td>
<td>49</td>
<td>a</td>
</tr>
<tr>
<td>3</td>
<td>30-70</td>
<td>27</td>
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<td>a</td>
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<td>30-69</td>
<td>27</td>
<td>49</td>
<td>a</td>
</tr>
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<td>5</td>
<td>17-74</td>
<td>21</td>
<td>49</td>
<td>a</td>
</tr>
<tr>
<td>6</td>
<td>35-70</td>
<td>23</td>
<td>4.8</td>
<td>a</td>
</tr>
<tr>
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<td>30-65</td>
<td>25</td>
<td>4.8</td>
<td>b</td>
</tr>
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<td>30-65</td>
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</tr>
<tr>
<td>12</td>
<td>13-52</td>
<td>25</td>
<td>4.8</td>
<td>b</td>
</tr>
</tbody>
</table>

6.2.2.2 Results for Silicon

The experimental results are shown in Figure 6.2. These ‘raw’ experimental data are as measured using the AFM and have not been adjusted to take into account the instabilities in the liquid layers as the tip and sample approach contact or the adsorbed water on the cantilever tip, and consequently they are the separation distances at which the liquid films become unstable and a jump to contact occurs.

It can be seen that although single sets of experimental data do not necessarily increase smoothly with increasing relative humidity, there is an overall trend of increasing adsorption with increasing relative humidity. Note that the scatter in the data is accentuated by the magnified scale of the ordinate.
It is expected that at higher temperatures separation distances will be less than at lower temperatures, due to a decreased tendency for adsorption. However inspection of the experimental data reveals that the separation distance is insensitive to temperature changes in this range. It can also be noted that the magnitude of the spring constant plays no role in the measurement of the separation distance. It is known that the cantilever tips will undergo wear during experiments (discussed in section 6.2.2.3) altering the effective tip radius, however this does not appear to affect the separation distances. The insensitivity of the measurements to cantilever and tip variations is expected and adds credence to the technique.

Figure 6.2 - Experimental data of separation distance as a function of relative humidity for silicon wafer.

6.2.2.3 Tip Wear
As mentioned in the previous section, it can be shown that the cantilever tips will undergo wear during experimentation. The wear can be attributed to the force applied to the tip while the tip and sample are in contact particularly in the upper section of the contact region of the AFM output curve where the tip is bent backwards.
Figure 6.3 and Figure 6.4 illustrate the amount of wear and the consequential change in tip radius that can occur. The cantilever tip shown in Figure 6.3 is unused and has a nominal tip radius of 12 nm. It is shown from two angles; in profile and as viewed from above. The same tip is shown in Figure 6.4 but has now been used to obtain ~2000 adsorption isotherm data points. The tip radius is now approximately 75 nm, again it is shown in profile and as viewed from above. The cantilever tip is a Pointprobe silicon ‘force modulation’ cantilever, supplied by LOT Oriel as detailed in section 3.3.

Figure 6.3 - Unused cantilever tip.

Figure 6.4 - Tip from Figure 6.3 after use for collection of ~2000 isotherm data points.
Experimental Results and Discussion

Figure 6.5 is a plot of separation distance against relative humidity for an unused and a used cantilever tip. Both sets of data were obtained on silicon wafer and at similar ambient conditions. The error bars in Figure 6.5 represent plus and minus twice the standard deviation, ($\pm 2\sigma$) based on the data from the twelve adsorption isotherms obtained on silicon wafer samples (section 6.2.2.1).

It can be seen that no significant difference between the two lines can be identified, within the realms of random error, at low humidity (< 55% RH). The two sets of data diverge at higher humidities (> 55% RH), however this is accentuated by the magnified scale of the ordinate and is not considered to be significant in the current work. Therefore the experiments show that the wear on a tip does not unduly affect the separation distance and hence the adsorbed layer thickness. This is to be expected as the separation distance is taken to be the sum of the distances moved by the tip and the sample from the point at which the tip jumps into contact with the liquid layer to the point of solid contact, and is independent of tip geometry. Note however, that the van der Waals force prior to contact is dependent on the geometry of the tip, increasing with tip radius, and consequently this may account for the increase in separation distance for the used tip at higher humidities.

Figure 6.5 - Separation distance as a function of relative humidity for used and unused cantilever tips on silicon wafer.
In this study, where needed in theoretical calculations, the tip radius is taken to be 75 nm, which allows for the wear on the tip to be taken into account.

6.2.3 Silicon Adsorption Isotherm

6.2.3.1 Layer thickness data

The thickness of the adsorbed water layers on the silicon wafer sample, \( t \), and the cantilever tip can be determined from the separation distances, \( d \), using the method of Forcada outlined in section 3.5.7.5 for similar solid surfaces.

The experimental separation distances, \( d \), measured using the AFM technique, are substituted into equation 3.19 where the function \( f \) has been set to zero, i.e.

\[
0 = \frac{A_{IL}}{2\pi(d-2t)^3} + \frac{A_{ILS}}{2\pi} \left( \frac{1}{t^4} - \frac{1}{(d-t)^4} \right)
\]  

(6.1)

The equation is then solved, using a quasi-Newton technique\(^1\), to give values of layer thickness, \( t \).

Figure 6.6, shows the separation distance data together with the adsorbed layer thicknesses and data for the total amount of water adsorbed (the water on the tip plus the water on the sample). It can be seen that, at a given humidity, the adsorbed layer thickness is approximately 28% of the total separation distance, and consequently the total amount of water adsorbed makes up just over half the separation distance at which the jump to contact occurs. It can also be seen that the scatter in the data appears less for the adsorbed layer thickness than for the separation distance data; this is due to a reduction in the absolute magnitude of the error with the reduction in the measured values.

\(^1\) Microsoft Excel Spreadsheet ‘solver’ function with default settings.
6.2.3.2 Fitted Data

The adsorbed layer thickness data from the twelve adsorption isotherms, for water on silicon, have been fitted using the form of the polarization theory equation (section 4.3), to produce an empirical expression from which the layer thickness at a given humidity can be determined.

From the polarization theory, section 4.3, the relationship between the thickness of an adsorbed water layer, \( t \), and the relative humidity/relative vapour pressure, \( p/p^o \) is given as:

\[
-\ln\left(\frac{p}{p^o}\right) = K_1K_3 + K_4
\]  

(6.2)

where \( K_1, K_3 \) and \( K_4 \) are constants.

The constants can be calculated in the experimental manner suggested by Bradley (1936). The value of \( K_4 \) is varied, by trial and error, until a plot of \( \ln[-\ln(p/p^o)-K_4] \)
Experimental Results and Discussion

against film thickness, $t$, is linear. $K_3$ and $K_4$ can then be determined from the slope of the straight line and the intercept with the vertical axis.

For the silicon adsorption isotherms when $t$ is measured in nm and the relative vapour pressure is in the range 0-1, $K_1 = 34.085$, $K_3 = 0.368$ and $K_4 = -2.517$. Equation 6.2 can be rearranged to give an expression for the fitted experimental data, from which the adsorbed layer thickness at a given humidity can be calculated.

$$ t = \frac{\ln\left(\ln\left(\frac{P}{P_o}\right) - (-2.517) \right) - \ln(34.085)}{\ln(0.368)} $$

(6.3)

$$ t = -\ln\left(-\ln\left(\frac{P}{P_o}\right) + 2.517\right) + 3.529 $$

For the polarization theory fit the correlation factor between the experimental data and the predicted values is 0.67.

Figure 6.7 - Fitted silicon adsorption isotherm
Experimental Results and Discussion

The fitted adsorption isotherm, for a range of relative humidity values corresponding to those at which experimental data were obtained, 10-70%, is shown together with the experimental data in Figure 6.7.

In the present study it would be possible to fit the experimental data using a linear model; the resulting correlation coefficient would be similar to the value for the polarization model. However, if adsorption isotherms are determined for a wider range of humidities a more flexible model is needed so that the shape of the isotherm can be adequately fitted. As noted in chapter 2 the polarization model provides a good fit for experimental data for water adsorption over a wider range of humidities; 0-95% (Badmann et al. 1981).

6.2.3.3 DLVO theory predictions

The DLVO theory, which is discussed in more detail in section 4.2, can be used to link the adsorbed water layer thickness, \( t \), to the relative vapour pressure of a system via the disjoining pressure, \( \Pi \). The disjoining pressure is defined in section 2.2.3.2.

A theoretical adsorption isotherm, developed using the DLVO theory, for the adsorption of water on silicon wafer is shown in Figure 6.8 together with the experimentally determined layer thickness data.

The DLVO prediction shown in Figure 6.8 has been calculated, using the method of solution outlined in section 4.2, for the situation where it is assumed that there is no solute present in the system. The presence of solute ions in the liquid layer has been shown in section 4.2 to increase the predicted adsorbed layer thicknesses by no more than 0.1 nm.

In the current study the following input parameters have been used for the solution of equations 4.3 and 4.1 to obtain the DLVO prediction for adsorbed layer thickness shown in Figure 6.8: relative permittivity of the adsorbate (water), \( \varepsilon = 78.5 \), temperature, \( T = 298 \) K, valency, \( z = 1 \), molecular volume of the liquid,
Experimental Results and Discussion

\[ v_m = 2.99 \times 10^{-29} \text{ m}^3/\text{molecule}, \text{ and Hamaker constant, } A = -0.92 \times 10^{-20} \text{ J (interaction of silicon with air across a water medium).} \]

It can be demonstrated that the adsorbed layer thickness, \( t \), will change with variation in the Hamaker constant, \( A \). It has been calculated that a 100 % increase (or decrease) of the Hamaker constant will lead to a 15 % - 20 % increase (or decrease) in the DLVO predicted adsorbed layer thickness.

Figure 6.8 - Comparison of DLVO prediction of adsorbed layer thickness with experimental data for silicon.

It can be seen from Figure 6.8 that adsorbed layer thicknesses predicted by the DLVO theory are significantly smaller than those measured experimentally. This major discrepancy has also been noticed by other investigators; Pashley and Kitchener (1979), Gee et al. (1990) and Derjaguin and Churaev (1974). The observations of these investigators have been discussed previously in section 2.2. Derjaguin and Churaev (1974) suggest the inclusion of an additional structural term, \( \Pi_s \), in the disjoining pressure expression to take account of any structuring in the water layer.
As the structural term $\Pi_S$ cannot be calculated due to the absence of theory for polar liquids it is generally taken to be the difference between the experimental measurements and theoretical predictions. In the present work this would suggest that the structural interaction forms approximately 90% of the total interaction, for the relative humidity range 10-70%. This seems highly unlikely especially as the influence of the structural interaction will decrease as the film thickness increases. Observation of the work of Gee et al. (1990) suggests that the structural term would account for 75% of their measured interaction at 76% relative humidity rising to 80% of the total interaction at a relative humidity of 93%. They suggest that some other force or some peculiarity of the experimental system is responsible for the thick water films obtained.

