Force Measurements between Titania Surfaces
Produced by Atomic Layer Deposition:
The van der Waals Enigma

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Declaration

The research presented in the thesis is my original work; however some aspects of this work were undertaken in collaboration with others. The XPS measurements in Chapter 3 were performed by Professor William Skinner of the Ian Wark Institute and Optical reflectometry measurements in this Chapter were performed by Mr Shaun Howard of the Department of Applied Mathematics. The work in Chapter 4 includes the results of calculations performed by Dr Drew Parsons of the Department of Applied Mathematics. XPS measurements described in Chapter 5 were performed by Dr Drew Evans of the Mawson Institute. Optical Reflectometry measurements of the CTAB adsorption to titania surfaces described in Chapter 6 were performed either by Mr Shaun Howard of the Department of Applied Mathematics or Mr Bo Wu of the Department of Chemical Physics at the University of Science and Technology of China.

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Abstract

The surface forces between colloidal particles are important in flotation, lubrication, adhesion, rheology, materials science and cell interactions. In order to perform a fundamental investigation of surface forces, model surfaces are usually employed instead of natural surfaces. This is because natural surfaces are unsuitable due to the degree of surface roughness, inappropriate geometry or chemical heterogeneity. Given that the number of materials for which model surfaces are available is small, it is advantageous to expand the range of model surfaces that are available. This will enable a wider range of properties to be investigated and provide analogs for materials that are of interest in industrial processes, as well as providing for more stringent tests of our theoretical understanding of surface forces. With this as the goal, Atomic Layer Deposition (ALD) has been applied to the production of model surfaces of mineral oxides for surface force measurements in this thesis.

Smooth surfaces of titania were produced using ALD and the surface forces measured in a range of conditions. Direct force measurements performed at the isoelectric point (IEP) of the titania surface revealed the van der Waals interaction. This measurement agreed with the calculated interaction predicted using Lifshitz theory. At pH values slightly above or below the IEP, a diffuse double layer repulsion was observed which is attributed to charging of the surface. At high pH, the forces were found to be repulsive up until contact, with no van der Waals attraction or adhesion being observed. It appears that the van der Waals attraction is either reduced at high pH or an additional repulsive force arises in these conditions. Reasons that could explain the absence of the van der Waals interaction at high pH include surface roughness, hydration of the surface or formation of a gel layer due to surface swelling. Surface roughness alone does not account for the absence of the van der Waals forces as the ALD prepared titania surfaces are very smooth. Neither do the hydration forces, as the expected dispersion forces should be exhibited at a range in which the hydration forces are absent. Formation of a gel layer through surface swelling is a possible explanation, however there is no evidence for this occurring as no change in the mechanical properties of the surfaces with pH were detected.
Surfactants are employed as a facile means to alter surface properties; they have applications in mineral processing, detergency and lubrication. Adsorption isotherms for the cationic surfactant cetyltrimethylammonium bromide (CTAB) on ALD titania surfaces were measured using optical reflectometry. Measurements were performed at a range of concentrations below and above the common intersection point where adsorption is dominated by electrostatic and hydrophobic interactions respectively, as well as above and below the IEP. Interestingly, significant levels of adsorption were observed below the IEP where the electrostatic interactions are unfavorable. The adsorption results were used to interpret the force measurements between titania surfaces in aqueous CTAB solutions, which were measured using the colloid probe technique at different pH and electrolyte concentrations. The surface force data was compared to DLVO theory. Poor fits are obtained when Lifshitz theory is used to determine the effective Hamaker constant for the dispersion forces. However, all of the data are fit well with a dispersion force of reduced magnitude.

The observation that the dispersion forces exhibited away from the IEP or in the presence of surfactant are much reduced has important implications for flocculation, adhesion and rheology of colloidal systems. Whilst several explanations for this anomaly have been proposed and tested in this thesis, the observation currently remains unexplained.
Publications

Refereed Journal Papers Included as Part of this Thesis

   *Surface Forces between Titanium Dioxide Surfaces in the Presence of Cationic Surfactant as a Function of Surfactant Concentration, Electrolyte Concentration, and pH*
   Langmuir, 30 (10), 2789–2798 (2014)

II. **R. B. Walsh**, D. Evans, V. S. J. Craig
   *Surface force measurements between Titanium Dioxide surfaces prepared by Atomic Layer Deposition in electrolyte solutions reveal Non-DLVO interactions: Influence of water and argon plasma cleaning.*
   Langmuir, 30 (8), 2093–2100 (2014)

    *Model Surfaces Produced by Atomic Layer Deposition*
    Chemistry Letters, 41 (10), 1247-1249 (2012)

    *Direct Measurement of van der Waals and Diffuse Double-Layer Forces between Titanium Dioxide Surfaces Produced by Atomic Layer Deposition.*

Refereed Journal Papers Not Included as Part of this Thesis

I. N. Eom, **R. B. Walsh**, G. Liu, D. F. Parsons and V. S. J. Craig
   *Surface forces in particle technology: Wet systems*
   Procedia Engineering, Accepted, (2014)

II. D. F. Parsons, **R. B. Walsh**, and V. S. J. Craig
    *Surface Forces: surface roughness in theory and experiment*

III. L. Ellis-Gibbings, V. Johansson, **R. B. Walsh**, L. Kloo, J. S. Quinton, and G. G. Andersson
   *Formation of N719 Dye Multilayers on Dye Sensitized Solar Cell Photocathode Surfaces Investigated by Direct Determination of Element Concentration Depth Profiles*

IV. E.-J. Teh, Y.-K. Leong, Y. Liu, V. S. J. Craig, **R. B. Walsh** and S. C. Howard
    *High Yield Stress Associated with Capillary Attraction between Alumina Surfaces in the Presence of Low Molecular Weight Dicarboxylic Acids*
Refereed Conference Proceedings

Additional Attractive Forces Between Alumina Particles Due to Low Solubility of Dicarboxylic Acids
XXV International Mineral Processing Congress (IMPC 2010) Brisbane, Australia, 6-10 September, pp 395-405

Effect of Low Molecular Weight charged molecules on the interactions between spherical alumina particles

Oral Conference Presentations

Australian Colloid and Interface Symposium 2013, Noosa, Australia, February 2013

25th European Colloid and Interface Society, Berlin, Germany, September 2011

Australian Colloid and Interface Symposium 2011, Hobart, Australia, February 2011

27th Australian Colloid & Surface Science Student Conference, Roseworthy, Australia, February 2010

Poster Presentations

I. R. B. Walsh, V. S. J. Craig, “Determination of interaction forces between mineral surfaces at high ionic strength”
International Fine Particle Research Institute Annual General Meeting, Chapel Hill, USA, July 2011

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Chapter 1: Measurement and analysis of surface forces

1.1 Introduction

Colloid science covers a wide range of different physical systems. A system is deemed to be colloidal in nature when small particles (typically <10 micron is size) of one material are dispersed throughout another.\(^1\) The phases of these systems can be any combination of solids, liquids or gases. Examples of colloidal systems include foams, cosmetics, paints, inks, milk and blood.

In a colloidal system a significant portion of the molecules of the dispersed phase, lie at or near the interface of the dispersion medium. Due to this proximity with the surface, the chemistry of the surface is important as the properties of these molecules, and those of the dispersing phase near the interface are different to those that occur in the bulk phase. Due to the large surface area of the interfacial region, these interfacial properties will dominate the behavior of the system.

The forces acting between the particles of the dispersed phase determine the stability of a colloid dispersion. In fact, colloidal particles in an aqueous medium are often thermodynamically unstable, due to the energetic cost of the interface. Despite this, colloidal systems are often seen to be stable for extended periods of time. Explaining this stability was the goal of colloid scientists over the first half of the twentieth century. Derjaguin and Landau\(^2\) and Verwey and Overbeek\(^3\), independently developed a theory of colloid stability which is now known as DLVO theory. This theory states that the total interaction between surfaces is the sum of the van der Waals forces which is attractive for a symmetric system and electrostatic forces which are repulsive for like particles. An important implication of the theory is that the repulsive forces serve only as a barrier to the attractive forces between surfaces, making colloid dispersions kinetically stable, depending on the height of the barrier. Relevant details of the DLVO theory with regards to surface force measurements are presented below.
1.1.1 DLVO Forces

DLVO theory states that the total interaction between two particles is the sum of the electrostatic force and the van der Waals force. In the case of two like surfaces, the electrostatic force is always repulsive while the van der Waals force is always attractive. Between two different surfaces, the electrostatic force can be attractive or van der Waals forces may be repulsive (e.g. an alumina particle in water interacting with a bubble).

1.1.1.1 Electrostatic Repulsion

When immersed in a polar medium, most surfaces will acquire a charge, through ionization of surface charge groups (such as carboxyl or amino groups) as a result of adsorption of ions to the surface or through the preferential dissolution of one type of ion into the medium. The magnitude of the charge at the surface is dependent on the properties of the solvent, such as dielectric constant, ionic strength and pH and the chemical nature of the surface. The distribution of ions in solution is influenced by the charge of the surface. Co-ions will be repelled from the surface and counter-ions will be attracted to the surface.

The most commonly accepted model to describe the distribution of ions is that attributed to Stern. This is a combination of the Helmholtz theory of adsorbed ions and the Gouy-Chapman model for an outer diffuse layer of ions. Figure 1.1 shows a schematic of the Stern model.

The region at the surface, which contains the surface charge and a compact layer of adsorbed counter-ions, is often called the Stern or Helmholtz Layer. The co-ions distribute themselves into a diffuse layer beyond the stern layer boundary, which is governed by the electrostatic forces and the random thermal motion of the ions. These two regions constitute the diffuse double layer.
Figure 1.1: Schematic of the stern double layer showing the change in potential as a function of distance. The potential decays linearly from the surface, through the inner layer of adsorbed counter ions, up to the stern layer. Outside the Stern layer, the potential decays exponentially away from the surface to zero through a diffuse layer of counter and co ions.

The boundary between the inner and outer layers is located a distance of about one hydrated ion from the surface (a few Å). In the Stern layer, the potential decays linearly from the surface up to the Stern layer boundary. Beyond this layer, the distribution of ions is described using the Gouy-Chapmen diffuse layer model. This model describes the counter-ions being attracted to the surface (and co-ions repelled from the surface) as a result of the potential at the Stern layer boundary. The attraction is balanced by the thermal diffusivity of the ions that results in an exponentially decaying distribution of ions (and electrostatic potential) from the surface according to Boltzmann statistics. A
A summary of the derivation of the Gouy-Chapman diffuse layer model described by Pashley, et al.\(^1\) is provided here.

Starting from Maxwell’s equations, the total electric field \( \vec{E}_t(\vec{r}) \) at the position vector \( \vec{r} \) is related to the local electric charge density \( \rho(\vec{r}) \) by,

\[
\nabla \cdot \vec{E}_t(\vec{r}) = \frac{\rho(\vec{r})}{\varepsilon_0 \varepsilon}
\]

[1.1]

For the case of the electric field a distance \( L \) from a charged flat surface, this becomes

\[
\frac{d^2 \psi(L)}{dL^2} = \frac{\rho(L)}{\varepsilon_0 \varepsilon}
\]

[1.2]

where \( \psi(L) \) is the electrostatic potential, \( \varepsilon_0 \) is the permittivity of free space and \( \varepsilon \) is the dielectric constant of the medium.

The local density of any ion of charge \( Z_i q \) (where \( q \) is the proton charge and \( Z_i \) is the valency of the ion) depends on the electrostatic potential energy. For an ion of charge \( Z_i q \) at \( L \) the electrostatic potential energy is simply given by \( Z_i q \psi(L) \). This is energy gained by moving a unit charge from a position of infinity to the position \( L \).