6.2.3.4 Comparison with previous investigators
Many investigators have studied the adsorption of water on silicon or similar materials, using several different measurement techniques. The results from various investigators are given in Table 2.1. Their results are also illustrated in Figure 6.9 together with the current AFM measurements for water adsorption on silicon wafer, (note Figure 6.9 is plotted on a vertical log scale). Figure 6.10 shows in more detail the results of those investigators who have studied adsorption at similar relative humidities to the range used in the current study (10-70%), together with the measurement technique by which the isotherm was obtained.

From Figure 6.9 and Figure 6.10, it can be seen that no two sets of data from previous investigators or the current work coincide, despite all materials having similar surface properties. However, the current adsorption isotherm does fall within the range of those previously measured.
Experimental Results and Discussion

Figure 6.9 - Comparison of current results with results from previous investigators.

Figure 6.10 - Detail of previous investigators.

Figure 6.10 shows that the adsorption isotherm for the current work is of the same form as those measured using gravimetric and ellipsometric techniques, *i.e.* gradual increase in layer thickness with increasing relative humidity up to ~80%. However, the values of layer thickness measured by the other investigators are between ~50-80% lower.
The exception is the isotherm published by Garbatski & Folman (1956) where the layer thicknesses are initially similar to those of the present work but then start to increase rapidly with increasing relative humidity. Due to the fundamental difference in the shape of the adsorption isotherm the work of Garbatski and Folman is not considered in subsequent discussions. The different form of the adsorption isotherm reported by Garbatski and Folman cannot be definitively explained. In their study they infer the film thickness from a change in electrical capacity between two closely spaced surfaces. However, the thicknesses obtained in this way are large and are then reduced by the use of a roughness factor. Garbatski and Folman extrapolate their data back to RH = 0.4 where they assume monolayer coverage. This point is then used as a reference from which the roughness factor is obtained. The assumption of monolayer coverage at RH = 0.4 and the use of such an extrapolation to produce a roughness factor may lead to errors in their reported data. Additionally, the electric field imposed by the proximity of the surfaces will result in an increased force of attraction between the polar molecules and the quartz surfaces. It is therefore suspected that the method itself promotes condensation, resulting in thicker adsorbed layers.

Previous investigators have noted and discussed the discrepancies between the different isotherms presented in Figure 6.9 and Figure 6.10, section 2.2.2.5. The differences in measured layer thickness values can be considered to arise from a number of sources; errors in measurement techniques, the possible presence of a surface ‘gel’ layer and the presence of surface contamination.

As discussed in section 2.2.2.2, many people have used ellipsometry to measure the thickness of liquid layers, yet for layers with a thickness of less than 20 nm it is not possible to determine both the thickness and the refractive index of the layer simultaneously (Pashley & Kitchener 1979). Consequently in the calculation of the thickness of adsorbed layers, using Drude’s equation (Beaglehole & Christenson 1992 equation 3), the refractive index is normally assumed to be the value of the bulk liquid. This leads to a potential error in published layer thicknesses measured using
ellipsometry. Most investigators agree that the value of the refractive index for a thin film will be greater than the bulk value, Gee (1990) suggests an increase of up to 14% in the refractive index. This would suggest that the reported layer thicknesses are greater than the true values. In which case the difference between the AFM results and the ellipsometry results may be even larger.

The difference between the current results and those of previous investigators may also be partly due to errors and additional factors that must be accounted for in the current measurement technique. The following potential sources of error are considered and discussed.

**AFM Output Curve**

In the present work, the layer thickness is calculated from data acquired from AFM output curves. In some cases the exact point at which the jump to contact starts or the point at which solid contact is made can be subjective. This may lead to a degree of error within the measured values and may account for some of the scatter within the experimental data, however this effect will be relatively small, ~1-2 pixel points leading to a maximum possible error of ±0.12 nm.

**Van der Waals and Electrostatic Contributions to the Separation Distance**

As discussed in Chapter 3, the separation distance will include contributions arising from van der Waals and electrostatic interactions. These interactions were shown to contribute less than 9% to the total separation distance and consequently have not been considered in the current work. However, had they been considered the layer thickness values would be an average of 0.2 nm smaller and consequently do not account for the difference between the results of the current study and those of previous investigations.

**Surface Roughness**

Scatter in the experimental data may also be caused by inhomogeneities on the sample surface, e.g. surface roughness. A rough surface will promote capillary
condensation in the ‘valleys’. Layer thickness will therefore appear to be larger if the AFM probe tip lands in a valley. There may also be some interaction between the side of the tip and asperities on the surface with the effect of increasing the measured layer thickness. However, as shown in Figure 6.1, the surface of the silicon wafer samples used in the current study are relatively flat with surface asperities which are significantly smaller than the radius of the cantilever tip and consequently the effect of surface roughness can be considered to be negligible.

Piezo Electric Crystal
During the calculation of adsorbed layer thickness, the movement of the sample is determined within the Nanoscope II software, via the use of a piezo electric crystal, which will expand or contract with an applied voltage. The crystal displacement is initially calibrated during the manufacturing process, however it is possible to recalibrate the piezo crystal using standard samples with steps of known height. For the current study, this calibration was carried out periodically by the SPM laboratory staff and no significant deviations were reported. Consequently, if the expansion behaviour of the piezo crystal has changed since the last calibration, perhaps an effect of aging, then this may lead to inherent errors in the calculated adsorbed layer thicknesses.

The displacement-voltage relationship for piezo crystals is frequently non-linear. This has been demonstrated, for example by Tyrrell and Cleaver (1998) with hysteresis between the expansion and withdrawal curves on a plot of crystal expansion against applied voltage. Tyrrell and Cleaver have corrected their AFM output curves to take account of the non-linearity of the piezo crystal and report that the contact gradient region of the output curve may be significantly affected with the error in the contact gradient values being up to 50%. This may explain the large range of contact gradient values, obtained for a rigid substrate, seen in the current work (section 3.5.4). In the current work it has not been possible to investigate the linearity or otherwise of the piezo crystal due to the limitations of the commercial AFM. However, a worst case scenario can be considered where the contact gradient
Polywater Layers

Barthel et al. (1996) measure the force vs. displacement profiles between silica surfaces in dry air. They suspect the presence of a polywater layer - a water layer contaminated by ionic or other species, having different properties, such as lower mobility and lower vapour pressure, compared with an adsorbed layer of water. The effect of this phenomenon has not been considered in the current work as it was not possible to perform experiments in dry conditions with the equipment available.
error is 50%. This error is calculated as the difference between the measured and the corrected contact gradient values divided by the corrected value and expressed as a percentage. Under these conditions the layer thickness can be calculated to be an average of 0.66 nm higher or lower than the current values.

Gel Layers
It has previously been proposed that the oxide layer on silicon surfaces (or on glass or quartz) may dissolve to a certain extent to form a ‘gel’ layer, (Iler 1979), which will lead to the observation of thicker films. If a gel layer was present it is expected that it could be observed on the AFM output curve by the contact region curve displaying two sections with different gradients relating to the different surface properties. During the collection of experimental data from AFM output curves no such variations in the contact region gradient have been observed. Also the increase in the observed layer thickness due to the presence of a gel layer has not been quantified but it is unlikely to be the cause of the large discrepancy between the present and previous isothenns, because the magnitude of the difference would suggest a very large gel layer; of a similar magnitude or greater than the adsorbed liquid layer. In this study no evidence to support the existence of gel layers has been observed.

Additional Contributions to the Interaction Between Liquid Films
Forcada also assumes that the overall interaction between the two liquid films can be attributed entirely to van der Waals interactions, no other forces such as an electric double layer effect, the surface tension or the viscosity of the liquid are considered. The inclusion of surface tension and viscosity terms would lead to increased layer thickness values as they would provide resistance to the formation of the localized perturbations of the liquid film and consequently the measured separation value, d, will be closer in magnitude to the predicted layer thickness, t.

In summary, the approach of Forcada (1993) used in the present work to determine the layer thickness from the measured separation distance, contains certain
Experimental Results and Discussion

simplifications of the system. A quantitative assessment of these simplifications would be very complex and is beyond the scope of this work.

**Increased Vapour Pressure Above the Cantilever Tip**

The thickness of adsorbed water layers is calculated from the experimental data for the distances at which the jump to contact occurs, according to the approach of Forcada (1993). This approach takes account of both the presence of a liquid layer on the cantilever tip and the instability of the liquid films as the tip and sample approach contact. However, it is assumed in this procedure that the thickness of the adsorbed water layer on the AFM cantilever tip is equal to that on the silicon sample. This may not be the case as the level of water adsorption on the cantilever tip may be affected by its highly curved surface. It can be shown from the Kelvin equation that the vapour pressure above a curved surface will be elevated. The Kelvin equation can be expressed as:

\[
\ln \left( \frac{P}{p} \right) = \frac{2 \gamma \nu}{RT_r} \tag{6.5}
\]

where
- \( P \) = vapour pressure over a curved surface
- \( p \) = vapour pressure over a flat surface
- \( \gamma \) = specific surface energy of the liquid (water) / air interface
  = 0.0728 J/m^2
- \( \nu \) = molar volume of water
  = 0.1 x 10^{-2} m^3/kg
  = 0.1 x 10^{-2} x 18/1000 m^3/mol
  = 1.8 x 10^{-5} m^3/mol
- \( T \) = temperature
  = 298 K
- \( R \) = Universal gas constant
  = 8.314 J/molK
- \( r \) = tip radius
  = 75 nm
For an adsorbed water layer on a cantilever tip:

\[
\ln\left(\frac{P}{p}\right) = \frac{2 \times 0.0728 \times 1.8 \times 10^{-5}}{8.314 \times 298 \times 75 \times 10^{-9}}
\]

\[
\frac{P}{p} = 1.014
\]  

(6.6)

This elevation in vapour pressure above a curved surface compared with that above a flat surface will lead to a reduction in the thickness of the water layer adsorbed on the cantilever tip. In the current work, where the difference in vapour pressure can be seen to be small (equation 6.6), this effect has been considered to be negligible. Consequently water adsorption is considered to occur equally on the planar sample surface and on the curved cantilever tip.