Since any ion next to a charged surface must be in equilibrium with the corresponding ions in the bulk solution, the electrochemical potential \( \mu \) of an ion at a distance \( L \) for the surface must be equal to the bulk value

\[
\mu_{i}^b = \mu_{i}^c
\]

[1.3]

or

\[
\mu_{i}^0 + k_B T \ln C_i(B) = \mu_{i}^0 + Z_i q \psi(L) + k_B T \ln C_i(L)
\]

[1.4]

where \( \mu_{i}^0 \) is the standard chemical potential of component ‘\( i \)’, \( C_i(B) \) and \( C_i(L) \) are the ion concentrations in the bulk and at a distance \( L \) from the surface, \( k_B \) is the Boltzmann constant and \( T \) is the temperature.
Rearrangement of this equation leads to the Boltzmann distribution (Equation 1.5), which describes the concentration of ions next to a charged surface that is immersed in an electrolyte solution.

\[
C_i(L) = C_i(B) \exp \left[ - \frac{Z_i q \psi(L)}{k_B T} \right]
\]

[1.5]

Using the Boltzmann distribution the net charge density \( \rho(L) \), at a distance \( L \) (for both counter and co-ions), can be obtained.

\[
\rho(L) = \sum_i Z_i q C_i(L) = \sum_i Z_i q C_i(B) \exp \left[ - \frac{Z_i q \psi(L)}{k_B T} \right]
\]

[1.6]

A substitution with Equation 1.2 gives

\[
\frac{d^2 \psi(L)}{dL^2} = \frac{q}{\varepsilon_0 \varepsilon} \sum_i Z_i C_i(B) \exp \left[ - \frac{Z_i q \psi(L)}{k_B T} \right]
\]

[1.7]

which is the Poisson-Boltzmann equation. In this derivation, ions are treated as point changes and the potentials at each plane \( L \) are uniformly smeared along that plane. These are usually reasonable assumptions.

In the case of a symmetrical electrolyte, that is a Z:Z electrolyte, Equation 1.6 becomes

\[
\rho(L) = Z q C(B) \left\{ \exp \left[ - \frac{Z q \psi(L)}{k_B T} \right] - \exp \left[ \frac{Z q \psi(L)}{k_B T} \right] \right\}
\]

[1.8]

By defining \( Y = Z q \psi(L)/k_B T \) this reduces to,

\[
\rho(L) = -Z q C(B) \{ \exp[Y] - \exp[-Y] \} = -2Z q C(B) \sinh Y
\]

[1.9]

which when applied to the Poisson-Boltzmann equation gives

\[
\frac{d^2 \psi(L)}{dL^2} = \frac{2Z^2 q^2 C(B)}{\varepsilon_0 \varepsilon k_B T} \sinh Y
\]

[1.10]
If the real distance $L$ is replaced with the scaled distance $X$ such that $X = \kappa L$ where $\kappa^{-1}$, which is called the Debye length, is defined as

$$\kappa^{-1} = \sqrt{\frac{\varepsilon k_B T}{q^2 \sum_i C_i(B)Z_i^2}}$$

[1.11]

then Equation 1.7 becomes the simple non-linear, second order differential equation:

$$\frac{d^2Y}{dX^2} = \sinh Y$$

[1.12]

Which gives the potential distribution next to a charged surface

$$Y = \left[ \frac{1 + Ye^{-X}}{1 - Ye^{-X}} \right]$$

[1.13]

where

$$\gamma = \left[ \frac{\exp(Y_0/2 - 1)}{\exp(Y_0/2 + 1)} \right]$$

[1.14]

An idea of what the theory predicts can be obtained by looking at the limit of low potentials, that is when $Y_0 \ll 1$. For 1:1 electrolytes, this corresponds to $\psi_0 < 25 \text{mV}$. In this case, Equation 1.13 will reduce to

$$\psi(L) \cong \psi_0 e^{-\kappa L}$$

[1.15]

which demonstrates the physical meaning of the Debye length. It is the distance at which the surface potential has fallen to $1/e$ of its original value. This is an indication of the decay length of the potential from the surface. Figure 1.2 shows some typical results for Equation 1.15, as the Debye length is varied. The Debye length is dependent on the electrolyte concentration. When the concentration is low the Debye length is large, as a result the potential decays slowly from the surface. At high electrolyte concentrations, the Debye length is small; therefore, the potential decays rapidly from the surface.
The interaction between diffuse double layers, as they come into contact will be dependent on the concentration of the counter and co-ions near the surfaces. For similarly charged surfaces, as they are moved together, the increase in concentration of similarly charged ions between the surfaces is unfavorable; as a result, a repulsive interaction occurs. The interaction energy of the repulsion between two flat surfaces of the same potential can be calculated using the algorithm developed by Chan, Pashley and White\textsuperscript{6}, which is summarized here.

Starting from the planar Poisson-Boltzmann equation for the scaled potential $Y\left(\frac{e\psi}{k_BT}\right)$ for a 1:1 electrolyte (Equation 1.12),

$$\frac{d^2Y}{dX^2} = \sinh Y$$

where $X\left(\frac{kd}{2}\right)$ is the scaled distance measured from the midplane (see Figure 1.3).
The first integration yields

\[
\frac{DY}{DX} = Q \text{ Sgn}(Y_m)
\]  

[1.16]

where \( Y_m \) is the scaled midplane potential and \( Q \) is defined to be

\[
Q = \sqrt{2(\cosh Y - \cosh Y_m)}
\]  

[1.17]

The derivative of \( Q \) with respect to the scaled potential is

\[
\frac{dQ}{dY} = \frac{\sinh Y}{Q}
\]

\[
= \frac{\text{Sgn}(Y_m)}{Q} \sqrt{\left(\frac{Q^2}{2} + \cosh Y_m\right)^2 - 1}
\]  

[1.18]

Using equations 1.16 and 1.18 the differential equation

\[
\frac{dX}{dQ} = \sqrt{\left(\frac{Q^2}{2} + \cosh Y_m\right)^2 - 1}
\]  

[1.19]
can be derived. If the value of $Q$ corresponding to the surface charge is known ($Q_s$), then for a given midplane potential $Y_m$, equation 1.19 can be solved from the midplane to the surface ($Q = 0$ to $Q = Q_s$) numerically using a fourth order Runge-Kutta method. Thus the scaled distance from the midplane ($X$) can be determined for a given $Y_m$. Repeating for a set of suitably chosen values of $Y_m$ will generate the corresponding scaled distances.

The electrostatic pressure for each value of $Y_m$ can be calculated using

$$P (L) = 2n k_B T (\cosh Y_m - 1)$$

[1.20]

Then the interaction energy ($E_p (L)$) per unit are can be calculated using

$$E_p (L) = \int_L^\infty P (L') dL'$$

[1.21]

The calculation of the electrostatic double layer force has two boundary conditions: the case of the surfaces having constant charge, and the case of constant potential at the surface. At the constant charge boundary condition, the charge on both surfaces is assumed to be fixed whereas the constant potential condition assumes that the potential is fixed and the charges will regulate as separation changes to maintain the constant potential of the surfaces. In the case of real surfaces, partial regulation occurs leading to forces that lie between the two boundary conditions. Depending on the boundary condition imposed $Q_s$ is calculated using

$$Q_s = \sqrt{2 (\cosh Y_s - \cosh Y_m)}$$

[1.22]

for the condition of constant potential, where $Y$ is $Y_s$ (the surface potential) or

$$Q_s = \frac{4\pi e}{\varepsilon k_B T} |\sigma|$$

[1.23]

for the constant charge condition calculated from the surface charge density ($\sigma$). Most surfaces will fall somewhere between these boundary conditions.
1.1.1.2 The Derjaguin Approximation

In this thesis, we make use of the Derjaguin approximation to compare the calculated DLVO force between two flat surfaces to the experimentally measured forces between a sphere and a flat surface. The interaction energy between two flat surfaces can be related to the force between two finite particles using a method described by Derjaguin. For two large spheres (radii $R_1$ and $R_2$) at a small distance $L$ apart (see Figure 1.4), so long as $R_1 \gg L$ and $R_2 \gg L$ the force can be obtained by integrating the force between small circular regions of area $2\pi x \, dx$ on one surface and the opposite surface, which is assumed to be locally flat and at a distance $Z = L + z_1 + z_2$. The net force between the two spheres is therefore

$$ F(D) = \int_{Z=L}^{Z=\infty} 2\pi x \, df(Z) $$

[1.24]

where $f(Z)$ is the normal force per unit area between the two flat surfaces.

Figure 1.4: The Derjaguin approximation, which related the force law $F(L)$ between two spheres to the energy of per unit area $E(L)$ of two flat surfaces.
Figure 1.5: A simple geometric model for determining the relationship between $L$ and $z$.

By applying simple geometry to the construction depicted in Figure 1.5, $L$ can be related to $z$. Pythagoras’ theorem states that

$$AC^2 = AB^2 + BC^2 = AD^2 + BD^2 + DC^2$$  \[1.25\]

Thus

$$4R^2 = z^2 + 2L^2 + (2R - z)^2$$  \[1.26\]

This is simplified to

$$L = (2r - z)z \approx 2Rz \text{ for } R \gg z$$  \[1.27\]

Therefore, the distance $Z$ becomes

$$Z = L + \frac{L^2}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$  \[1.28\]

and
\[ dZ = \left( \frac{1}{R_1} + \frac{1}{R_2} \right) L \, dL \]  \hspace{1cm} [1.29]

so the equation 1.24 becomes

\[ F(L) \approx \int_{L}^{\infty} 2\pi \left( \frac{R_1 R_2}{R_1 + R_2} \right) f(Z) \, dZ = 2\pi R_{eff} \, E_p(L) \]  \hspace{1cm} [1.30]

where

\[ R_{eff} = \frac{R_1 R_2}{R_1 + R_2} \]  \hspace{1cm} [1.31]

In the case of a sphere of radius \( R \) near a flat surface (\( R_2 \gg R_1 \)) so

\[ R_{eff} \approx R_1 = R \]  \hspace{1cm} [1.32]

Therefore,

\[ F(L) = 2\pi R E_p(L) \]  \hspace{1cm} [1.33]

1.1.1.3 Van der Waals forces between surfaces

The van der Waals force, also known as dispersion forces, is responsible for the attractive component of DLVO theory. Dispersion forces have their origin in quantum mechanics and arise because all molecules have a finite dipole moment due to the instantaneous position of the electrons around the nucleus. These instantaneous dipoles momentarily polarize nearby atoms or molecules resulting in an attraction from the interaction between the induced dipoles. These induced dipole-induced dipole interactions are the principal contribution to the van der Waals force as they are present between all types of molecules.\(^4\)

The interaction free energy due to van der Waals forces between two molecules is proportional to the inverse sixth power of the separation between them. Between molecules, these forces decay within 1-2 nm, but in the case of macroscopic objects, depending on geometry, the force can be proportional to an inverse second or third
power, with separation. As a result the van der Waals interaction can be significant in colloidal systems.

Hamaker argued that the attraction between two surfaces can be calculated by summing the energy of all the atoms in one surface with all the atoms in the other and thus obtain the two body potential for surfaces. For two planar surfaces the interaction free energy due to van der Waals interactions is

\[ E_{vdW} (L) = -\frac{A}{12\pi L^2} \]  

[1.34]

where \( L \) is the separation between the surfaces and \( A \) is the Hamaker constant. The force can then be determined by application of the Derjaguin Approximation (Equation 1.33).

Using a pairwise addition is not justifiable, as ignoring the influence of nearby atoms or molecules is not reasonable for solids interacting across a medium. Lifshitz theory completely circumvents this additivity problem by treating particles as a continuous medium. This allows the calculation of the forces using bulk properties such as the dielectric constants and the refractive indicies of the media. An effective Hamaker constant, based on Lifshitz theory, for two media 1 and 2 across a third medium 3 can be approximated using

\[
A \approx \frac{3}{4} k_B T \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right) \left( \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right) + \frac{3h}{4\pi} \int_{\nu_1}^{\nu_2} \left( \frac{\varepsilon_1 (i\nu) - \varepsilon_3 (i\nu)}{\varepsilon_1 (i\nu) + \varepsilon_3 (i\nu)} \right) \left( \frac{\varepsilon_2 (i\nu) - \varepsilon_3 (i\nu)}{\varepsilon_2 (i\nu) + \varepsilon_3 (i\nu)} \right) d\nu
\]

[1.35]

where \( \varepsilon_1, \varepsilon_2 \) and \( \varepsilon_3 \) are the static dielectric constants of the three media, \( \varepsilon (i\nu) \) are the values of \( \varepsilon \) at imaginary frequencies, \( h \) is the planck and

\[
v_n = \left( \frac{2\pi k_B T}{h} \right)^n
\]

[1.36]

with \( n \) being the refractive index.

The first term of Equation 1.35 gives the zero frequency energy van der Waals interaction and includes the dipole-dipole and the dipole-induced dipole contributions. The second term gives the induced dipole-induced dipole contribution of the dispersion energy. Equation 1.35 is an approximation that only describes the first two terms of an
infinite series. The other terms of the series are small and are commonly ignored for simplicity, generally resulting in an error of less than 5%.

1.1.1.4 DLVO Interaction between two surfaces

The total interaction energy between surfaces according to DLVO theory is simply the sum of the electrostatic double layer and van der Waals components.

\[ E_{\text{Total}} = E_{\text{Elec}} + E_{\text{vdW}} \]

An example of the total interaction energy for a DLVO interaction between two identical surfaces along with the electrostatic contribution and the van der Waals contribution is shown in Figure 1.6.

![Figure 1.6](image)

Figure 1.6: The total interaction energy as well as the electrostatic and van der Waals components for a sphere-flat system as a function of separation at the constant potential boundary condition. A surface potential of 20 mV, an ionic strength of $10^{-3}$ M and a Hamaker constant of 10 zJ (1 zJ = $10^{-21}$ J) were the parameters used in these calculations.

At small separations, the van der Waals attraction increases following a power law sharply while the repulsive electrostatic component increases exponentially. Therefore, at small separations the van der Waals attraction will be the dominant contribution to the total interaction energy as a power law increases faster than an exponential. In addition, at large separations the van der Waals attraction will dominate the interaction although it may be too small to have a significant effect. At intermediate distances, the
electrostatic contribution may dominate the interaction depending on the magnitude of the surface potential and the Debye length.

For DLVO type interactions, the expectation is that for a surface that has a small surface charge, the force profile will be dominated by the van der Waals force (see Figure 1.7). As the surface charge increases, the diffuse double layer repulsion strengthens and at sufficient surface charge, the electrostatic repulsion will dominate at large separations. At small separations the van der Waals attraction will dominate.

![Figure 1.7: Comparison of the interaction energy versus separation for a DLVO calculation for high and low surface potentials. Solid lines represent the constant charge boundary condition, dashed line are the constant potential boundary condition. At low surface potentials, the force is dominated by the van der Waals interaction. At high surface potentials, the diffuse double layer force dominates at large separations and the van der Waals dominates at small separations. A Hamaker constant of 10 zJ was used in these calculations.](image)

While the DLVO theory is highly successful in describing some colloidal systems, it should be noted that there are instances in the literature where DLVO theory has proven inadequate, disagreeing with experimental observations. This inadequacy is the result of the simplicity of the theory. DLVO describes a system where only a diffuse double layer repulsion and a dispersion attraction are present between the surfaces and the solvent is a continuum. To explain experimental measurements DLVO theory often requires an expansion to include other non-DLVO forces, for example short ranged
repulsive forces due to a layer of water hydrating the surfaces or long ranged hydrophobic interactions. A more detailed explanation of some of these non-DLVO forces is described below.

1.1.2 Non-DLVO Forces

DLVO theory often adequately describes the interactions between surfaces at low salt concentrations and low surface potentials. However there are many instances where non-DLVO behavior has been observed.\textsuperscript{12-14} To give some examples, force measurements between silica surfaces have shown that the van der Waals attraction is not observed at small separations.\textsuperscript{15} The long ranged attraction observed between hydrophobic surfaces is another.\textsuperscript{16} Several of these non-DLVO interactions are described below.

1.1.2.1 Hydration Forces

Solvent-surface interactions can induce ordering of the adjacent liquid molecules. In the case of a surface exposed to an aqueous environment the surface is said to induce a hydration layer at the surface. When two hydrated surfaces are brought into contact the disruption of the hydration layers gives rise to a repulsive force. This force decays exponentially with separation and has a decay length of \( \sim 0.25 \) nm\textsuperscript{17, 18}, as a result the force is only observed at separations less than 3 nm in direct force measurements. The hydration force has been observed between silica surfaces,\textsuperscript{15, 19} explaining the absence of the van der Waals attraction from the force profile and it has been observed for mica\textsuperscript{20} and alumina\textsuperscript{21} surfaces as well. It should be noted that the origin of the hydration force is still a matter of debate, with an alternative theory being that of a steric repulsion arising due to a “gel layer” present on the silica surfaces.\textsuperscript{22}

1.1.2.2 Hydrophobic Forces

When hydrophobic surfaces have been immersed in aqueous solutions, an attractive force has been observed. This force has a longer range than the van der Waals attraction predicted by DLVO theory. This hydrophobic attraction has been observed in a number of experiments.\textsuperscript{11, 16, 23-29} The strength and range of the attraction does not agree from one experiment to another, particularly when different techniques are employed in the measurements. As a result, the mechanism of the hydrophobic force is not understood.
and still debated. The longer, stronger hydrophobic forces are widely believed to be related to the presence of nanobubbles on the surfaces.

1.1.2.3 Heterogeneous Charge Surface Forces

In rare cases, hydrophilic surfaces that have a net neutral charge immersed in aqueous solutions have exhibited attractions stronger then those that would result from the van der Waals force. By modeling the surface charge as a heterogeneous mixture of both positive and negative charges, this attraction can be explained.

Miklavecic et al. noted that in the case of heterogeneous charging, the interactions between such surfaces will always be attractive. That is, the distribution of the charge sites of the surface plays no part in the observed attraction. Such a force is fitted to an exponential function such as

\[ E_{\text{Het}} = B e^{-2q_{\text{min}}L} \]  

[1.37]

Where \( B \) is a parameter dependent on the density of charges at the surface, \( L \) is the separation distance between surfaces and \( q_{\text{min}} \), the decay length, which is defined as

\[ q_{\text{min}} = \left[ \left( \frac{\pi}{\alpha} \right)^2 + \kappa^{-2} \right]^{\frac{1}{2}} \]  

[1.38]

where \( \kappa^{-1} \) is the Debye length and \( \alpha \) is the size of the charge patches on the surface. This value for \( q_{\text{min}} \) places limits on the decay length of the force. When \( \alpha \ll \kappa^{-1} \) (the charge patches are small compared to the Debye length) then the decay length will be dictated by the size of the patches. In the case when \( \alpha \gg \kappa^{-1} \) (patches are much larger than the Debye length) then the decay length will be dictated by the Debye length. The factor of 2, which occurs in the exponential function of Equation 1.37, places a limit on the decay length of the force, such that the maximum decay length will be half the magnitude of the Debye length.

1.2 Measuring Surface Forces

Although theories for predicting the interactions between surfaces have been around since the mid twentieth century, high quality, reliable measurements in liquid environments have only been obtained in the last 50 years.
Experimental methods for measuring surface forces, such as DLVO forces, include several direct and indirect methods. Direct methods involve measuring the force as a function of the separation, where the separation is controlled by some mechanical means.\textsuperscript{33} These are difficult measurements to perform due to the short range and small magnitude of the forces, as well as the need to produce a system free of contamination. Indirect measurements involve studying interactions by measuring the properties imparted to a surface by the surface interaction. For example, measuring adhesion, surface tension or wetting in order to study van der Waals forces. These kinds of measurements are hampered by factors such as particle alignment in the system and interpretation of results. Despite these issues, a number of techniques have been developed to determine the forces applicable to colloidal systems. Three common methods for measuring surface forces, the SFA, TIRM and the AFM, will be described briefly below.

### 1.2.1 Surface Force Apparatus

Various methods have been developed to measure the full force laws between two surfaces with a high distance resolution (less than a nanometer). In 1968, Tabor and Winterton\textsuperscript{34} developed an apparatus for the measurement of the van der Waals force between mica surfaces. Later, Israelachvili and Adams\textsuperscript{10} modified the design to allow these types of measurements to be performed in liquid environments. This device is now known as the Surface Force Apparatus (SFA).

The SFA is designed as a force balance. In a force balance, one surface is held rigidly while the other is mounted on a spring. The surfaces are moved towards or away from each other and allowed to come to the equilibrium position, where the force imparted by the surface is balanced by the restoring force of the spring. The deflection of the spring ($\Delta d$) is measured and converted to a force ($F$) using Hooke’s Law.

$$F = -k\Delta d$$

[1.39]

where $k$ is the spring constant.

In the SFA, smooth mica sheets are glued to two glass half cylinders arranged in a crossed-cylinder geometry (equivalent to a sphere-flat geometry). The separation between the surfaces is measured using white light interferometry (FECO).\textsuperscript{35} Surface separation is controlled through the use of piezoelectric transducers. Due to its design,
the SFA has limitations. Surfaces need to be atomically smooth over a large area and FECO measurements of the surface separation need to be possible. Originally this limited measurements to transparent materials such as mica\textsuperscript{20} and sapphire\textsuperscript{36} but by applying the FECO in reflectance technique, measurements between transparent material and reflective material have been performed\textsuperscript{37}.

\subsection{1.2.2 Total Internal Reflection Microscopy}

Total Internal Reflection Microscopy (TIRM) was developed in 1987 by Prieve, Luo and Lanni as a technique for the measurement of the forces, in liquid, between a particle and a surface\textsuperscript{38}. In TIRM, a particle is allowed to settle under gravity to the equilibrium position near a surface. At this point, the force between the surface and the particle are balanced by gravity. The particle does not remain stationary at equilibrium, rather, it will move due to Brownian motion. The probability of finding the particle at any particular location depends on the potential energy at that location, with low potential energy regions being the most probable location of the particle. The relationship between the potential energy $\phi(L)$ of a location and the probability of the particle being located at that point $p(L)$ is given by the Boltzmann equation

$$p(L) = G \exp \left[ - \frac{\phi(L)}{kT} \right]$$

[1.40]

where $G$ is a normalization constant such that $\int p(L) \, dL = 1$

In TIRM, an evanescent wave is generated at the interface between the surface and the liquid using a laser at an angle such that total internal reflection occurs. This evanescent wave illuminates the liquid in a non-uniform way. When a particle of different refractive index to that of the liquid settles near the interface, some of the evanescent wave is scattered. The intensity of the light scattered by the particle is sensitive to the proximity of the particle to the surface. Monitoring the proximity of the particle to the surface over time produces a probability distribution, which is related to the potential energy (Equation 1.40).

This technique is sensitive enough to detect changes in the distance between the surface and the particle as small as 1 nm and forces as small as 0.1 pN. However, it is incapable of measuring interactions as strong as those that have been reported for AFM or SFA measurements\textsuperscript{39}.
1.2.3 Atomic Force Microscope

The Atomic Force Microscope (AFM) was developed by Binnig, Quate and Gerber in 1986\textsuperscript{40} as an alternative to the Scanning Tunneling Microscope (STM). Unlike the STM, the surfaces placed in the AFM do not need to be conductive, but the instrument has similar principles of operation. As a result, the AFM can be used to image a wide range of materials, including mineral oxides, semiconductors and biological samples, with better than nanometer resolution.

The AFM in its simplest mode of operation produces an image by maintaining a cantilever beam at a constant deflection using a feedback loop. A sharp tip is attached to the end of the beam as a sensing probe and is moved over the surface in a raster pattern, creating a height image of the sample. An optical lever system is used to measure the deflection of the tip.

While originally a technique used for imaging, the AFM has since been developed into an instrument for direct measurements of surface forces. Ducker \textit{et al.}\textsuperscript{15} and Butt \textit{et al.}\textsuperscript{41} developed the colloid probe technique, where a particle is attached to the cantilever as a sensing probe and the cantilever is ramped in the direction normal to a surface.

This technique allowed the investigation of materials that were previously difficult or unsuitable for study with instruments like the SFA. The colloid probe technique has been used to study materials such as silica\textsuperscript{15}, gypsum\textsuperscript{42}, gold\textsuperscript{43}, alumina\textsuperscript{21}, titania\textsuperscript{44}, cellulose\textsuperscript{45} and polystyrene\textsuperscript{46}.

1.3 Force Measurements

Over the years, there have been a large number of publications on the subject of force measurements. The studied range of materials is extensive\textsuperscript{13, 15, 21, 43-51}. However, it is notable that most of the measurements involve a select few materials, mostly silica and mica or modifications of these surfaces. This is mostly due to the difficulty in finding surfaces of appropriate geometry with a minimum of surface roughness\textsuperscript{52}.

The most interesting and least well understood surface forces are short ranged (up to a few nanometers). When rough surfaces are used for force measurements, an uncertainty in the interactions between the surfaces will occur. This makes the determination of the origins of the interaction at small separations almost impossible. Silica and mica are two of the few materials that can be obtained smooth enough for use as model surfaces for
accurate measurements at small separations. As a result, most of the surface force measurements have been performed using these materials, although there is a great deal of interest in others.