**Capillary Bridges**

Another possible cause of the discrepancy between the large layer thicknesses measured in the current work and the smaller values of previous investigators is that the intrusive nature of the AFM technique results in an increase in the amount of water in the system. As the tip and sample come into contact a liquid bridge will form. If the mean radius of curvature, \(r_{ave}\), of the liquid bridge is smaller than that determined from the Kelvin equation, for a given relative humidity, water will condense into the capillary (note, values of \(r_{ave}\) will be negative due to the overall concave geometry of the liquid bridge). When the liquid bridge breaks, on retraction of the tip, the extra water from the capillary will be added to that already present on the surfaces and hence a thicker layer will be measured the next time the tip and sample come into contact. The AFM system is dynamic with the tip and sample continuously moving in and out of contact, consequently it is a complex task to determine accurately the extent of this effect, however it is possible to make an approximation. Orr *et al.* (1975) have studied the geometry and properties of liquid...
bridges formed between a sphere and a flat surface and publish a table which relates the filling angle, $\psi$, to the mean curvature of the liquid bridge.

Figure 6.11 - Geometry of adsorbed layers as tip and sample come into contact.

In the current work, the filling angle, $\psi$, has been taken to be the angle at which an adsorbed layer on a probe tip and an adsorbed layer on a sample surface intersect when the two solid surfaces are brought into contact, (Figure 6.11). This definition ignores the presence of any displaced water, however if the layer thicknesses are small the majority of the water will be bound in the surface monolayer. Orr et al. define the mean curvature as $2Hr$, where $H = 1/r_{ave}$. From the tabulated data of Orr et al. (1975) it is possible to determine the mean radius of curvature for a liquid bridge formed between adsorbed layers of any thickness, $t$.

Separately, it is possible to determine the mean radius of curvature, $r_{ave}$ of a stable liquid bridge, when the rate of condensation and evaporation into and out of the liquid bridge are equal, at any given humidity, $p/p^0$, by the use of the Kelvin equation.

$$\ln\left(\frac{p}{p^0}\right) = \frac{2\gamma v}{RT_r_{ave}}$$ (6.7)

where $\gamma$ = specific surface energy of the liquid (water) / air interface

$\gamma = 0.0728$ J/m$^2$

$v$ = molar volume of water

$v = 1.8 \times 10^{-5}$ m$^3$/mol
Experimental Results and Discussion

\[ T = \text{temperature} \]
\[ = 298 \text{ K} \]
\[ R = \text{Universal gas constant} \]
\[ = 8.314 \text{ J/molK} \]

Table 6.2 compares the mean radii of curvature predicted from the Kelvin equation (equation 6.7) at a range of humidities and the mean radii of curvature determined from adsorbed layer thicknesses using the data of Orr et al. (1975). The adsorbed layer thicknesses correspond to those measured using the AFM technique and to those reported by Badmann et al. (1981) measured gravimetrically at those given relative humidity values. Adsorbed layer thicknesses have been back calculated for the mean radii of curvature predicted by the Kelvin equation from the tabulated data of Orr et al..

Table 6.2 - Comparison of mean radii of curvature and layer thickness for different measurement / prediction techniques.

<table>
<thead>
<tr>
<th>Measurement Technique</th>
<th>RH = 0.2</th>
<th></th>
<th>RH = 0.4</th>
<th></th>
<th>RH = 0.6</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kelvin equation prediction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( r_{\text{ave}} ) (nm)</td>
<td>( t ) (nm)</td>
<td>( r_{\text{ave}} ) (nm)</td>
<td>( t ) (nm)</td>
<td>( r_{\text{ave}} ) (nm)</td>
<td>( t ) (nm)</td>
</tr>
<tr>
<td></td>
<td>-0.65</td>
<td>0.23</td>
<td>-1.14</td>
<td>0.55</td>
<td>-2.05</td>
<td>1.39</td>
</tr>
<tr>
<td>Gravimetric (Badmann et al. 1981)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.72</td>
<td>0.29</td>
<td>-0.88</td>
<td>0.41</td>
<td>-1.07</td>
<td>0.52</td>
</tr>
<tr>
<td>AFM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-3.85</td>
<td>2.11</td>
<td>-4.85</td>
<td>2.30</td>
<td>-5.16</td>
<td>2.42</td>
</tr>
</tbody>
</table>

It can be seen from table 6.2 that if the water layer adsorbed on a silicon surface is initially of the thickness measured by Badmann et al. (1981) then for relative humidities greater than \(~ 40 \%\) the use of the atomic force microscope will cause water to condense into the liquid bridge formed between the cantilever tip and the sample. This will increase the thickness of the adsorbed layers and the mean radius.
of curvature of the meniscus formed when the tip and sample are in contact, up to the critical values predicted by the Kelvin equation. For example, at 60 % RH, the layer thickness is initially 0.52 nm and this will increase through capillary condensation to 1.39 nm as predicted by the Kelvin equation. However, the value of the layer thickness measured using the AFM technique (t = 2.42 nm) is still substantially larger than the value predicted by the Kelvin equation.

For relative humidities less than ~ 40 % no water will condense into the capillaries as the critical mean radii of curvature, predicted by the Kelvin equation, have already been exceeded.

Consequently, it can be concluded that if the ambient thickness of the adsorbed layer, prior to experimentation is low i.e. ~ 0.5 nm and the relative humidity is above ~ 40%, then contact between the AFM probe and the sample will cause capillary condensation and the amount of water in the system will increase. However, this effect does not altogether account for the large layer thickness measured, at all humidities, using AFM.

This approach provides an approximation of the effect of capillary condensation. As well as the dynamic nature of the system i.e. the cantilever moving into and out of contact with the surface, the effect of sample roughness and the irregularity of the cantilever tip have not been considered. It is also to be noted that although Fisher and Israelachvili (1981) have proved the validity of the Kelvin equation for water down to a mean radius of 5 nm this analysis suggests mean radii that are less than 5 nm and hence the validity of the Kelvin equation may be questioned. Additionally, the water that is displaced as the tip and the sample come into contact has not been considered in the determination of the filling angle, however with the low values of the initial layer thickness this discrepancy is considered to be small.

One can also question the physical significance of water layer thicknesses of less than 0.5 nm. This is a statistical value, and in reality implies the presence of clusters of
molecules on specific active sites. The Kelvin equation is clearly not valid under these circumstances. However, the local spatial inhomogeneity caused by the presence of the probe tip on the surface is expected to increase the surface potential thereby promoting the nucleation of water molecules. Once sufficient nucleation has occurred, the liquid layer will become mobile and a meniscus will form. Repeated contact and removal of the tip from the surface will tend to pull water into the capillary from the surrounding surface. It is this mechanism that is suspected to possibly account for the excessively large measured values of layer thickness using AFM. This hypothesis could not be tested because the Nanoscope II does not allow individual contacts to be made.

Surface Contamination

A possible explanation of the large difference between the adsorption isotherm of the present work and those of previous investigators: Hagymassy et al. (1969), Gee et al. (1990), Badmann et al. (1981) and Beaglehole & Christenson (1992), is the presence of surface contamination. The method of preparation of the sample surfaces in the current experiment is somewhat different to previous investigators. Gee et al. and Beaglehole & Christenson use similar cleaning methods for their respective samples, quartz and silicon. In both sets of experiments the samples are lightly etched using a HF/HNO₃ solution, to remove any surface contaminants. The use of a HF/HNO₃ solution to etch the sample surface was not suitable for the current study; although the silicon wafer sample could easily undergo this treatment, it was not deemed suitable for the AFM cantilevers due to the small size of the tips.

In the present work, the silicon wafer and the cantilever tips were cleaned by submersion in propan-2-ol for 20 minutes to remove any surface grease, rinsed using distilled water and left to dry. It is possible that there will be a residual layer of the organic solvent on the sample using this method if the samples are not rinsed sufficiently.

The cleaning method used in this study could be improved by exposing the samples to UV light of wavelengths 184.9 nm and 253.7 nm, (Vig 1985 and Baunack & Zehe
1989). Under the influence of the short wavelength UV radiation ($\lambda = 184.9$ nm) ozone ($O_3$) is formed from oxygen. Long wavelength radiation ($\lambda = 253.7$ nm) will decompose the ozone forming highly reactive atomic oxygen which will oxidize any residual hydrocarbons on the sample surface (such as remaining solvent), together with ensuring the sample is completely dried. Due to difficulties encountered in finding a supplier of the UV lamp emitting the desired wavelengths of light (UV-C), this cleaning technique has not been attempted in the present work. It would perhaps be an interesting subject for further study.

Previous investigators have debated the influence of surface contamination on the thickness of adsorbed layers and report seemingly conflicting outcomes. Pashley & Kitchener (1979) and Gee et al. (1990) suggest that the presence of surface contamination will lead to the formation of thinner films, whereas Beaglehole & Christenson (1992) suggest that thicker adsorbed layers would be observed.

The effect that surface contamination will have on the adsorbed layer must depend on the nature of the contaminant molecules and the context in which they are considered. If, for example, the contamination is considered to be a collection of molecules on the sample surface prior to the formation of the liquid film, the nature of the effect on the adsorbed film thickness will depend on the hydrophobicity of the contaminant molecules. If the contaminant is hydrophobic in nature then it can be expected to hinder the formation of the adsorbed film and consequently the observed layer thickness will be less than expected. However, if the contaminant is hydrophilic in nature, perhaps containing hydroxyl groups (e.g. organic solvents such as propanol) then film formation is promoted and thicker films will be observed.

Another context in which contamination can be considered is if the contaminant materials are dissolved within the liquid layer forming an electrolyte solution. As discussed in section 4.2 the presence of electrolyte ions in the liquid film will cause an increase in the layer thickness, however the analysis in section 4.2 suggests that this effect will not be significant.
In summary, the adsorbed layer thickness values of the silicon adsorption isotherm measured in the present study are larger than previously measured isotherms for the same range of relative humidity. The differences may be due to errors in previous investigators measurements or errors within the current technique, such as the calculation of layer thickness from the separation distance or presence of surface contamination, however the most probable cause is the induced condensation arising from the presence of the probe tip.

6.2.4 *Half separation distance*

As discussed in sections 3.5.7 and 6.2.1 the 'half separation distance' for silicon, \( \frac{1}{2}d_{Si} \), is needed for the calculation of adsorbed layer thickness on materials other than silicon. An empirical expression for the half separation distance as a function of relative humidity has been developed by fitting data from the adsorption isotherm experiments.