It would be advantageous to increase the number of model surfaces that are available for study. This would enable a wider range of properties to be investigated and provide analogs for materials that are of interest in industrial processes as well as providing for more stringent tests of our theoretical understanding of surface forces.

1.4 Surface Preparation

Roughness is the main problem that prevents the production of model surfaces suitable for force measurements for most materials. Being able to produce smooth surfaces would allow previously unavailable materials to be studied. A possible approach is to grow thin films of the materials of interest onto substrates of the appropriate geometry. There are a variety of techniques that can be used to grow thin films of materials; some of these are described here.

1.4.1 Sputter Deposition

Sputtering is a process whereby atoms are ejected from a solid target due to bombardment by energetic particles. For sputtering to occur, the energy of the incoming particles must be sufficient to exceed the thermal energy of the target ($>\!\!>\!\!> 1\text{eV}$). The atoms sputtered from the target are ejected into the chamber in the gas phase. These sputtered atoms tend to deposit on all surfaces of the chamber, therefore a thin film of the sputtered material will be deposited onto a substrate placed within the chamber, the composition of which is very close to that of the source material. Sputtering has the advantage of being useful for the deposition of a wide range of materials; even materials with very high melting points are easily sputtered. The disadvantage of sputtering is that the surfaces produced are often quite rough, making them unsuitable for accurate force measurements.

1.4.2 Chemical Vapour Deposition

Chemical Vapour Deposition (CVD) is a chemical process, which is used to produce high purity films. In CVD a substrate, typically a silicon wafer, is exposed to one or more volatile precursor chemicals. These chemicals react with or decompose at the substrate to produce a thin film of the desired material. The advantage of CVD is that
the gas phase transport of the chemical reactants allows a surface of any geometry to be coated. In addition, the films are of high quality and high purity. The disadvantage of CVD is the roughness of the films that are produced.\textsuperscript{55}

1.4.3 Atomic Layer Deposition

Atomic layer deposition (ALD) is similar to CVD but provides additional control over the growth rate of the film. ALD involves splitting CVD into two half reactions. This keeps the chemical precursors separate during the reaction. Commonly, the half reactions will involve the deposition of two different atoms on the surface; for example, first a metal, then oxygen, with a purge of the chamber by an unreactive gas between reactions. By having two half reactions, the film is grown one atomic layer at a time, providing control over the film growth as fine as $\sim 0.1$ Å per cycle. Film thickness is therefore dependent on the number of deposition cycles that are applied. Like CVD, the reactants are introduced to the reaction chamber as a vapour phase. Provided the exposure of the precursor is of sufficient quantity and duration, a defect free, conformal coating of the substrate will result. The consequence of this is a surface with comparable roughness to the bare substrate, even for complex geometries, making the coating of flat surfaces as well as particles straightforward.

ALD has many advantages when applied to the production of surfaces for force measurements. The range of materials that can be grown is extensive.\textsuperscript{56} ALD can also be performed at high\textsuperscript{57} or low\textsuperscript{58} temperatures, allowing the coating of temperature sensitive substrates.\textsuperscript{59, 60} The disadvantage of this process is the deposition time. ALD is a slow process compared to CVD, due to the use of two half reactions to produce the film. However, for the purpose of producing surfaces for force measurement, deposition time is not a significant issue. ALD is ideal for smooth surface production.

1.5 Materials Investigated in this thesis

Using ALD, model surfaces of mineral oxides can be grown onto smooth silica substrates to produce surfaces for force measurements. Here we will discuss the mineral oxides chosen for study.

1.5.1 Aluminium Oxide

Alumina is interesting from a fundamental perspective because, unlike most materials which are negatively charged at neutral pH, alumina is positively charged at neutral pH.
Although the isoelectric point (IEP) of alumina is high (~pH 9),\textsuperscript{61} it is still possible to perform measurements at those pH’s without damage to the surface or the instrument. Therefore, it is expected that the van der Waals interaction at the IEP may be directly measured. The handling of aluminium oxide (alumina) slurries is important to the production of aluminium. By measuring and understanding the forces between alumina surfaces we can improve the processing of colloidal alumina.

1.5.2 Titanium Dioxide

Titanium Dioxide (titania) is a technologically and industrially important mineral oxide. It is primarily used as a light scattering pigment by utilizing the dielectric properties that result in a high refractive index.\textsuperscript{62} It has further application in optical coatings, in solar cells, as a photocatalyst and as the outermost surface of titanium implant materials where it is responsible for adsorption of the extracellular matrix that confers biocompatibility. Titania is suitable for fundamental surface science studies as it is a chemically stable material, has low solubility in water and has an IEP that is readily accessible (~pH 5).\textsuperscript{63} This IEP allows neutral, positively and negatively charged surfaces to be studied. Due to the high refractive index (i.e. high dielectric strength), titania exhibits a large dispersion force; this is reflected in a large Hamaker constant. The dispersion forces are almost an order of magnitude greater in strength then those between silica surfaces.\textsuperscript{64} The accessible IEP of titania should allow for direct measurement of the van der Waals interaction.

1.5.3 Hafnium Dioxide and Zirconium Dioxide

Hafnium and Zirconium are chemically very similar. They occur together in nature and are difficult to separate; separation is necessary for the uses to which they are put. Hafnium has high neutron absorption properties while zirconium has low neutron absorption. Hafnium dioxide (Hafnia) and zirconium dioxide (Zirconia) are therefore used in different parts of nuclear reactors and contamination of either by the other will compromise their effectiveness. Therefore, the ability to separate them cost-effectively is of significant interest. An examination of the force profiles of these materials may provide insight into better techniques for separation.
Chapter 2: Materials and Methods

The goal of this work is to develop the techniques required to produce smooth surfaces using Atomic Layer Deposition (ALD) and to investigate the forces between those surfaces in a range of conditions; electrolyte, pH, surfactant concentration. This chapter describes the materials and experimental techniques used to create surfaces using the ALD technique and the experimental methods used to characterize the deposited films as well as measure the surface forces. The software developed to aid in the analysis of force measurements is also described.

A detailed description of materials and chemicals which were used is provided in §2.1. The principles of ALD as described in §2.2 along with the equipment and general methodology used to produce mineral oxide surfaces. The techniques used to characterize the deposited films are described in §2.3. The optical reflectometer (OR) which is described in §2.5 was used to examine the stability of the deposited films in aqueous environments as well as the adsorption of surfactants. The AFM instrument and the methodology used to obtain images of surfaces and perform surface force measurements is described in §2.6. Finally, §2.7, details the analysis software that was created to analyze the surface force measurements. The software was written to perform the conversion of the raw AFM voltage measurements into force-separation data, as well as perform analysis and theoretical fitting of the force measurements.

2.1 Materials

2.1.1 Substrates

In order to determine the forces that occur at small separations between surfaces, the surface roughness needs to be minimized. In this work, ALD was used to grow smooth films of mineral oxides onto substrates to create surfaces for accurate surface force measurements.

To that end, boron-doped (100) silicon wafer (MEMC, U.S.) was used as the substrate for the flat surfaces to be used for force measurements. The spherical substrates used for the production of colloids for colloid probes were borosilicate spheres of monomodal size distribution with radius of (10 ± 0.1 µm) supplied by Duke (borosilicate glass...
Due to the expense of the monomodal particles, these were substituted for Ballotini spheres and coated using ALD for the zeta potential measurements. For OR measurements, silicon wafers with a surface silica layer 320 nm thick were used as substrates. The oxide layer was required so that the final surfaces would have the optical properties to optimise the sensitivity of the OR to material adsorption.

Prior to ALD, all of the substrates were exposed to radio frequency discharge water plasma. This treatment had the duel effect of cleaning the surface of organic contamination and creating an excess of hydroxyl chemical groups on the surface; these are the bonding sites for the ALD reaction process. This water plasma treatment was performed using an in-house plasma reactor. Substrates were exposed to a 30 W plasma for a period on 90 s followed immediately by exposure to 50 W plasma for a period of 30 s.

2.1.1.1 ALD Precursors

Metal sources used in the ALD system were purchased from SAFC Hitech (Bromborough, UK). The metal sources were of high purity (99.999%) and were delivered in sealed containers that could be installed in the ALD without exposure to the atmosphere. Metal sources are organometallic compounds, most of which were toxic and/or highly reactive when exposed to the atmosphere. Milli-Q grade water was used as the oxygen source.

2.1.1.2 Solution Preparation

The accuracy of the measurement of surface properties is reliant on the removal of all contaminants from the system. Ensuring that the chemicals and containers contain as little contamination as possible was essential to the success of the measurements. As such, the water used in measurements was cleaned by filtering first with a cotton filter; then a carbon filter; then a reverse osmosis filter, before finally being filtered with a Millipore Gradient filtration unit which also exposes the water to UV treatment. The resistivity of the produced Milli-Q water was greater than 18.2 MΩ.

All glassware used to prepare solutions was soaked in a 10 % w/w solution of NaOH for at least 10 min and then rinsed with copious quantities of Milli-Q water. Glassware cleanliness was determined by the wetting properties of the glass surface. Glassware
that was completely wet by water was considered clean. Dirty glassware was washed repeatedly with 10 % w/w NaOH until clean.

Analytical Reagent grade salts and surfactants were used throughout this investigation. Before solution preparation, the salts were baked at 400 °C for at least 16 hours to remove organic impurities. Prepared salt solutions were bubbled with high purity nitrogen to remove surface active contaminants following the method described by Parkinson.\textsuperscript{65} The solution was then extracted from below the air/water interface using a glass syringe and steel needle and used immediately. Surfactants were purified using appropriate methods to remove contamination. Cetyltrimethylammonium bromide (CTAB) was purified via recrystallization with acetone, twice. Sodium dodecyl sulfate (SDS) was purified using the method described by Casson et al.\textsuperscript{66}. First, the SDS was dissolved in water, then acidified and separated with hexane. The aqueous phase was neutralized and cooled below the Krafft point to obtain crystals. These crystals were recrystallized twice with 1:1 water/ethanol and once with pure ethanol. The purified SDS crystals were stored in a freezer. All ethanol used in the work was distilled prior to use.

\subsection{AFM Measurements}

The flat surfaces and colloid probes used for force measurements were cleaned using water plasma to remove surface contamination. Short low power treatments were used to remove surface organic contamination while minimizing the grafting of hydroxyl chemical groups at the surface. The AFM fluid cell, tubing and O-ring were washed with distilled ethanol and blown dry with nitrogen gas before use. The nitrogen gas was sourced from the boil-off from a liquid nitrogen tank.

\section{Atomic Layer Deposition (ALD)}

\subsection{Introduction}

ALD was originally developed in the mid 1970s by Suntola and his co-workers as a means to deposit high quality thin films in electroluminescent flat panel displays\textsuperscript{67}. This technique is capable of producing a conformal coating of material onto a substrate and is now a common method of producing thin films for microelectronic device production.\textsuperscript{68}
The ALD process involves a two-stage chemical reaction between a substrate and precursor chemicals in a controlled manner to deposit a film of material onto the substrate. In this study, the ALD process was used to coat substrates with mineral oxide thin films appropriate for the study of surface forces, zeta potential and surfactant adsorption.

### 2.2.1 Methodology and equipment

The basic components of the type of ALD reactor system used in this work are represented in Figure 2.1. The ALD system is made up of four parts: the reaction chamber, a vacuum system, an inert carrier gas and the precursors. High purity nitrogen gas is pumped through the reaction chamber continuously during the deposition process, functioning as an inert carrier gas. The precursor chemicals are introduced into the nitrogen flow for short periods so that they are carried to the reaction chamber. The precursors react with the surface of the substrates to grow the film. The vacuum system maintains the chamber in a low-pressure environment and removes the excess precursor and reaction products from the reaction chamber.

![Figure 2.1: Schematic of an ALD reactor.](image)

An inert carrier gas is constantly flowing through the chamber. Precursors are introduced into the gas flow using valves attached to source containers. The precursor chemicals react with substrates present in the chamber to deposit a thin film of material on the substrates. The system is maintained at low pressure using a vacuum pump, which also removes excess precursor and reaction products from the system.
During a typical deposition process, the sequence of events for the process is typically as follows,

Stage 1. Precursor 1 exposure,
Stage 2. Purge,
Stage 3. Precursor 2 Exposure,
Stage 4. Purge,
Stage 5. Repeat.

This sequence can be extended to include more precursor reactions to allow the creation of more complex, layered films. During deposition, the reaction chamber can be heated to facilitate film growth and precursors are heated as needed to vaporize the chemicals for transport into the reaction chamber. In the case of the mineral oxides produced in this work, precursor 1 was a metal organic compound and precursor 2 was Milli-Q water. An illustration of an ALD process for the production of a TiO$_2$ is shown in below.

Prior to exposure, the substrate is terminated with hydroxyl surface groups.

The metal organic precursor is introduced into the chamber. This precursor reacts with the hydroxyl surface groups binding the metal to the surface.
The system is then purged with nitrogen gas to remove excess precursor and reaction products from the chamber.

Water vapour is introduced into the chamber; this reacts with the organic groups attached to the metal on the surface, forming one layer of hydroxyl terminated metal oxide.

The system is purged again with nitrogen to remove excess water vapour and reaction products from the chamber.
The previous four stages are repeated until a film of the desired thickness has been deposited onto the substrate.

![Diagram](image)

Figure 2.2: Example of Atomic Layer Deposition process for the creation of titania film.

The gas phase nature of the reaction allows the precursor chemicals access to all of the surfaces exposed in the reaction chamber. This and the self-limiting nature of the reaction allows the film to grow evenly over the entire surface, coating any surface roughness conformably and without defects in the film.

In this work, thin films of mineral oxides were prepared using a Savannah 100 (Cambridge Nanotech) ALD system. Prepared cylinders of high purity (>99.9%) metal organic compounds were acquired from SAFC Hitech for use as the metal sources. The metal organic compounds utilized were trimethylaluminium, titanium isopropoxide, tetrakis(dimethylamido) hafnium(IV) and tetrakis(ethylmethylamido) zirconium(IV) to produce alumina (Al$_2$O$_3$), titania (TiO$_2$), hafnia (HfO$_2$) and zirconia (ZrO$_2$) respectively. The oxygen source, prepared using Milli-Q grade water, was prepared in-house as it was a non-hazardous material. Deposition processes were carried out at temperatures ranging from 80 °C to 250 °C. Precursors were used according to need; some were used at room temperature, others were heated to between 75 °C and 130 °C depending on the chemical and the film being produced.

### 2.3 Surface Characterization

The surfaces were characterized using a variety of techniques: AFM imaging, X-Ray Reflectivity (XRR), X-Ray Diffraction (XRD), zeta potential and OR were used to determine the surface roughness, film thickness, crystal structure, surface charging properties and film stability in aqueous environments respectively.
The principles of XRD, XRR and zeta potential measurements and analysis are described in sections 2.3.1, 2.3.2 and 2.3.3 respectively. The OR instrument is described in §2.5. The AFM imaging is described in §2.6.

2.3.1 X-Ray Diffraction

X-ray diffraction (XRD) is a technique used for the determination of the atomic or molecular structure of a crystal. For different crystal phases of a material, the spacing between atomic planes will be different. The distances between planes of atoms in a crystal can be determined using XRD. When an x-ray beam illuminates a surface, the light is scattered elastically by the electrons in the material. For a regular array of scattering points, like the atoms of a crystalline material, the scattered light will reflect and interfere constructively in a few specific directions and destructively in all others. The direction of the constructive interference (angle) \( \theta \) of two adjacent parallel planes of atoms, separated by a distance \( d \) (see Figure 2.3) for a wavelength \( \lambda \) is provided by Bragg’s Law:

\[
2dsin\theta = n\lambda
\]

[2.1]

where \( n \) is an integer.

Figure 2.3: Illustration the derivation of Bragg’s Law. An incident x-ray beam is scattered by the atoms of a material. The interference of the reflected x-rays is constructive when the additional path length between atom layers of the material \( 2dsin\theta \) is equal to an integer multiple of the wavelength \( \lambda \).
Measuring the intensity of the scattered light for a sample over a range of angles allows the directions of constructive interference for the crystal to be determined. This is known as a diffraction pattern or spectra. For unknown materials these spectra are analyzed to determine the spacing and crystal structure of a material. The oxides that are examined in this work have been studied in the past; therefore, crystal structure of the deposited films can be determined by comparing measurements with literature spectra.

Measurements of XRD spectra were made using a PANalytical X’Pert Pro diffractometer located at the Australian Nuclear Science and Technology Organization (ANSTO) and a instrument of the same model located within the Department of Electronic Materials Engineering in the Research School of Physics and Engineering at the Australian National University Both instruments employ a Cu Kα (8048 eV) X-ray source. XRD spectra were measured over an angle range of 20-80°.

2.3.2 X-Ray Reflectometry

The thickness of the film deposited on the surface is important for the theoretical prediction of the van der Waals force and for determining the optical properties of the surface for OR measurements. The thickness of the deposited films was determined using X-Ray Reflectometry (XRR).

XRR involves reflecting an X-ray beam off a surface and measuring the intensity of the X-rays reflected in the specular direction (reflected angle equals incident angle). The reflectivity ($R$) of the reflected beam is measured as a function of the momentum change perpendicular to the surface $Q_z$, which is defined as the ratio of the reflected and incident intensities.

$$Q_z = \frac{(4\pi \sin \theta)}{\lambda}$$

The measured reflectivity depends on the variation in the scattering length density (SLD) profile perpendicular to the interface. Although SLD is a continually varying function within a material, the interface function can be approximated by a slab model, where layers with a thickness $d_n$, a SLD $\rho_n$ and roughness $\sigma_{n,n+1}$ are sandwiched together between the substrate and the ambient materials.
The measured spectra are compared to the prediction of Fresnel reflectivity to determine the thickness and scattering properties of the different layers of the surface. If the interfaces between the layers are not perfectly sharp, then the theory will deviate from the experimental measurements. The theory can be analyzed to obtain a density profile of the surface, which can be used to determine the thickness and SLD of each layer as well, and the deviation of the data from the theory for a flat interface can be used to determine the roughness of the interfaces between layers. This is typically done by convoluting Gaussian noise with the density profile.

Measurements of films thickness were made using the PANalytical X’Pert Pro diffractometer located at ANSTO or at the Department of Electronic Materials Engineering at ANU. The measurements were analyzed to determine film thickness, scattering length density and roughness of the different interfaces in the surface. The Igor based program Motofit written by Nelson was used to perform this analysis.

2.3.3 Zeta Potential

The zeta potential is a measure of the surface potential of a particle at the shear plane. It is generally thought to be ~ equal to the potential at the stern layer and slightly less than the surface potential (see §1.1.1.1 for a description of surface potential and zeta potential). The zeta potential of a surface provides an indication of the charge on a surface under specific solution conditions. By measuring the zeta potential over a range of pH the isoelectric point of a surface, the point where the zeta potential is zero can be determined.

The zeta potential is determined by imposing a potential difference over a colloidal suspension. This will cause charged colloidal particles to move towards the electrode of opposite charge. The velocity of the colloids is related to the zeta potential (ζ) using the Smoluchowski equation:

\[ \zeta = \frac{\mu \eta}{\varepsilon_0 \varepsilon} \]

[2.3]

where \( \mu \) is the velocity and \( \eta \) is the dynamic viscosity of the medium. This theory is true for a spherical particle in a medium with a Debye length much less than the radius of the particle.
The zeta potential measurements in this work were performed using a Zetasizer Nano ZS instrument (Malvern Instruments, U.K). Colloidal suspensions were prepared in 10^{-3} M NaCl solutions. An automated titration unit, fitted with a pH probe, adjusted the pH of the colloidal suspensions using HCl and NaOH solutions over a range of pH and recorded the zeta potential. The software provided with the instrument calculates the zeta potential from the velocity using the Henry equation: \[ \mu = \frac{2 \varepsilon \zeta f(K\alpha)}{3\eta} \] \[ [2.4] \]

where \( f(K\alpha) \) is Henry’s function which is generally approximated to 1.5 for aqueous media and moderate electrolyte concentrations, giving the Smoluchowski equation (Equation 2.3).

### 2.3.4 Nano-Indentation

Indentation is a common technique for the testing of the mechanical properties of small volume of materials. To perform nano-indentation a load is applied to a surface, using an indenter tip with a geometry known to high precision and, the depth of penetration is measured. These measurements can be plotted to create a load displacement curve, which is used to extract the mechanical properties of the material. \[76\]

The gradient of the load displacement curve is indicative of the stiffness \((S)\) of the material. This stiffness is related to the reduced modulus \((E_r)\) of the system by

\[ E_r = \frac{\sqrt{\pi} S}{2 \sqrt{A}} \] \[ [2.5] \]

where \(A\) is the projected area of the of the indentation which can be determined from the penetration depth and the geometry of the tip.

This reduced modulus can then be related to the young’s modulus using

\[ \frac{1}{E_r} = \frac{(1 - \nu^2)}{E} + \frac{(1 - \nu_i^2)}{E_i} \] \[ [2.6] \]
where $E_i$ is the modulus of the tip, $\nu_i$ is the Poisson’s ratio of the tip, $E$ is the modulus of the sample and $\nu$ is the Poisson’s ratio of the sample.

### 2.4 Surface Tension

Water and surfactant purity were tested using surface tension measurements. Water produced by the Milli-Q purification system was checked periodically to ensure the surface tension was 72 mN/m.$^{77}$ Surfactants were considered clean if no minimum was observed in the surface tension measurements near the critical micelle concentration.$^{78}$ Both the surface tension and the contact angle reported in the work were performed using KSV-CAM 200 contact angle goniometer.

### 2.5 Optical Reflectometry

#### 2.5.1 Introduction

Optical Reflectometry (OR) provides a means to follow the adsorption or desorption of molecules like proteins, polymers and surfactants, onto a surface with a high temporal resolution, allowing a quantitative determination of the material absorbed to a surface along with the kinetics of the adsorption. The technique is a form of ellipsometry that does not require any moving parts during operation and is highly suited to kinetic measurements.

#### 2.5.1 Instrument and Operation

In this work, the OR used follows the design of Dijt et al.$^{79}$, see Figure 2.4. This instrument was custom built within the Department of Applied Mathematics by Shaun Howard$^{80}$ and involves using a stagnant point flow cell where material is delivered to the point of measurement at the surface, through a diffusion-only process.
Figure 2.4: Schematic of an optical reflectometer. A beam of lineally polarized light from a laser is reflected from a surface of interest. The p and s components of the reflected light are measured with photodiodes. Upon adsorption or desorption of materials at the surface, the ratio of the p and s components of the reflected light is changed. This change in ratio is converted to adsorbed surface excess using equation 2.7.

OR utilizes a linearly polarized laser beam, which is reflected off the surface at a location of interest. The reflected beam is split into the parallel (p) and perpendicular (s) polarizations using a beam splitter and the intensity of each beam is measured with photodiodes that are attached to a computer using a data acquisition system. Adsorption of material to the surface causes a change in the ratio of the p and s polarizations of the reflected light. This ratio can be translated into a surface excess $\Gamma$ of adsorbed material using

$$\Gamma = \frac{\Delta S}{S_0 A_s}$$

[2.7]

where $S_0$ is the baseline ratio of the reflectivities of the p and s components ($S_0 = (R_p / R_s)$), $\Delta S$ is the change in ratio of the polarizations ($S - S_0$) and $A_s$ is the sensitivity parameter, obtained from a calculation of the Fresnel optical model of the system, which is solved using the matrix method of Abelès. The sensitivity parameter is dependent on the optical properties of both the surface and the adsorbing material.
In this work, the substrate used when preparing surface for OR measurements were silicon wafers with a 320 nm thick surface layer of silica. A film of mineral oxide was deposited onto this substrate using ALD to create surfaces with the desired chemistry. The oxide layer is used to optimise the optical system such that the measurement is sensitive to changes in the amount of adsorbed material but insensitive to the conformation of the adsorbed material.

2.6 Atomic Force Microscope

2.6.1 Introduction

The AFM was first developed in 1986 as a method to image non-conducting surfaces.\textsuperscript{40} Since that time the instrument has evolved such that it is capable of measuring surface forces,\textsuperscript{15, 82} mechanical properties\textsuperscript{83, 84} and electrical properties\textsuperscript{85-87} of a sample. In this study the AFM has been used as an imaging tool to determine the roughness of surfaces as well as a tool to measure surface forces in aqueous environments.