The data have been fitted using the polarization theory, section 4.3. The theory can be expressed as in equation 6.2 but now the layer thickness, \( t \), is replaced by the half separation distance, \( \frac{1}{2}d_{Si} \). When the half separation distance is measured in nanometers and the relative vapour pressure is in the range 0.1-0.7, \( K_1 = 96.559, K_3 = 0.368 \) and \( K_4 = -0.993 \). Equation 6.2 can be rearranged to give an expression for the fitted experimental data, from which the half separation distance at a given humidity can be calculated.

\[
\frac{1}{2}d_{Si} = \frac{\ln\left( -\ln\left( \frac{P}{P_0} \right) - (-0.993) \right) - \ln(96.559)}{\ln(0.368)}
\]

\[
\frac{1}{2}d_{Si} = -\ln\left( -\ln\left( \frac{P}{P_0} \right) + 0.993 \right) + 4.571
\]

The correlation factor between the experimental data and the predicted values is 0.68.
Experimental Results and Discussion

The fitted half separation distance data for a range of relative humidity values corresponding to those at which experimental data were obtained, 10 - 70 %, are shown together with the experimental data in Figure 6.12.

Figure 6.12 - Fitted half separation distance data for silicon wafer.

As discussed in section 6.2.3.3, it would be possible to fit the data using a linear model, however for the reasons mentioned previously the polarization theory model has been chosen. The empirical expression in equation 6.8 can now be used in the calculation of adsorbed layer thickness on other materials at any relative humidity value within the range 10-70%.

6.3 Lactose
6.3.1 Introduction

In this study, experiments have been performed on three forms of α-lactose monohydrate; laboratory grown crystals, granulac and classified lactose. Granulac and classified lactose are commercially available forms of lactose commonly used within the pharmaceutical industry. The sample materials are discussed in more detail in chapter 5.
Experimental Results and Discussion

In the following section, 6.3.2, water adsorption isotherms, obtained experimentally using the AFM technique, are presented for each of the three forms of lactose. The differences between the isotherms are discussed in section 6.3.3.

6.3.2 Experimental Results

For each sample material ten sets of experimental data were obtained using the AFM measurement technique, giving an average of 180 points per isotherm. The experiments were performed over a range of ambient temperatures. A summary of the range of experimental ambient temperatures for each sample material is given below in Table 6.3.

Table 6.3 - Range of Experimental Ambient Temperatures.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal</td>
<td>25</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>Granulac</td>
<td>24</td>
<td>28</td>
<td>21</td>
</tr>
<tr>
<td>Classified</td>
<td>22</td>
<td>25</td>
<td>20</td>
</tr>
</tbody>
</table>

From the experimental data the adsorbed layer thicknesses have been calculated using the three step strategy for a two component system proposed in section 3.5.7.7. First, the half separation distance associated with the cantilever tip is determined from experimental data for the tip interacting with a surface of the same material, i.e. a silicon sample. Second, the separation distance for a two component system is determined experimentally. This distance is assumed to be the sum of the half separation distance for the cantilever tip and the half separation distance for the sample. Consequently, the half separation distance for the sample can be calculated. Finally, a theoretical separation distance is determined for the sample material, equal to twice the half separation distance, and from this the adsorbed water layer on the sample surface can be determined. A sample calculation, for an adsorbed layer on a lactose crystal sample, is given in appendix 2.
The adsorbed layer thicknesses have been averaged with respect to the relative humidity. Averaged layer thicknesses are presented for given humidities ± 2.5% RH. The resulting water adsorption isotherms are shown in Figure 6.13.

The scatter in the experimental data, which results in error bars of ± 10% may partly be due to inhomogeneities across the sample surfaces. It is known that α-lactose monohydrate crystals, and consequently the milled material, will contain a small quantity of the β form of lactose, together with other impurities such as phosphates. This is discussed in greater detail in section 5.2.1.

Figure 6.13 - Lactose adsorption isotherms.

6.3.3 Discussion

6.3.3.1 Introduction

It can be seen, from Figure 6.13, that the adsorption isotherms for the three forms of α-lactose monohydrate show distinctly different levels of water uptake. Lactose crystals appear to adsorb the largest amounts of water, with classified lactose showing the lowest levels. The values for granulac lie between the other two isotherms. There
Experimental Results and Discussion

is no overlap of the measured values except at high relative humidity values (> 60%) where the isotherms of the classified lactose and of the granulac begin to converge.

Table 6.3 indicates that the adsorption isotherms for each lactose sample were determined for approximately the same range of temperatures, and consequently the different levels of water uptake cannot be attributed to variation in temperature. These differences may however be due to variations in the surface topography, contamination and process history of the three samples, as discussed in the following sections.

6.3.3.2 Surface Topography

It can been seen from both AFM images and SEM images that the three lactose samples have very different surface structures.

The lactose crystal, illustrated in Figure 6.14, Figure 6.15 and Figure 6.16 has a very flat surface with small protrusions no more than a few nanometers in height.

Figure 6.14 - SEM image: lactose crystal.
Figure 6.15 - SEM image: area of top face of lactose crystal.

![SEM Image](image)

Figure 6.16 - AFM image: area of top face of lactose crystal.

![AFM Image](image)

One of the individual granulac particles used in the AFM experiment to determine adsorbed layer thickness is shown in Figure 6.17. A more detailed SEM image of an area on this particle is shown in Figure 6.18. An AFM image of a similar area of a
Experimental Results and Discussion

particle surface is shown in Figure 6.19. Note Figure 6.18 and Figure 6.19 are not images of the same area.

Figure 6.17 - SEM image: granulac particle.

Figure 6.18 - SEM image: close up of granulac particle.
Figure 6.19 - AFM image: close up of granulac particle.

Although the granulac lactose has a wide size distribution, including a large amount of fine material (Figure 5.2) it can be seen from the SEM images, Figure 6.17 and Figure 6.18, that there is a relatively small amount of fine material or debris on the particle surfaces.

One of the individual classified particles used to obtain the adsorption isotherm is shown in Figure 6.20. An SEM image of a small area, giving more detail of the surface structure of this particle is shown in Figure 6.21. An AFM image of a similar area of a classified lactose particle surface is shown in Figure 6.22. Note Figure 6.21 and Figure 6.22 are not images of the same area.
Figure 6.20 - SEM image: classified lactose particle.

Figure 6.21 - SEM image: close up of classified lactose particle.
Experimental Results and Discussion

Figure 6.22 - AFM image: close up of classified lactose particle.

It can be seen that although the classified lactose has a smaller size distribution (Figure 5.4), which is not surprising as the material has been sized, there is a large amount of surface debris on the particles, which leads to an apparent increase in the particle surface roughness.

The mean values of surface roughness have been determined, using Nanoscope II software from the AFM images of the three samples, Figure 6.16, Figure 6.19 and Figure 6.22, and are given in Table 6.4. The roughness has been determined on several 200 nm x 200 nm squares of the sample and the values have been averaged. The roughness has only been determined for small surface regions as these correspond to the contact area of the AFM tip (tip radius 75 nm), i.e. the point at which the isotherms were measured. The roughness values given are the 'root mean square' values, $R_{RMS}$, determined using equation 6.9, where $z_i$ is the height of the point $i$, $z_{ave}$ is the average $z$ value for the surface and $N$ is the number of points considered.
Experimental Results and Discussion

\[ R_{\text{RMS}} = \sqrt{\frac{\sum (z_i - z_{\text{ave}})^2}{N}} \]  

Table 6.4 - Average surface roughness.

<table>
<thead>
<tr>
<th>Lactose sample</th>
<th>Average Roughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal</td>
<td>0.80 nm</td>
</tr>
<tr>
<td>Granulac</td>
<td>1.64 nm</td>
</tr>
<tr>
<td>Classified</td>
<td>1.48 nm</td>
</tr>
</tbody>
</table>

It can be seen that although the observed amount of surface debris on the two milled lactose samples is different, at the level at which the adsorption isotherms are obtained the surface roughness values are very similar. The lactose crystal displays a lower level of surface roughness, approximately half that of the milled lactose samples. It is possible that the variation in surface roughness will account, although probably not totally, for the observed differences in the adsorption isotherms for the different samples.

There will undoubtedly be variations in the amount of adsorbed water across a sample. Water will accumulate in hollows on the surface where the effect of the local radius of curvature will enhance condensation, and it is expected that there will be lower levels of water adsorption on protrusions on the sample surface. In the present study, the surface regions selected to be sampled are relatively flat and away from large hollows and protrusions as these may affect the contact between the tip and the sample, \textit{i.e.} sampling in a hollow may cause multiple tip contacts due to the geometry of the cantilever tip. Nevertheless probe contact on the rougher sample surfaces will naturally occur on an asperity, and there will therefore be a certain quantity of adsorbed moisture below the asperity that the probe tip does not experience. Consequently measured layer thickness is expected to be lower than for smooth surfaces, as observed in the present experimental results.
6.3.3.3 Contamination

In general, the surface energy will be dependent on the chemical nature of the sample material surface and the level of surface contamination. All three samples are nominally \( \alpha \)-lactose monohydrate, although different manufacturing procedures may lead to different levels of impurities within the material.

It is known that \( \alpha \)-lactose monohydrate will contain a small percentage of \( \beta \)-lactose (Wade and Weller 1994), the exact percentage may vary between different \( \alpha \)-lactose sources. The effect of the presence of \( \beta \)-lactose within the sample is not known, it may promote or inhibit adsorption. It is known, however, that \( \beta \)-lactose is significantly more soluble than \( \alpha \)-lactose and that both forms will mutarotate to give an equilibrium \( \alpha : \beta \) ratio in solution. The presence of the dissolved lactose ions in the adsorbed liquid layer will increase the layer thickness as predicted by the DLVO theory. Consequently, a higher \( \beta \)-lactose concentration at the surface of an \( \alpha \)-lactose monohydrate sample will lead to an increase in adsorbed layer thickness. But, as discussed in section 4.2, this effect is predicted to be small, increasing the layer thickness by no more than 0.1 nm.

The possible effects of surface contamination have been discussed in detail in section 6.2.3.4. No attempt has been made to clean the three forms of lactose sample used in the present study and as a result it is likely that surface contamination will have an effect on the levels of adsorption. However, it is not possible to quantify this effect, without the use of a separate technique to identify and measure the levels of surface contaminants.