2.6.2 Instrumentation and Operation

The basic components of the AFM are illustrated in Figure 2.5. In a typical imaging experiment, a sharp tip or colloidal particle is attached to the end of a flexible cantilever beam. A laser beam is focused onto the top of the cantilever beam which reflects the beam into a position sensitive photodiode detector. During imaging, the sample is moved in a raster pattern using a piezoelectric scanner. As the sample is moved, the cantilever beam will deflect in response to surface topography. An electronic feedback system is used to adjust the cantilever height above the sample such that the feedback parameter for the cantilever is kept constant.
In the case of force measurement experiments, the cantilever is moved in the direction normal to the surface without horizontal translation. The deflection of the cantilever is measured as a function of the travel distance of the piezoelectric stage. This deflection vs. distance is converted to force vs. separation using the method described in §2.6.4.

2.6.3 Imaging

Originally, imaging was performed where the surface and tip were kept in a state of constant deflection while in contact. This method is now known as contact mode. Problems arise with this technique when there are attractive forces present between the tip and sample. In the presence of an attraction, the sample and tip adhere, which applies a lateral force on the cantilever that can lead to errors in the deflection measurements and therefore errors in the height image. Contact mode imaging also has drawbacks in that it can easily damage delicate samples due to the force applied by the cantilever tip and the tip wears quickly.

Dynamic or tapping mode has been developed as a means to improve AFM image quality. In tapping mode the tip is oscillated at or near the resonant frequency of the cantilever, using a small piezoelectric motor in contact with the cantilever substrate. The amplitude of an oscillating tip, which is moved near a surface, is damped based on the proximity of the tip to the surface. This change in amplitude is used as the feedback parameter to keep the tip at a constant height from the surface. Ideally, in tapping mode...
imaging, the surfaces and tip do not make contact. Therefore, it is a better technique for imaging attractive surfaces and delicate sample.

In this work, two AFMs have been used for imaging. Initially a Digital Instruments Multimode Nanoscope III AFM with Phase extender box was used for tapping mode imaging of surfaces. Once available a Bruker Multimode Nanoscope VIII AFM was used in ScanAsyst mode to image surfaces.

2.6.4 Force Measurement

When using an AFM for force measurements the surface is ramped up and down in the direction normal to the substrate. The response of the position sensitive photodiode (cantilever deflection) is measured as a function of the distance traveled by the surface. This produces a measurement similar to that shown in Figure 2.6.

Figure 2.6 Schematic of photodiode response as a function of sample travel. The curve when the surfaces are approaching is shown in red and the retraction curve in blue.

Figure 2.6 depicts what may be expected from a DLVO type force profile. At large separations there is no force acting between the sample and the tip so there is no deflection of the cantilever. At smaller separations, the force is repulsive between the surfaces and the cantilever responds by bending away from the sample. This is generally referred to as the non-contact region. When the attractive force exceeds the sum of the repulsive force and the spring constant of the cantilever, there is a jump into contact between the surfaces. Once in contact, any further movement of the sample results in an equal change in the deflection of the cantilever (assuming the surfaces are
hard relative to the cantilever). This is described as the region of constant compliance
and is equated with a zero separation between the sample and tip. An adhesion of the tip
and sample can be observed as the sample and tip are retracted to the starting position.
Depending of the material of the sample and tip and the ambient conditions the
magnitude of the adhesion may be small, large or absent.

The photodiode response $\Delta p$ is converted to the deflection of the cantilever $\Delta d$ by
calibrating the optical response of the cantilever,

$$\Delta d = p_c \Delta p$$

[2.8]

where $p_c$ is the gradient of the compliance region. Converting the deflection to a force
is achieved by applying Hooke’s Law

$$F = -k \Delta d$$

[1.39]

The movement of the sample $\Delta h$ is converted to the separation between the surfaces ($L$)
by the addition of the cantilever deflection, i.e.

$$L = \Delta h + \Delta d$$

[2.9]

A constant is added to the separation values such that the now vertical compliance
region is set to zero separation. A similar addition of a constant to the force values is
applied, such that at large separations the force is zero. The resulting force-separation
curve will appear similar to the example shown in Figure 2.7.
Figure 2.7: The curve shown in Figure 2.6 converted into a force-surface plot. The curve when the surfaces are approaching is shown in red and the retraction curve in blue.

When presenting surface force measurements generally the normalized force is presented. This is achieved by the dividing the force by the radius of the probe used in the measurements \((F/R)\). When using the colloid probe method of force measurements this is the radius of the colloid on the cantilever tip. Presenting data in the form of normalized force allows comparison with theoretical calculations to be simple, due to the Derjaguin approximation (see §1.1.1.2).

2.6.4.1 Colloid Probe Manufacture

Surface force measurements in this work were performed using the colloid probe technique described by Ducker \textit{et al.}\textsuperscript{15} and Butt \textit{et al.}\textsuperscript{19}. To perform this type of measurement a colloid needs to be attached to the tip of an AFM cantilever. This was achieved using a three-way stage manipulator (see Figure 2.8). The cantilevers employed were CSG10 or CSG11 rectangular type cantilevers supplied by ND-MDT, which have a nominal spring constant of 0.1 N/m and 0.03 N/m respectively.
Figure 2.8: Three-way manipulation stage used to attach colloids to AFM cantilever tips (left). An AFM cantilever is held in a clamp above a surface with glue drops and colloids on it (right). The cantilever is gently pressed onto a glue drop, then onto a colloid to produce colloid probes.

A cantilever tip is pressed onto a drop of glue (Epikote 1004, Shell) melted using a hot plate. Excess glue is removed by gently tapping the tip against a surface using the manipulation stage. The glue coated cantilever tip is then pressed onto a colloid and the glue allowed to cool and harden.

Care needs to be taken when attaching the colloid, particularly in regard to the amount of glue that is used. Too little glue and the colloid might break off during transit between storage and instrument, or even during force measurement. Too much glue and the colloid may be submerged in the glue, preventing the determination of the colloid position or size or the force measurements themselves.

2.6.4.2 Cantilever Calibration

To determine the force that occurs between surfaces in an AFM force measurement, the spring constant of the cantilever needs to be determined. While there are a variety of methods to do this, in this work, the thermal tune method was used.

In this technique, first the optical lever needs to be calibrated to determine the conversion of the photodiode response of the AFM to a deflection of the cantilever. The
gradient of a force curve compliance region provided this. Then the thermal fluctuations of the cantilever are measured in the frequency domain. The resonant frequency of the cantilever is then fitted to a Lorentian line shape and the background noise is subtracted away. The area under the peak is the power spectrum \( P \) of the cantilever, which can be related to the spring constant \( k \) using,

\[
k = \frac{k_B T}{P}
\]

[2.10]

The drawback of the thermal tune method is the need to calibrate the optical lever of the system. Measuring a force curve brings the cantilever tip into contact with a hard surface, which can lead to damage or blunting of the tip. However, in this work a colloid will be attached to the cantilever, after spring constant measurement, replacing the tip. Therefore, any damage to the tip is irrelevant to the forces measurements described here.

Spring constants were determined using an Asylum MFP-3D (Asylum Research, Santa Barbara, USA) instrument. The MFP-3D software has a function to measure the spring constant with the thermal tune method.

2.6.4.2.1 Off end Correction

Changing the position of a probe of a cantilever will change the spring constant. Most methods for spring constant determination assume that the tip of the cantilever is at the end of the cantilever beam (see Figure 2.9a). This is rarely the case when a colloid has been attached to the cantilever (see Figure 2.9b).
Figure 2.9: Example of AFM cantilevers. a) is a bare cantilever (no colloid), b) is a cantilever with the colloid attached. The position of the cantilever probe is changed by the addition of the colloid to the tip.

A correction to the spring constant was developed by Sader et al.\textsuperscript{92} to account for the change in position of the contact point of the cantilever. This correction states that the spring constant of a colloid probe $k$ can be determined using

$$k = k_E \left( \frac{x}{x - \Delta x} \right)^3$$

[2.11]

where $x$ is the length of the cantilever, $\Delta x$ is the change in position of the cantilever probe (see Figure 2.9b) and $k_E$ is the end tip spring constant. In the case of a colloid probe, $\Delta x$ is the distance from the end of the cantilever to the center of the colloid. This correction was applied to all of the spring constants used in this work. It should also be noted that this correction only applies to cantilevers of rectangular type geometry. Therefore, the cantilevers used in the force measurements performed in this study were of this type.
2.6.4.3   **Electron Microscope Imaging of Colloid Probes**

The position of the colloid attached to the cantilever is important for the correction to the spring constant; the radius of the colloid is used to determine the normalized force. Both were measured using electron microscopy. A Zeiss UltraPlus analytical Field Emission Scanning Electron Microscope (FESEM) at the ANU Centre for Advance Microscopy was used to measure the position and size of the colloid attached to the AFM cantilevers.

![Figure 2.10: A FESEM image of a colloid mounted at the tip of a V-shaped cantilever.](image)

Measurement of the position of the colloid was made from the base of the cantilever to the probe/end of the cantilever to minimize errors in the measurements. The colloid diameter was measured at three different points then averaged to determine the radius.

### 2.7 Analysis Software (The Force)

Computer software was developed to simplify the processing and analysis of the force measurements. This software is designed to convert AFM measurements of photodiode response-piezo movement to force vs. separation and then facilitate the analysis of the forces between the surfaces. The analysis systems that are available at this time in the software are DLVO theory fitting of the experimental data, a minimum value finder for determining the depth of an adhesion and a system to fit the spring constant to the measurement.
This program, which has been named *The Force*, was created using the *LabVIEW Professional Development System*. This allows *The Force* to be compiled for use in any of the three major operating systems (*Microsoft Windows*, *Macintosh OS X* or *Linux*). A compiled copy of this program for both *Microsoft Windows* and *Macintosh OS X* is provided on the attached disk designated Appendix 2. A copy of the un-compiled program code is also provided on the Appendix 2 disk.

### 2.7.1 Conversion to Force-Separation

The conversion of the AFM measurement of piezo travel vs. photodiode response into a normalized force-separation data set is achieved using the method described in §2.6.4. To perform the conversion for data measured with a Nanoscope AFM three parameters need to be known: the spring constant of the cantilever, the radius of the colloid and the scan size of the measurement. The spring constant and the radius of the colloid are used to convert the photodiode response to the normalized force. The scan size is the total distance the sample traveled during measurement and is used to determine the distance the sample has traveled at each step of the measurement.

When converting the measurements to force versus separation, there are three adjustable parameters: a compliance value, a separation zero value and a force zero value. The compliance value changes the slope of the compliance region; this is adjusted until the compliance region is vertical (indicating that additional applied force to the cantilever does not change with separation of the surfaces). The force zero value is set such that at large separations the force between the surfaces is zero. Finally, the separation zero is used to set the separation of the compliance region to zero (separation is zero when the surfaces are in contact). Each of these parameters is adjusted using a slider style input value that updates the converted data on the screen in real time. This enables accurate and quick data analysis compared to previous methods in which the output of a particular set of variables would be evaluated and repeatedly corrected. An image of the user interface of this section of *The Force* is shown in Figure 2.11.
Figure 2.11: User interface of the data conversion section of The Force.

To allow for faster processing of the data files, a predictive function was added to estimate the initial value of the fitting parameters. The compliance values are estimated by determining the gradient of the expected compliance region. The separation zero values are estimated by averaging the separation values of the expected compliance region. The force zero values are estimated by averaging the force at large separations (where it is assumed there is no force between the surfaces). The user also has the choice of adjusting each of the parameters separately for when the surfaces are approaching or retracting or to link them so that they are set concurrently. After the data has been converted there is a save function to output that data in the form of a text file.

2.7.2 Data Analysis

After the experimental data has been converted into a force-separation curve it can be analyzed in different ways within the same program. Currently The Force has three data analysis methods available: DLVO theory fitting to the data, a minimum value finder and a spring constant fitting system.

2.7.2.1 DLVO

For surface force measurements, a standard analysis is a comparison with DLVO theory. The Force has a DLVO calculation built in that uses the algorithm described by Chan et al.\textsuperscript{6} which is summarized in §1.1.1.1. There are three fitting parameters
provided in the DLVO analysis: the non-retarded Hamaker constant, the Debye length and the surface potential/charge.