6.3.3.4 Process History

The propensity for moisture adsorption will also be dependent on the process history of the samples. The two commercial forms of lactose studied, granulac and classified, have both been milled. Milling is likely to cause residual stresses within the crystalline particles, which would be expected to increase the sample surface energy. Milling may also cause an increase in the presence of \( \beta \)-lactose at the surface.
Experimental Results and Discussion

and possibly the formation of anhydrous $\alpha$-lactose due to localized high temperatures; although this can be expected to rehydrate in the presence of a humid environment. Because the conditions of milling, by the commercial manufacturers are not known, it is impossible to draw any definite conclusions about the role milling has on the different levels of adsorbed water measured for granulac and for classified lactose. However, it is possible that the higher proportion of anhydrous material expected on the surface of the milled material may effectively retain the adsorbed moisture, leaving less to be detected as a surface film. This could account for the lower measured values of layer thickness for the milled samples.

The laboratory grown $\alpha$-lactose monohydrate crystals have not undergone any destructive techniques such as milling, however the crystal surface may still have areas of residual stress which arise from growth defects. The level of water adsorption on the crystal may be dependent on the choice of face studied. In the current work water adsorption has been measured on the 100 crystal face.

In summary, it is not possible to determine the precise cause of the different levels of water adsorption for the three lactose samples. However, a range of phenomena that may be responsible has been discussed qualitatively. Where possible the effect on the adsorbed layer thickness has been surmised. It is thought that the lower values of adsorbed layer thickness detected for commercial lactose samples are the result of a higher level of surface roughness.

6.4 Dynamic Vapour Sorption Experiments

6.4.1 Introduction

Two attempts, using different sample materials, have been made using dynamic vapour sorption (DVS) to validate the AFM technique, developed in the current study, for the measurement of adsorption isotherms.
Experimental Results and Discussion

Aluminium foil was selected as the sample material for the first experiment as it provided a single flat surface and would be directly equivalent to the sample used for the AFM study. Aluminium foil provided a lightweight material with a stable surface oxide layer hence the quantity of the material used in the DVS experiments and the water uptake could be maximized. Unfortunately, the DVS experiments, kindly performed by Surface Measurements Systems\(^2\), failed to give any conclusive results due to limits in the sensitivity of the measurement equipment (quoted displayed resolution 0.1 \(\mu\)g).

Classified lactose was selected for the second experiment. The choice of the lactose powder as the second sample increased the complexity of the experiment as the surface area of the sample needed to be accurately determined by independent means. Furthermore, there was a possibility of capillary condensation occurring within the bulk sample, which would lead to falsely large values of film thickness.

6.4.2 DVS Technique

In the dynamic vapour sorption approach, the sample to be investigated is placed on an ultrasensitive microbalance which is exposed to a continuous flow of air with a predetermined and constant relative humidity. As humid air passes over the sample a region of constant moisture concentration is established around the sample. This region allows the rapid establishment of a water vapour adsorption (or desorption) equilibrium by maximizing the mass transport of water vapour to and away from the sample. By monitoring the sample mass as a function of time and by varying the relative humidity an adsorption isotherm can be determined.

6.4.3 Aluminium Experiments

6.4.3.1 DVS Experimental Results

DVS experiments were performed on a DVS.1 instrument by Surface Measurement Systems Ltd, (SMS). An aluminium foil sample of mass 120 mg was used in an

\(^2\) Surface Measurement Systems Ltd. 3 Warple Mews, Warple Way, London. W3 0RF
experiment to measure the adsorption isotherm between 0 and 70% relative humidity. It is reported by SMS that the uptake of water was almost beyond the detection limit of the instrument (quoted displayed resolution 0.1 µg) and was virtually indistinguishable from background noise.

6.4.3.2 AFM Experimental Results
Ten adsorption isotherm experiments were performed on aluminium foil, 5 on the dull side and five on the shiny side. There was no observable difference between the data obtained on either side of the aluminium foil. The adsorbed layer thicknesses were determined from the experimental data using the three step strategy for a two component system proposed in section 3.5.7.7. First, the half separation distance associated with the cantilever tip is determined from experimental data for the tip interacting with a surface of the same material, i.e. a silicon sample. Second, the separation distance for a two component system is determined experimentally. This distance is assumed to be the sum of the half separation distance for the cantilever tip and the half separation distance for the sample. Consequently, the half separation distance for the sample can be calculated. Finally, a theoretical separation distance is determined for the sample material, equal to twice the half separation distance, and from this the adsorbed water layer on the sample surface can be determined. A sample calculation, for an adsorbed layer on a lactose crystal sample, is given in appendix 2.

The adsorbed layer thickness values have been averaged with respect to the relative humidity, to give an averaged layer thickness at a given humidity ± 2.5%. The error associated with the averaged values is no more than ± 13%. The averaged layer thickness values and the experimental data are shown in Figure 6.23. It can be seen that the thickness of the adsorbed liquid layer increases with increasing humidity.
6.4.3.3 Comparison of AFM and DVS adsorption isotherms

As reported in section 6.4.3.1, the DVS experiments proved inconclusive, as the level of adsorption could not be distinguished from the equipment background noise. This suggests that the thickness of the adsorbed water layers are small and probably smaller than those measured using the AFM technique. If the water layer thicknesses measured using the AFM technique were observed using DVS an uptake of water of ~35 µg would be observable between relative humidity values of 0% and 70%. This leads to the conclusion that the AFM technique over predicts the thickness of adsorbed water layers, as discussed in section 6.2.3.4. The DVS experimental results could possibly be improved by the use of a greater mass of sample material (maximum capacity 1.5 g) and hence an increase in the surface area available for adsorption.
6.4.4 Classified Lactose Experiments

6.4.4.1 DVS Experimental Results

A DVS experiment was performed on a Surface Measurement Systems DVS-1 instrument at Rhône-Poulenc Rorer\(^3\). A 61.63 mg (at 0% RH) sample of classified lactose was used to measure the adsorption isotherm between 0 and 90% relative humidity. The resulting isotherm gave the change in mass of the sample as a function of relative humidity and hence the uptake of water. This was converted to an adsorbed layer thickness using equation 6.10.

\[
\begin{align*}
t &= \frac{M}{\rho A} \\
M &= \text{change in mass of the sample between 0 % RH and the current value of RH (kg)} \\
\rho &= \text{density of water (kg m}^{-3}\text{)} \\
A &= \text{surface area of the sample (m}^2\text{)} \\
A &= \text{surface area of the sample (m}^2\text{)}
\end{align*}
\]

The surface area of the classified lactose sample was determined from the linear portion of a BET plot measured using an Omnisorp 100 CX at the University of Surrey\(^4\).

The surface area of a 1.5 g classified lactose sample was found to be 1.12 m\(^2\)/g. It has been assumed that the surface area of this sample was representative of this batch of classified lactose and consequently the sample used for the DVS analysis.

A plot of adsorbed layer thickness against relative humidity, measured using DVS and AFM, is given in Figure 6.24.

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\(^3\) kindly performed by Linda Randall, Rhône-Poulenc Rorer, London Road, Holmes Chapel, Cheshire.

\(^4\) kindly performed by Mr Michael Reiger, Department of Chemical and Process Engineering, University of Surrey.
Figure 6.24 - Classified Lactose Adsorption Isotherms.

6.4.4.2 AFM Experimental Results
The adsorption isotherm determined using the AFM technique given in Figure 6.24 is that previously detailed in section 6.3.2.

6.4.4.3 Comparison of AFM and DVS Adsorption Isotherms
Figure 6.24 illustrates the two adsorption isotherms measured using the AFM and DVS techniques. It can been seen that the DVS technique reports significantly lower levels of water adsorption compared with the values from the AFM technique. The difference in magnitude of the adsorbed layer values is similar to the difference observed in Figure 6.10 between the adsorbed layers measured using AFM on a silicon sample and the values reported by other investigators using gravimetric techniques.

The discussions of 6.3.2.4 concerning the origin of this difference are in general also applicable in this case, e.g. errors in interpretation of the AFM output curve, non-linearity of the piezo crystal, effect of the curvature of the cantilever tip, inherent errors in the theoretical adjustment and the effect of surface contamination. The fact
that the AFM measurements exceed the gravimetric measurements for both the smooth silicon sample and the much rougher lactose samples suggests that the difference is inherent in the technique. The explanation is thought to lie with the promotion of water nucleation and subsequent capillary condensation due to the presence of the probe tip on the surface.

A rough surface will promote capillary condensation in the 'valleys'. Layer thickness will therefore appear to be larger if the AFM probe tip lands in a valley. There may also be some interaction between the side of the tip and asperities on the surface with the effect of increasing the measured layer thickness. Although the average roughness of the classified lactose sample is smaller than the radius of the cantilever tip (Table 6.4) it can be seen, from Figure 6.22, that there are some large asperities which may come into contact and subsequently interact with the side of the cantilever tip.

Lactose is a partially soluble material which will dissolve to some extent and may form a 'gel' layer, of 'soft' partially dissolved material, which will lead to observation of thicker films. If a gel layer was present it is expected that it could be observed on the AFM output curve by the contact region curve displaying two sections with different regions relating to the different surface properties. During the collection of experimental data on the lactose samples no such variations in the contact regions have been observed.

6.5 Conclusions
A range of experiments was carried out to measure the separation distances at which the tip and sample jump into contact at a range of relative humidities, using the AFM technique. The adsorbed layer thicknesses on the cantilever tip and sample were then calculated from these separation distances. It was seen that the cantilever spring constant and the cantilever tip radius (representing the level of wear on the tip) do not effect the level of water adsorption. It was also observed from the AFM experiments that the effect of variation in temperature, for the range studied 21-27 °C is negligible.
A comparison made between the adsorbed layer thickness, calculated using the DLVO theory (assuming no solute ions are present), and the AFM determined silicon isotherm reveals that the DLVO theory predicts adsorbed layers which are significantly smaller than those measured experimentally. Previously, Deijaguin and Churaev (1974) have suggested that the inclusion of a structural term, $\Pi_s$, in the DLVO theory will account for this difference. However, in the current work the structural term would have to comprise an unrealistically large percentage of the total layer thickness.

The adsorbed layer thicknesses for the silicon sample were fitted using the polarization theory equation to produce a single silicon isotherm. This silicon adsorption isotherm has been compared with values of adsorbed layer thickness measured by previous investigators. The form of the isotherm is similar to other investigators but the current values are larger than those previously observed. Physical effects to which the difference in magnitude may be attributed have been considered and where possible quantified:

- Subjective interpretation of the AFM output curves - $\pm 0.12$ nm.
- Non-linearity of the piezo crystal within the AFM. - ‘worst case scenario’ $\pm 0.66$ nm.
- Roughness of the sample surface causing differential adsorption - the silicon wafer samples are flat, with respect to the cantilever tip, consequently this effect has been considered to be negligible.
- The highly curved cantilever tip causing an increase in vapour pressure above the tip leading to increased adsorption - the increase in vapour pressure has been calculated and found to be negligible.
- Presence of surface ‘gel’ layer - no evidence has been found in the current work to support the presupposition that surface ‘gel’ layers exist.
- Formation of capillary bridges as the tip and sample come into contact promoting condensation of water - the mean radius of curvature of the capillary bridge has been calculated, for gravimetrically determined adsorbed layers (< 1 nm) to be comparable to those predicted by the Kelvin equation for condensation. At such
small distances the validity of the Kelvin equation is very doubtful. However, water nucleation at the site of contact between the probe and the surface is expected, due to an increase in the surface potential resulting from the imposed spatial inhomogeneity. Consequently, water is expected to condense at the contact site increasing the observed adsorbed layer thickness.

- Contamination may be present on the sample surface, which may inhibit or promote the adsorption of water. All silicon samples have been cleaned during the preparation procedure, however an improved cleaning technique is suggested for future studies.

Adsorption isotherms have been determined for three forms of $\alpha$-lactose monohydrate. It was observed that each form of lactose gave a different level of water adsorption. Laboratory grown crystals exhibited the greatest levels of moisture adsorption. Commercially produced milled $\alpha$-lactose displayed lower levels of water adsorption, with the classified lactose recording lower levels of water adsorption than the granulac lactose.

The experiments for each form of lactose were performed over similar ranges of temperature and consequently it can be concluded that the variation in adsorption level are not due to temperature variations.

The surface topography of each sample was analyzed through the use of SEM photographs and AFM images of the surface. The laboratory grown crystals record a roughness of about half that of the commercial lactose samples. The lower values of layer thickness detected for commercial lactose samples is thought to be the result of the increased roughness: adsorbed water is in the ‘valleys’ and is undetected by the probe which lands on the ‘hills’.

All three samples are nominally $\alpha$-lactose monohydrate however the different histories of the samples may lead to different levels of contamination / impurities, which in turn may affect the adsorbed layer thicknesses:
Experimental Results and Discussion

- α-lactose monohydrate contains a small percentage of β-lactose. Due to differences in solubility a higher β-lactose concentration at the surface of an α-lactose monohydrate sample will lead to an increase in the adsorbed layer thickness. The DLVO theory predicts this increase will be no more than 0.1 nm.

- α-lactose monohydrate may contain other impurities, such as phosphates. These may affect the level of water adsorption.

Two experiments, using aluminium foil and classified lactose, have been performed using dynamic vapour sorption (DVS) to validate the AFM technique, developed in the current study, for the measurement of adsorption isotherms.

The aluminium foil DVS experiment was performed by Surface Measurement Systems. It was reported that the uptake of water on the aluminium sample (120 mg) was beyond the detection limit of the instrument (DVS-1) i.e. less than 0.1 μg. It was found that an adsorption isotherm could be determined for aluminium foil using the AFM technique. If the water layer thicknesses measured using the AFM technique were observed using DVS an uptake of water of ~35 μg would be observable between the relative humidity values of 0% and 70%.

The lactose DVS experiment was performed at Rhône-Poulenc Rorer. The reported change in mass of the sample, as a function of relative humidity, was related to the adsorbed layer thickness via the use of sample area, which was from the linear region of a BET plot measured at the University of Surrey.

The adsorption isotherm determined using DVS was compared to the adsorption isotherm determined for classified lactose using the AFM technique. It was observed that the adsorbed layer thicknesses determined using AFM are significantly larger than those measured using DVS. The difference in magnitude is similar to the difference in magnitude between the AFM determined silicon isotherms and adsorption isotherms determined by previous investigators using gravimetric techniques.
In summary, adsorption isotherms have been determined for silicon wafer, three forms of lactose (crystal, classified and granulac) and aluminium foil using the AFM technique.

The silicon isotherm has been compared to isotherms reported by previous investigators, measured using ellipsometric and gravimetric techniques, and has been found to give significantly larger values of adsorbed layer thickness. The causes of the discrepancy have been discussed and where possible quantified. It has not been possible to identify any one factor which would account for the large magnitude of the AFM measured values. However, condensation induced by the physical presence of the probe appears to be the most probable cause.

The adsorption isotherms for each of the three forms of lactose show different levels of water uptake. Possible contributory factors have been discussed but the cause has not been determined. However, the smaller measured values for the commercial samples is thought to be the result of surface roughness.

An adsorption isotherm for classified lactose has been determined using dynamic vapour sorption (DVS). The adsorption isotherms for classified lactose measured using DVS and AFM have been compared. The AFM technique reports significantly larger values of adsorbed layer thickness. The cause of this discrepancy is again attributed to condensation induced by the presence of the probe on the surface.
7. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

In the present study a method has been developed, from a technique originally proposed by Mate et al. (1989), by which the thickness of adsorbed water layers can be determined on individual particles using atomic force microscopy (AFM). The current work has addressed several issues that were either unresolved or not considered by Mate et al., i.e. the inclusion of the cantilever displacement in the calculation of layer thickness, the presence of a liquid layer on the AFM cantilever tip, and the instability of the liquid films as the tip and sample approach contact. Using this current technique, adsorption isotherms at individual points on a sample surface can be determined by measurement of adsorbed layer thickness as a function of relative humidity.

In the current method an experimentally measured separation distance, \( d \), is determined from the AFM output curves. The separation distance is taken to be the sum of both the distances moved by the AFM cantilever tip and the sample during the 'jump-on' region, from the point at which a rapid cantilever displacement is initiated to the point of solid contact.

In air, under ambient conditions, the separation distance is dominated by the thickness of the adsorbed water layers on both the tip and the sample. However there will also be contributions from: (i) a cantilever deflection, \( d_{\text{def}} \), just prior to the onset of the jump arising from van der Waals interactions between the tip and the sample, (ii) an initial jump as the tip jumps into contact with the water layer, \( d_{\text{VDW}} \), again arising from van der Waals interactions, and (iii) attraction of the two adsorbed layers causing localised thickening of the adsorbed water layers (bulges). The effect of electrostatic contributions has been considered to be negligible as doping within the cantilever tip combined with the presence of the adsorbed water layer will act to dissipate any charge.
The van der Waals contributions \( d_{\text{def}} \) and \( d_{\text{VDW}} \) to the separation distance have been determined experimentally by comparing the cantilever deflection in the jump region measured in ambient conditions with the deflection measured under water. Under water the separation distance has been attributed solely to van der Waals interactions as there will be no adsorbed layers. The repulsive contribution of the electrostatic double layer will be small except at very small tip/sample separations, however at these separations all smaller than that at which the ‘jump’ to contact is initiated. It has been experimentally determined that the van der Waals interactions contribute approximately 9% of the cantilever displacement measured in air. In the current study this contribution to the separation distance has not been considered in the theoretical analysis of the experimental data.

The van der Waals contributions to the cantilever displacement has also been determined theoretically and it has been found that the theoretical value lies within the same range as the experimentally determined values. It has also been shown that the cantilever displacement prior to the van der Waals interaction induced jump, \( d_{\text{def}} \), is exactly half of the van der Waals interaction jump distance, \( d_{\text{VDW}} \).

The AFM sampling rate is defined as the number of times the tip and sample move in and out of contact per second. For the Nanoscope II AFM, used in the current study, the sampling rate can be varied between 0.1 Hz and 25 Hz. It has been shown that at sampling rates greater than 2.5 Hz an increased separation distance is observed (for a given humidity). The increase in separation distance is attributed to the formation of a region of increased adsorbed layer thickness. This occurs when the liquid neck, formed as the cantilever tip is withdrawn from the sample surface, breaks and the liquid which was contained within the neck does not have time to return to a stable equilibrium position before the tip re-engages the liquid layer. In the current study a sampling rate of 1 Hz has been used for all experimental measurements, to avoid this effect.
Conclusions

Forcada (1993), while relating the separation distance to the activity of the adsorbed liquid, provided a method by which the thickness of the adsorbed layers, on identical surfaces, can be determined from the separation distance. In the present study, systems have been studied in which the cantilever tip and sample are made of different materials. It has been shown that the theoretical approach of Forcada cannot simply be extended to include non-symmetrical systems (i.e. where the cantilever tip and sample are made of different materials). Consequently, a three step process has been proposed for the calculation of layer thickness for a two component system. First, the half separation distance associated with the cantilever tip is determined from experimental data for the tip interacting with a surface of the same material, i.e. a silicon sample. Second, the separation distance for a system with dissimilar solid surfaces is determined experimentally. This distance is assumed to be the sum of the half separation distance for the cantilever tip and the half separation distance for the sample. Consequently, the half separation distance for the sample can be calculated. Finally, a theoretical separation distance is determined for the sample material, equal to twice the half separation distance, and from this the adsorbed water layer on the sample surface can be determined.

Adsorption isotherms can be obtained for a single point on a sample surface by measuring the thickness of the adsorbed water layer, using an atomic force microscope and subsequent analysis, as the relative humidity of the surrounding environment is varied. In the current study, adsorption isotherms are obtained by measuring the adsorbed layer thickness in a closed chamber as the relative humidity is either ramped up or down. It has been demonstrated that the layer thickness values determined using this dynamic method are comparable to values measured after prolonged exposure (23 hours) to a constant relative humidity and consequently it can be concluded that the equilibrium thickness of the layer appears to be established effectively instantaneously.

A study has been made of a range of theoretical models used to predict layer thickness. Of the models discussed in this study the DLVO theory is the only truly
theoretical model. The DLVO theory can be used to predict the thickness of adsorbed water layers as a function of relative humidity via the use of the disjoining pressure. The disjoining pressure is considered to be made up of two components: a van der Waals interaction, and an electrostatic interaction. The electrostatic contribution is discussed for a system containing solute ions in the liquid layer and for a system without solute ions in the liquid layer. The difference in the magnitude of the predicted adsorbed layer thicknesses between the two systems is no more than 0.1 nm. This is significant in relative terms but much less so when compared with present and previous experimental data.