The Hamaker constant describes the magnitude of the van der Waals force between the surfaces and can be found for many systems in the literature\textsuperscript{93}. In the case of this work, these values were calculated using an algorithm developed and implemented by Dr. Drew Parsons of the Department of Applied Mathematics, ANU, which is described in the article by Walsh \textit{et al.}\textsuperscript{94} and summarized in §4.2.1.1. The Debye length and surface potential are used as fitting parameters in the model of the electrostatic force between the surfaces and are determined by fitting the total DLVO theory to the experiment data according to the user’s judgment.

After the DLVO force between the surfaces has been modeled, the DLVO curve can be saved in a text format file to allow the plotting of the data using other programs. An image of the DLVO modeling user interface is shown in Figure 2.12.

![Figure 2.12: User interface for the DLVO modeling section of The Force.](image)

2.7.2.2 \textit{Finding Minimum Values}

The magnitude of an adhesion can be determined using the minimum value finding system of \textit{The Force}. This system allows the user to select a section of the force-separation data set. The force will then determine the most negative force in that section and the separation at which it occurs. Most commonly this is used to determine the primary adhesion between surfaces but can be used to look at secondary, tertiary, etc.
adhesions as well. The values of the minimum force for multiple sections of a data set or multiple data sets can be saved in a table for quick analysis at a later date.

2.7.2.3 *Spring Constant fitting*

When the force is attractive between the surfaces it is common for the magnitude of the attractive force to exceed the spring constant of the cantilever. This results in a mechanical instability and data in this region does not reflect the interaction between the surfaces. When the attraction (or repulsion) exceeds this limit, the force observed in the data shows a linear region, which has a gradient equal to the spring constant.

Attractive forces having a magnitude similar to the spring constant, are easily confused with real attractive forces, which exceed the spring constant limit in force measurements. By comparing the slope of these regions of the force with the spring constant it is a simple matter to determine whether the magnitude of the force is less than or greater than the spring constant. If the slope of the data is less that the spring constant then the data is real, otherwise it should be ignored or removed.

A spring constant fitting system has been added to *The Force* to allow the user to compare the spring constant to the measured forces. A line with the gradient of the spring constant is calculated. The y-intercept (adhesive force) is the fitting parameter.

This analysis system can also be used to determine the magnitude of the adhesion for a force curve where the data has been truncated (see Figure 2.13). If an adhesion between surfaces is large enough, the deflection in the cantilever will be greater than that which the instrument can measure, which results in the adhesion information being “cut off” in the data set. Provided a section of the linear spring constant region of the adhesive pull off is visible then a spring constant fitting will allow the magnitude of the adhesion to be extrapolated from the available data.
Figure 2.13: Example of truncated data produced during an AFM measurement. Red dots mark experimental data. The black line represents the spring constant extrapolation to determine the adhesive force between the surfaces. In this case, the adhesive force was found to be 1.8 mN/m.
Chapter 3: Model Surfaces Produced by Atomic Layer Deposition

3.1 Introduction

Investigation of surfaces relevant to colloid and surface science usually require that model surfaces be employed for measurements. This is because natural surfaces are often unsuitable due to surface roughness, inappropriate geometry or chemical heterogeneity.

Consequently, there is a strong interest in expanding the range of model surfaces beyond those that are currently available for study. This would allow a wider range of properties to be investigated as well as provide analogs for systems that are of technical interest for industry and other disciplines.

This chapter describes the preparation of mineral oxide surfaces suitable for use in force measurements using Atomic Layer Deposition (ALD). These surfaces are characterized to determine roughness, thickness and crystal structure of the deposited layer as well as the surface charging properties to ensure they are suitable to be employed as model surfaces.

To determine the optimal method for growing mineral oxide films of alumina, titania, hafnia and zirconia with ALD, the effect of film thickness and reactor temperature on the properties of the films was investigated. These recipes were developed using examples provided by Cambridge NanoTech as well as examples from literature references. 57, 58, 95, 96

3.2 Results and Discussion

3.2.1 Alumina (Al₂O₃) Surfaces

Layers of alumina were grown using trimethylaluminium (TMA) as the aluminium source and Milli-Q water as the oxygen source for the ALD process. Neither of the precursors were heated, as the vapour pressure is sufficient at room temperature for the ALD process. The layers were deposited with the reaction chamber heated to 200 °C using 0.015 s pulse times for both TMA and water. The chamber purge time between
half reactions was 8 s. The effect of the variation of the film thickness on the properties of the film was examined by creating surfaces coated with layers of various thicknesses. The layer thickness is controlled by the number of ALD deposition cycles.

3.2.1.1 Characterization

A key factor for determining the suitability of an ALD deposited layer for use as a model surface is the roughness of the surface. Roughness complicates the interpretation of force measurements as it introduces uncertainty in the position of zero separation, which is ill defined, and also will effect the manifestation of the forces. It is important to determine the effect of the thickness of the deposited layer on the roughness. To do this we prepared ALD films of alumina which were deposited using either 100 deposition cycles or 952 deposition cycles that were imaged using the AFM, see Figure 3.1. The root mean square (RMS) roughness of surfaces was determined by analyzing the images using the computer software package Gwyddion.97
Figure 3.1: AFM images of thin films of alumina deposited onto silicon wafer using ALD. The top image is a thin film produced with 100 deposition cycles, the bottom image is for a film produced with 952 cycles.

The roughness of a surface with a 100-cycle alumina layer is 0.25 nm, whilst the surface with a 952-cycle layer has a roughness of 0.26 nm. There is no significant difference between the roughness of the surfaces coated with thick or thin layers of alumina. The roughness is low and comparable to the roughness of the substrate\textsuperscript{98} making them both suitable to use as model surfaces.
3.2.1.1 Film Thickness

To calculate the van der Waals force present between such ALD prepared surfaces, the thickness of the deposited layers needs to be determined. Determining the thickness also allows the calculation of the sensitivity parameter for performing quantitative measurements material adsorption using the Optical Reflectometer (OR), see §2.5.

XRR measurements were employed to determine the thickness of the alumina layers. An example of an XRR measurement for a 952-cycle alumina layer coated silicon wafer is shown in Figure 3.2.

![Graph](image.png)

**Figure 3.2:** XRR measurements of an alumina layer grown with 952 deposition cycles of ALD onto a silicon wafer. Modeling of the surface using the program *Motofit* determined that the thickness of the alumina layer was 110.4±6.1 nm with an SLD of 3.08±0.07×10⁻⁵ Å⁻² and a roughness of 0.56±0.02 nm.

Analysis of this measurement was performed using the software package *Motofit*. The thickness of the 952-cycle film was determined to be 110.4±6.1 nm with a scattering length density (SLD) for the alumina layer of 3.08±0.07×10⁻⁵ Å⁻², and a surface roughness of 0.57±0.02 nm. This SLD indicates the electron density of the film is similar to that of bulk alumina (3.33±×10⁻⁵ Å⁻²). Modeling of the 100-cycle film determined a thickness of 11.4±0.1 nm using an SLD of 3.04±0.04×10⁻⁵ Å⁻² and a roughness of 0.58±0.01 nm. The alumina layers have an average deposition rate of 0.12 nm/ALD cycle.
3.2.1.1.2 Film Crystallinity

To further characterize the films, XRD spectra were measured to examine the crystallinity of the surface. This can influence a range of properties, including the density, refractive index, and surface-charging properties. XRD measurements of the alumina films were performed over a 2θ range of 20-80˚ and are shown in Figure 3.3.

![XRD spectra of silicon wafer with an alumina film made with 100 and 952 deposition cycles.](image)

Figure 3.3: XRD spectra of silicon wafer with an alumina films made with 100 and 952 deposition cycles. Diffraction peaks of the silicon wafer substrate are observed along with peaks for α-phase alumina crystal structure.

Measured spectra were compared with literature powder diffraction spectra\textsuperscript{70, 71, 100} to determine the crystal phases present in the surfaces. Diffraction peaks observed at 62˚ and 66˚ are consistent with the (122) and (030) reflections of the alpha crystal form of alumina.\textsuperscript{101} Also observed in the spectra are diffraction peaks that correspond to the crystal structure of the silicon/silica substrate of the alumina coated sample. The diffraction peaks for the substrate materials of the 110 nm layer of alumina have lower intensity compared with those of the 11.4 nm layer due to the screening of the substrate by the thicker film.

3.2.1.1.3 Elemental Composition

To ensure that the alumina films that were being produced by the ALD were in fact \( \text{Al}_2\text{O}_3 \), XPS, measurements were performed. William Skinner of the Ian Wark Institute in Adelaide performed the measurements using a Kratos Axis Ultra spectrometer, which
employed a monochromatic Al Kα x-ray source (1486.6 eV), and provided analysis. The composition of the ALD alumina sample is summarized in Table 3.1.

Table 3.1: Atomic composition of ALD produced alumina films determined using XPS

<table>
<thead>
<tr>
<th>Surface Element</th>
<th>% Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>28.4</td>
</tr>
<tr>
<td>Total Oxygen</td>
<td>51.8</td>
</tr>
<tr>
<td>Oxide Oxygen</td>
<td>41.7</td>
</tr>
<tr>
<td>Hydroxyl Oxygen</td>
<td>10.1</td>
</tr>
<tr>
<td>Carbon</td>
<td>19.8</td>
</tr>
</tbody>
</table>

The ratio of aluminium to the oxide portion of the oxygen signal indicates a slight deviation from stoichiometric alumina, which is likely the result of incompletely reacted TMA trapped in the film during deposition. The carbon present in the film will either be the result of unreacted TMA or adventitious hydrocarbon adsorbed from the atmosphere. The valence band of the XPS spectra exhibits two nearly symmetric peaks at binding energies of 5.5 and 10 eV, see Figure 3.4, which is consistent with the alpha phase of alumina.102
Figure 3.4: Measured XPS valance band of Al₂O₃ films (top). The bottom image are measurements reported by Thomas et al. of the XPS valance bands of alumina phases where (a) the band for gibbsite, (b) is bayerite, (c) is nordsstrandite, (d) is boehmite, (e) is α-alumina and (f) is γ-alumina. The measured symmetric peaks for the ALD prepared alumina surface are consistent with an α-alumina crystal phase.

3.2.1.1.4 Film Stability in aqueous solutions

Optical Reflectometry (OR) is designed to monitor the adsorption of molecules, polymers and particles to a surface with high temporal resolution. However, it can also
be applied to investigate the stability of a surface or film in a medium. In a normal OR measurement, the solvent is passed through the measurement cell until the p/s signal stabilizes. This is the point where the equilibrium between the surface and the solvent is achieved and is the baseline for the system. A surface with a 110 nm layer of alumina was placed in the OR with water flowing through the measurement cell and the ratio of the p/s signal was measured to observed the baseline of the system, see Figure 3.5.

![Figure 3.5: Optical reflectometry measurements of an alumina surface in water showing ratio of p and s polarizations of the reflected light versus time. A stable baseline is not achieved over the measured period](image)

What is evident from these measurements is that a constant baseline signal is not observed. Over the span of the five hours shown the p/s signal does not stabilize. In fact, the instability of the p/s ratio continued for more then 24 hours. Any change in the signal represents a change in the optical properties of the surface, either through adsorption or desorption of material at the surface. The continuously unstable baseline observed for the alumina surface lead to the conclusion that the alumina layer dissolves over time. While the OR technique was not designed to measure a rate of dissolution of the surface, it was possible to estimate it to be approximately 0.5 nm per hour.

Two approaches were explored to stabilize the alumina surface in water: annealing of the surface and using an adhesive layer between the alumina and substrate. Annealing the surface at 400 °C for at least 10 hours had no effect on the stability of the alumina. To test the use of an adhesive layer a thin layer of alumina was grown onto a titania
(TiO$_2$) layer. An OR suitable wafer was coated with 5 nm of titania using ALD, then 5 cycles of alumina, approximately 0.5 nm, was deposited onto the titania layer. This surface was monitored using OR, see Figure 3.6. To determine whether the alumina layer dissolved completely from the surface a $10^{-3}$ M CTAB solution was introduced into the measurement cell periodically and then replaced with water. The adsorption and desorption of CTAB appears as spikes in the data. Due to the opposite charge of the titania and alumina surfaces at neutral pH, the cationic surfactant CTAB will adsorb more strongly to the titania surface. Thus observation of the magnitude of the spike enables the chemistry of the surface to be inferred.