The validity of the polarization model as a predictive theory is doubtful, however it has been used successfully by previous investigators to fit experimental adsorption isotherm data (Bradley 1936, Garbatski & Folman 1956 and Badmann et al. 1981). In the current study, the form of the equation of the polarization theory has been used to fit experimental data to produce a single convenient empirical expression, but the theory has not been used to predict values of adsorbed layer thickness.

Previous investigators have found that the BET model can be used to fit experimental data for adsorption of a polar liquid on a polar surface. It is shown, in the current work, that the form of the model equation, where the model constant c becomes infinitely large, gives an upper limit to the predicted thickness of adsorbed layers. These maximum values fall below the experimentally measured values for adsorbed water thickness (for all the systems considered in this study) and consequently the BET model has not been used to fit the experimental data of the current study.

The FHH model has been used to fit some of the experimental data of the current study. Previous investigators suggest that the value of the constant N should be in the range 2-3, however the value obtain in the present work is 7.9, which is outside the expected range. This indicates that the FHH theory does not provide a suitable model for use in this work.
Silicon wafer was selected to be an ‘ideal’ sample as it is relatively flat and has a stable surface oxide layer. Adsorption isotherms for silicon/silicon oxide have been published by several other investigators and consequently the results of the current work have been compared both with these previous isotherms and also with theoretical predictions of the layer thickness.

A range of experiments was carried out to measure the separation distances at which the tip and sample jump into contact, and consequently to quantify the amount of water adsorbed on silicon wafer samples at a range of relative humidities, using the AFM technique. It was seen that the cantilever spring constant and the cantilever tip radius (representing the level of wear on the tip) do not effect the level of water adsorption. Of the two contributions to the separation distance; adsorbed layer thickness and van der Waals interactions, the spring constant and tip radius are not expected to effect the layer thickness but they will effect the van der Waals contribution. However, the van der Waals contribution to the separation distance is small (< 9%) and any variations due to differences in spring constant and tip radius are insignificant.

It was also observed from the AFM experiments that the effect of variation in temperature, for the range studied 21-27 °C is negligible. However, the effect of variation in temperature is expected to be significant if a wider range had been studied.

A comparison has been made between the adsorbed layer thickness calculated using the DLVO theory (assuming no solute ions are present) and the AFM determined silicon isotherm. It can be seen that the DLVO theory predicts adsorbed layers which are significantly smaller than those measured experimentally. Derjaguin and Churaev (1974) suggest that the inclusion of a structural term, $\Pi_s$, in the DLVO theory will account for the difference between the predicted and measured adsorbed layer values. However, in the current work the structural term would have to comprise an unrealistic percentage of the total layer thickness. Consequently, it can be concluded
Conclusions

that there must be some other phenomenon responsible for the large water layer observed.

The silicon adsorption isotherm has been compared with values of adsorbed layer thickness measured by previous investigators. The form of the isotherm is similar to other investigators but the current values are larger than those previously observed. The discussion focussed on additional factors which may need to be accounted for in the current AFM technique both at the experimental stage and in the interpretation and theoretical translation of the data. Where possible the magnitude of each effect on the adsorbed layer thickness has been quantified.

Physical effects which may effect the experimental data include:

- Subjective interpretation of the AFM output curves - leading to a potential variation in layer thickness of ± 0.12 nm.
- Non-linearity of the piezo crystal within the AFM. - the magnitude of the effect has been quantified by consideration of a ‘worst case scenario’ from a study performed by previous investigators (Tyrrell & Cleaver 1998). Under these conditions the adsorbed layer may be 0.66 nm less than determined in the current work.
- Roughness of the sample surface causing differential adsorption - the silicon wafer samples are flat, with respect to the cantilever tip, consequently this effect has been considered to be negligible.
- Presence of surface ‘gel’ layer - no evidence has been found in the current work to support the presupposition that surface ‘gel’ layers exist.
- The highly curved cantilever tip causing an increase in vapour pressure above the tip leading to decreased adsorption, i.e. a thinner layer coating the probe tip - the increase in vapour pressure has been calculated and found to be negligible.
- Formation of capillary bridges as the tip and sample come into contact promoting condensation of water - the mean radii of curvature of the liquid bridge calculated from the Kelvin equation, at different relative humidities, have been compared to those calculated for adsorbed liquid layers determined gravimetrically.
Conclusions

At layer thicknesses of less than 5 nm the application of the Kelvin equation is dubious and the formation of a meniscus is unlikely. However, the spatial inhomogeneity arising from the presence of the probe on the surface is expected to increase the surface potential therefore promoting nucleation of water. Once sufficient water has gathered, (> 1 monolayer), the liquid layer will become mobile and a meniscus will form. Repeated contact and removal of the tip from the surface will tend to pull water into the capillary from the surrounding surface. It is this mechanism that is suspected to account for the excessively large measured values of layer thickness using AFM.

- Contamination may be present on the sample surface, which may inhibit or promote the adsorption of water. All silicon samples have been cleaned during the preparation procedure, however an improved cleaning technique is proposed.

In the current AFM technique, the experimentally measured separation distances are translated theoretically into adsorbed layer thicknesses, using an approach based on the work of Forcada (1993). This approach contains certain system simplifications which may lead to errors in the calculated values of adsorbed layer thickness:

- It has been assumed that the separation distance can be attributed solely to the effect and presence of the adsorbed liquid layers. The contribution of van der Waals interactions (and electrostatic interactions) to this distance has been quantified by conducting an experiment under water, where there will be no adsorbed layers. It has been found that van der Waals interactions make up approximately 9% of the separation distance when measured in air. In this study the contribution of van der Waals interactions to the separation distance has not been considered in order to simplify the theoretical considerations. However, if the contribution of van der Waals interactions to the separation distance had been included it has been determined that the adsorbed layer thicknesses would be an average of 0.2 nm lower.
• In the work of Forcada (1993) it is assumed that the overall interaction between the two liquid films can be attributed entirely to van der Waals interactions, no other forces such as the electric double layer effect, the surface tension or the viscosity of the liquid are considered. If the electric double layer effect were to be included an increased liquid layer thickness would be expected due to the repulsive nature of the effect. The inclusion of surface tension and viscosity terms would also lead to increased layer thickness values as they would provide resistance to the formation of the localised perturbations of the liquid film and consequently the measured separation value will be closer to the predicted layer thickness.

Several of the other investigators, with whom the current data has been compared, measure adsorption isotherms using ellipsometry, which is generally considered to be a reliable technique. However, evidence has been uncovered that points to inherent errors in the measurement of thin films using ellipsometry. For thin films (<20 nm) it is not possible to determine both the layer thickness and the refractive index, consequently the refractive index of the film is taken to be that of the bulk material and it can be concluded that the resulting layer thicknesses are therefore approximate.

Lactose was also selected as a sample material due to its wide use and great importance to the pharmaceutical industry. Adsorption isotherms have been obtained for three forms of α-lactose monohydrate. Milled lactose available commercially was selected, granulac and classified lactose, together with ‘ideal’ laboratory grown lactose crystals.

It was observed that each form of lactose gave a different level of water adsorption. Laboratory grown crystals exhibited the greatest levels of moisture adsorption. Commercially produced milled α-lactose displayed lower levels of water adsorption, with the classified lactose recording lower levels of water adsorption than the granulac lactose.
Conclusions

The experiments for each form of lactose were performed over similar ranges of temperature and consequently it can be concluded that the variation in adsorption level are not due to temperature variations.

Surface topography was considered as a possible cause of the variation in water adsorption. The surface structure of each sample was analyzed through the use of SEM photographs and AFM images of the surface. The measured surface roughness for the commercial lactose samples was determined to be about twice that for the laboratory grown crystal. This correlates with the measured layer thickness; the rougher samples exhibit smaller layer thicknesses because the probe tip will contact asperities and adsorbed water in the ‘valleys’ on the surface will go undetected by the probe.

All three samples are nominally α-lactose monohydrate however the different histories of the samples may lead to different levels of contamination / impurities, which in turn may effect the adsorbed layer thicknesses:
- α-lactose monohydrate contains a small percentage of β-lactose. Due to differences in solubility a higher β-lactose concentration at the surface of an α-lactose monohydrate sample will lead to an increase in the adsorbed layer thickness. The DLVO theory predicts this increase will be no more than 0.1 nm.
- α-lactose monohydrate may contain other impurities, such as phosphates. These may affect the level of water adsorption.

Two experiments, using different sample materials, have been performed using dynamic vapour sorption (DVS) to validate the AFM technique, developed in the current study, for the measurement of adsorption isotherms.

The first experiment was performed with aluminium foil as the sample material, selected because it provided a flat stable surface and the DVS sample would be directly equivalent to the sample used for the AFM study. It was reported that the uptake of water on the aluminium sample (120 mg) was beyond the detection limit of
the instrument (DVS-1) \( i.e. \) less than 0.1 \( \mu g \). It was found that an adsorption isotherm could be determined for aluminium foil using the AFM technique. If the water layer thicknesses measured using the AFM technique were observed using DVS an uptake of water of \( \sim 35 \mu g \) would be observable between the relative humidity values of 0\% and 70\%.

The second experiment was performed using classified lactose. The use of a powder added complexity to the experiment as there was the possibility of capillary condensation between the particles at higher humidity levels, however this was not observed for the sample for relative humidity values up to 70\%. DVS was used to measure the change in mass of the classified lactose sample as function of relative humidity. The change in mass of the sample was related to the adsorbed layer thickness via the use of sample area, which was determined for a typical classified lactose sample from the linear region of a BET plot.

The adsorption isotherm determined using DVS has been compared to the adsorption isotherm determined for classified lactose using the AFM technique and reported previously. It can be observed that the adsorbed layer thicknesses determined using AFM are significantly larger than those measured using DVS. The difference in magnitude is similar to the difference in magnitude between the AFM determined silicon isotherms and adsorption isotherms determined by previous investigators using gravimetric techniques. The discussions concerning the origin of the difference in layer thickness for the silicon isotherms can also be applied to the discrepancy between the AFM and DVS adsorption isotherms.

In summary, adsorption isotherms have been determined for silicon wafer, three forms of lactose (crystal, classified and granulac) and aluminium foil using the AFM technique.

The silicon isotherm has been compared to isotherms reported by previous investigators, measured using ellipsometric and gravimetric techniques, and has been
found to give significantly larger values of adsorbed layer thickness. The causes of the discrepancy have been discussed and where possible quantified. The most likely cause of the difference is thought to be due to induced capillary condensation arising from the physical presence of the probe.

The adsorption isotherms for each of the three forms of lactose show different levels of water uptake. Possible contributory factors have been discussed but the precise cause has not been determined. The smaller measured values for the commercial samples are thought to be the result of surface roughness.

An adsorption isotherm for classified lactose has been determined using dynamic vapour sorption (DVS). The adsorption isotherms for classified lactose measured using DVS and AFM have been compared. The AFM technique reports significantly larger values of adsorbed layer thickness.

In the current work, it has been proposed that the difference observed in the level of water adsorption between the current AFM data and previously published data, measured using ellipsometry or gravimetric techniques, may primarily be due to the physical presence of the probe tip on the sample surface causing a spatial inhomogeneity and an increase in surface potential. This may lead to nucleation of water molecules and once sufficient water has gathered the formation of a liquid meniscus and capillary condensation. However, this effect has not been quantified in the current study. In order to progress the validation of the AFM technique, as an accurate method of determining adsorption isotherms, this effect needs to be quantified. The prediction of the increase in the surface potential around the probe tip and a subsequent statistical mechanics analysis of the water nucleation and the formation of a capillary meniscus should be considered as an area for future study.

The interactions occurring between the cantilever tip, the sample surface and the adsorbed water layers also need to be analysed in greater detail, in order to improve
the accuracy of the theoretical translation of the separation distances to adsorbed layer thicknesses. The dynamic nature of the system also needs to be addressed.

It has been shown, for the lactose samples, that surface roughness will affect the level of the adsorbed layer detected. It is suggested that an analysis be performed to study the potential effect of variation in surface roughness and the reduced detection of surface water lying in 'valleys', in order to quantify the effect.
REFERENCES


References


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Herrington, B.L., (1934), Some physico-chemical properties of lactose. J. Dairy Sci., 17, 533-542.


References


Appendix 1 - CALCULATION OF HAMAKER CONSTANT

The assumption of additivity in van der Waals interaction expression and in the conventional definition of Hamaker's constant ignores the influence of neighbouring atoms on the interaction between any pair of atoms and consequently makes the assumption essentially incorrect (Visser 1976). The problem of additivity can be avoided by the use of Lifshitz theory (Lifshitz 1956). In this theory the atomic structure is ignored and the forces between large bodies, now treated as continuous media, are derived in terms of bulk properties namely, the optical characteristics of the material with respect to the whole electromagnetic spectrum. Israelachvili (1991) comments that the original Lifshitz theory (Lifshitz 1956) requires knowledge of quantum field theory for its understanding. He goes on to comment that this is the probable reason that the theory was initially ignored until it was shown that the essential equations could be derived using much simpler theoretical techniques. The various approaches to the calculation of the Hamaker constant are reviewed by Israelachvili & Tabor (1973), Mahanty & Ninham (1976) and Visser (1976). Israelachvili (1991) suggests the simplest of which is a modified additivity approach.

Using this approach, Hamaker's constant can be calculated with relative ease. For two macroscopic phases, 1 and 2, interacting across a medium, 3, Hamaker's constant can be calculated from equation A1.1.

\[
A \approx \frac{3}{4} kT \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right) \left( \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right) + \frac{3h\nu_e}{8\sqrt{2}} \left( \frac{n_1^2 - n_2^2}{(n_1^2 + n_3^2)^{1/2}} \right) \left( \frac{n_2^2 - n_3^2}{(n_2^2 + n_3^2)^{1/2}} \right) \left( \frac{n_1^2 + n_3^2}{(n_1^2 + n_3^2)^{1/2}} + \frac{n_2^2 + n_3^2}{(n_2^2 + n_3^2)^{1/2}} \right)
\]

(A1.1)

Here

\(\varepsilon =\) dielectric constant (relative permittivity)

\(n =\) refractive index

\(h =\) Plank's constant

\(\nu_e =\) main electronic absorption frequency in the UV range \(\approx 3 \times 10^{15}\) s\(^{-1}\) and is assumed to be the same for all 3 phases.
A summary of the variables used; dielectric constant, refractive index and main electronic frequency, for the materials used in the current work, are given in Table 1.

Table 1 - Summary of optical properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dielectric Constant $\varepsilon$</th>
<th>Refractive Index $n$</th>
<th>Adsorption Frequency $v_e \left(10^{15} \text{ s}^{-1}\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1</td>
<td>1</td>
<td>3.0</td>
</tr>
<tr>
<td>Water</td>
<td>78.5</td>
<td>1.333</td>
<td>3.0</td>
</tr>
<tr>
<td>Silicon Oxide $^a$</td>
<td>3.81$^o$</td>
<td>1.458$^o$</td>
<td>3.2$^o$</td>
</tr>
<tr>
<td>Aluminium Oxide $^b$</td>
<td>11.6</td>
<td>1.75</td>
<td>3.0$^d$</td>
</tr>
<tr>
<td>Lactose</td>
<td>6$^o$</td>
<td>1.517$^l$</td>
<td>3.0$^d$</td>
</tr>
</tbody>
</table>

unless stated values have been taken from Israelachvili (1991)

a - native oxide layer on silicon wafer

b - native oxide layer on aluminium foil

c - Comprehensive Inorganic Chemistry V1 (1973)

d - estimated - based on general value (Israelachvili 1991)

e - estimated - based on values for crystalline solids (Israelachvili 1991)

f - Whittier (1944)

In the current work the Hamaker constants have been determined from equation A1.1 using Mathcad PLUS 5.0. The values of Hamaker constants for the systems relevant to this work are given in Table 2.

Due to the assumption in equation A1.1 that the adsorption frequency, $v_e$, is the same for all the materials, the general value of $3.0 \times 10^{15} \text{ s}^{-1}$ is used in all the calculations despite the fact that the value for silicon oxide is slightly higher.
### Table 2 - Hamaker Constants

<table>
<thead>
<tr>
<th>Phase 1</th>
<th>Medium 3</th>
<th>Phase 2</th>
<th>Hamaker Constant x 10^{-20} J</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>air</td>
<td>water</td>
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</tr>
<tr>
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<td>silicon oxide</td>
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</tr>
<tr>
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<td>7.60</td>
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<td>water</td>
<td>lactose</td>
<td>1.11</td>
</tr>
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<td>air</td>
<td>-0.92</td>
</tr>
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</tr>
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</tr>
<tr>
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<td>water</td>
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<tr>
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<td>air</td>
<td>lactose</td>
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</tr>
<tr>
<td>silicon</td>
<td>water</td>
<td>lactose</td>
<td>0.85</td>
</tr>
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</table>

The system considered in section 3.5.3, for the calculation of the van der Waals interaction force, is a silicon tip interacting with a silicon surface across a water and air medium. This can be treated as a silicon oxide/water/silicon oxide system for the purpose of Hamaker constant calculation. The air layer is assumed to be equivalent to a vacuum and has no effect on the Hamaker constant. In reality the presence of the molecules in the air, compared with an absence of molecules in a vacuum, will cause a slight retardation in the interaction and consequently the Hamaker constant will be lowered slightly.
Appendix 2 - CALCULATION OF ADSORBED LAYER THICKNESS

From the experimental data the adsorbed layer thicknesses, on lactose samples, can be calculated using the strategy for dissimilar solid surfaces proposed in section 3.5.7.7. This appendix provides a sample calculation for the determination of adsorbed layer thickness on a lactose crystal at a relative humidity of 50 %.

The half separation distance associated with the cantilever tip is determined from experimental data for the tip interacting with a surface of the same material, i.e. a silicon sample.

An empirical expression, equation 6.7, for the half jump distance as a function of relative humidity has been developed, for a silicon/silicon interaction by fitting data from adsorption isotherm experiments conducted on silicon wafer samples (sections 6.2.3 & 6.2.4).

\[
\frac{1}{2}d_{s1} = \ln(-\ln\left(\frac{\rho}{\rho_0}\right) + 0.993) + 4.571 \quad \text{(nm)} \tag{6.7}
\]

At a relative humidity of 50 % (p/p° = 0.5)

\[
\frac{1}{2}d_{s1} = 4.047 \text{ nm}
\]

The separation distance for a two component system is determined experimentally.

A separation distance has been determined using AFM for the interaction between a silicon cantilever tip and a lactose crystal sample at a relative humidity of 50 %.

\[
d_{\text{total}} = 12.691 \text{ nm}
\]
This distance is assumed to be the sum of the half separation distance for the cantilever tip and the half separation distance for the sample. Consequently, the half separation distance for the sample can be calculated.

\[ d_{total} = \frac{1}{2}d_{s1} + \frac{1}{2}d_{s2} \]

\[ \Rightarrow \quad \frac{1}{2}d_{s2} = 12.691 - 4.047 \text{ nm} \]

\[ \frac{1}{2}d_{s2} = 8.644 \text{ nm} \]

A theoretical separation distance can then be determined for the sample material, equal to twice the half separation distance.

\[ d_{s2} = 17.288 \text{ nm} \]

This value for separation distance can then be used to calculate the adsorbed layer thickness using equation 3.18 where the function \( f \) is set to zero.

\[
f = \frac{A_{IL}}{2\pi(d-2t)^4} + \frac{A_{ILS}}{2\pi} \left( \frac{1}{t^4} - \frac{1}{(d-t)^4} \right) \tag{3.18}
\]

For water adsorption on lactose surfaces, the solid being considered is lactose, the liquid is water and the intervening medium is air. Consequently, \( A_{IL} \) is the Hamaker constant for two water layers interacting in air and \( A_{ILS} \) is the Hamaker constant for a lactose surface interacting with air across a water layer.

\[ A_{IL} = 3.73 \times 10^{-20} \text{ J} \]

\[ A_{ILS} = -1.47 \times 10^{-20} \text{ J} \]

Substituting the value of the separation distance, \( d = 17.288 \times 10^{-9} \text{ m} \) and the values for the Hamaker constants \( A_{IL} \) and \( A_{ILS} \) into equation 3.18, where the function is set to zero gives:
This equation is then solved iteratively, using a quasi-Newton technique (Microsoft Excel Spreadsheet 'solver' function with default settings), to give a value of adsorbed layer thickness, $t$.

Equation 3.18 can be solved using this iterative technique for the example of the adsorbed layer thickness measured on a lactose crystal sample at 50 % RH.

$$t = 5.27994753012576 \times 10^{-9} \text{ m}$$

Consequently, the thickness of an adsorbed water layer on a lactose crystal surface, at 50 % relative humidity, has been calculated to be 5.280 nm.