![Figure 3.6: Optical reflectrometry of CTAB adsorbing to a thin alumina film on a titania film. The ratio of p and s polarizations versus time is shown. The surface was exposed to CTAB for 2 min periodically (see spikes). The depth of the spikes increases over time indicating that CTAB is adsorbing more strongly and titania is being exposed due to dissolution of alumina.](image)

Over approximately 90 min, the baseline signal stabilizes at a p/s value of approximately 1.015. The increase in the size of the spikes in the data with time indicates that the level of CTAB adsorbing is increasing due to increased exposure of the titania layer. After a period of 4-5 hours, the alumina film has completely dissolved. We concluded that using an adhesive layer failed to stabilize the alumina layer.

An alternative means to prevent the dissolution of the alumina layer is to employ molecules that adsorb to the alumina surface and stabilize or passivate it. OR
measurements performed in the presence of a strongly adsorbing additive demonstrated that the alumina surface could be passivated by the adsorption of molecules, thereby preventing the dissolution of the layer.\textsuperscript{103} We conclude that the alumina layers produced via ALD are useful as model surfaces for surface studies in aqueous solution only when they are used in the presence of passivating molecules.

3.2.1.2 Summary

Whilst alumina surfaces that are smooth enough to be used as model surfaces can be produced using ALD, the instability of the alumina in water means they are unsuitable for use in many situations of interest. It is unknown whether the dissolution of the alumina surfaces is an obstacle for all alumina surfaces or is just a problem for ALD prepared alumina.

3.2.2 Titania (TiO$_2$) Surfaces

Titania films were produced using titanium isopropoxide and Milli-Q water as the precursors. The water source was used at room temperature, while the titanium isopropoxide was heated to 80 °C. Films were deposited using a 0.015 s pulse of the titanium source and 0.015 s pulse of water. The chamber was purged or a period of 10 s between the ALD half reactions.

3.2.2.1 Characterization

It has been documented that the properties of ALD prepared layers are strongly influenced by the deposition temperature employed.\textsuperscript{104, 105} Titania films grown at low temperatures have been observed to have amorphous crystallinity,\textsuperscript{18} while films deposited at higher temperatures have been seen to form anatase and rutile crystal structures.\textsuperscript{106, 107} These differences in crystal structure should effect the roughness and charging properties of the surface. AFM images of titania films deposited using ALD at 250 °C are presented in Figure 3.7 for layers deposited using 280 and 2200 deposition cycles.
Figure 3.7: AFM images of ALD titania films produced at 250 °C. The titania layers were deposited using 280 cycles (top) and 2200 cycles (bottom).

The titania films deposited using 2200 deposition cycles were found to have an RMS roughness of 8.2 nm, which is better than the titania surfaces that were previously employed in studies using titania colloidal particles\textsuperscript{44} but still less than ideal for a model surface. The thinner films deposited using 280 cycles were found to have a roughness of 0.24 nm, which is considerably smoother. However, films of this thickness may be too thin, leading to the dispersion forces manifest between the surfaces being affected by the substrate materials as the film is not thick enough to present a dispersion force similar to a bulk material, see §4.2.1.1.
To produce thicker layers of titania that are more likely to remain smooth, films of titania were deposited at 80 °C where the layer should have an amorphous crystal structure. An AFM image of a titania film deposited at 80 °C using 1600 deposition cycles is shown in Figure 3.8.

![AFM image of a titania film deposited at 80 °C using 1600 deposition cycles.](image)

The RMS roughness of these low temperature films is 0.47 nm. This is much lower than the layers of similar thickness deposited at 250 °C. These smooth thick films of titania are ideal for use as model surfaces for force measurements.

3.2.2.1.1 Film thickness

The thickness of the deposited layers of titania were determined using XRR so that accurate calculations of the van der Waals force as well as the sensitivity parameters for OR measurements could be made. The XRR measurement of a 280 cycle titania film deposited at 250°C is shown in Figure 3.9.
Figure 3.9: A plot of an XRR measurement for a titania surface deposited at 250°C using 280 cycles showing the intensity (R) versus Q along with the model of the surface determined using *Motofit*.

The thickness of the titania layer was determined using *Motofit* to be 10.6 nm using a SLD of $2.78 \times 10^{-5}$ Å$^{-2}$ and a roughness of 0.62 nm. In comparison XRR measurements of titania films made at 250°C with 2200 cycles are difficult to model due to the high roughness of the titania surface. This results in uncertainty in determination of the thickness and properties of the layer (see Figure 3.10). An approximate thickness of the titania layer was determined by performing a Fast Fourier Transform of the data. This estimated the layer thickness to be 82 nm.
Figure 3.10: XRR plot showing the intensity versus $Q_z$, for a titania surface deposited at 250°C using 2200 cycles. Motofit\textsuperscript{74} was unable to model the surface due to the roughness of the surface. A fast Fourier transform of the data approximated the film thickness to be 82 nm.

XRR measurements of titania layers deposited at 80°C using 1600 cycles provided high quality data, which were modeled using Motofit. The thickness of the layer was determined to be $102 \pm 0.05$ nm using an SLD of $2.32 \pm 0.03 \times 10^{-5}$ Å\textsuperscript{-2} and a roughness of $0.73 \pm 0.01$ nm. The SLD used in the models of the titania layers indicates that the electron density of the titania is similar to that of bulk titania ($3.08 \times 10^{-5}$ Å\textsuperscript{-2}).\textsuperscript{99}

3.2.2.1.2 Film Crystallinity

To determine whether there is a difference in the crystal structure between the titania layers deposited at high and low temperatures, XRD measurements were performed. Spectra of titania surfaces deposited at 250 °C and 80 °C are shown in Figure 3.11. These spectra were compared with powder diffraction spectra from the literature\textsuperscript{71,100,108} to determine the crystallinity of the materials on each surface.
Layers deposited at 250 °C present diffraction peaks at 25° and 43° that are consistent with the (101) and (112) diffraction peaks of the anatase form of titania. The peak observed at 33°, corresponds to the (200) peak of the silicon wafer substrate. In the layers deposited at 80 °C, no diffraction peaks consistent with forms of titania are observed, indicating that the titania layer is amorphous. The (200) silicon diffraction peak is still observed.
This difference in the crystallinity of the layers deposited at high and low temperature can explain the difference in the roughness observed in the AFM images. When the titania forms a crystal, a preferred direction for deposition results. This leads to the surface becoming rougher as the thickness increases. The amorphous surface has no preferred direction of deposition and therefore changes in roughness with thickness are much smaller.

3.2.2.1.3 Elemental composition

The elemental composition of titania films were determined using XPS by William Skinner at the Ian Wark Institute in Adelaide. A summary of the composition of the films deposited at 80 °C and 250 °C is presented in Table 3.2.

<table>
<thead>
<tr>
<th>Surface Element</th>
<th>% Quantity 80°C</th>
<th>% Quantity 250°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>18.5</td>
<td>23.8</td>
</tr>
<tr>
<td>Total Oxygen</td>
<td>47.9</td>
<td>54.3</td>
</tr>
<tr>
<td>Oxide Oxygen</td>
<td>36.4</td>
<td>47.9</td>
</tr>
<tr>
<td>Hydroxyl/Water</td>
<td>11.5</td>
<td>6.4</td>
</tr>
<tr>
<td>Carbon</td>
<td>13.9</td>
<td>21.9</td>
</tr>
</tbody>
</table>

The ratio of metal to oxide in both cases indicated near stoichiometric titania for layers deposited at both high and low temperatures. The carbon present in the surface is likely the result of reaction products trapped in the film during the deposition process or adventitious hydrocarbon absorbed from the atmosphere (discussed in more detail in §5.2.4). The detection of no other elemental signals confirms the absence of other contaminating impurities.

Fine scans of the binding energy positions of the Ti 2p3/2 photoelectron peaks that are present at 459.7±0.2 eV are presented in Figure 3.12 for both samples.
Figure 3.12: Binding energy measurements of the Ti 2p 3/2 peak of the ALD titania samples using XPS. The presence of the peak at a value of 458.7±0.2 eV is typical for Ti(IV).

These peaks are consistent with either anatase or rutile forms of titania in terms of the Ti site electronic environment\textsuperscript{109} and no contribution is observed for Ti(III) at 457.3 eV.

3.2.2.1.4 Film stability

The stability of the titania films in an aqueous environment was determined using OR. Surfaces were prepared by depositing a 10 nm film of titania onto a silicon wafer with a 320 nm silica layer. Upon immersion into an aqueous environment, a stable baseline was achieved over a wide range of pH. Additionally, surfaces immersed in water for 60 hours showed no change in appearance or roughness, as measured by AFM imaging. Therefore, the titania surfaces were deemed stable for surface force measurements.

3.2.2.1.5 Zeta Potential

The charging properties of the titania surfaces produced by ALD were examined, to ensure that the composition of surface charge groups for this type of titania is comparable to samples of titania that have been studied in the past.\textsuperscript{61,110}

Zeta potential measurements were performed to measure the charging properties of the titania surfaces. These measurements were performed using ballotini silica particles (mean size of 30 µm) coated with a 10 nm layer of titania. The titania coated particles were suspended in a 10⁻³ M NaCl solution and the zeta potential was measured over a
range of pH using a Zetasizer ZS instrument. These zeta potential measurements are shown in Figure 3.13.

![Zeta potential vs pH](image)

Figure 3.13: Zeta potential as a function of pH for ballotini silica particles coated with 10 nm of titania using ALD in a $10^{-3}$ M NaCl solution.

The isoelectric point (IEP) of the particles was found to be at pH 5.1, which agrees with previously published measurements for clean rutile titania surfaces\textsuperscript{110}. The titania produced by ALD is therefore found to have comparable surface charging properties to those of previously available titania samples.

### 3.2.2.2 Summary

ALD produced titania films that are deposited at 250 °C are in the anatase form, which causes the roughness of these surface to increase with the thickness of the layer deposited. While thin layers (<10 nm) deposited at this temperature are smooth enough for force measurements, they do not have the van der Waals properties of bulk titania. Thicker layers are too rough for accurate force measurements at small separations. Depositing the films at 80 °C produces amorphous titania which is very smooth. These surfaces have sufficiently low roughness for force measurements even when the layer thickness is large (>50 nm). A summary of the deposition conditions along with the properties of the ALD films employed is presented in Table 3.3.
Table 3.3: Summary of titania surface produced using ALD

<table>
<thead>
<tr>
<th>Growth Temperature (˚C)</th>
<th>Number of cycles</th>
<th>Thickness (nm)</th>
<th>Roughness (nm RMS)</th>
<th>Crystal Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>280</td>
<td>16</td>
<td>0.24</td>
<td>Anatase</td>
</tr>
<tr>
<td>250</td>
<td>2200</td>
<td>82</td>
<td>8.2</td>
<td>Anatase</td>
</tr>
<tr>
<td>80</td>
<td>1600</td>
<td>102</td>
<td>0.47</td>
<td>Amorphous</td>
</tr>
</tbody>
</table>

The titania surfaces produced by ALD are stable in water and have similar charging properties to those of titania samples that have been used in previous studies. Using ALD is an effective way to produce model surfaces of titania for use in the study of surface properties.

3.2.3 Hafnia (HfO₂)/Zirconia (ZrO₂)

Hafnia layers were produced using tetrakis(dimethylamido) hafnium(IV) and Milli-Q water as the precursors. Tetrakis(ethylmethylamido) zirconium(IV) and Milli-Q water were used as the precursors for depositing zirconia layers. The hafnium precursor was heated to 75 ˚C and the zirconium source was heated to 130 ˚C; the water source was not heated. The hafnia layers were grown using a 0.15 s pulse of the hafnium source, a 0.015 s water pulse and 60 s purge times for each cycle. Zirconium layers were deposited using 0.2 s zirconium pulses, 0.015 s water pulses and 60 s purge times.

3.2.3.1 Characterization

3.2.3.1.1 Roughness

AFM images of hafnia and zirconia layers, deposited at 250 ˚C using 600 deposition cycles are presented in Figure 3.14.
The RMS roughness of the hafnia surfaces is 1.8 nm over an area of 1 µm² while the roughness of the zirconia surface is 3.1 nm for the same area. The roughness of these surfaces, due to the propensity of these materials to become crystalline, is suitable for some surface studies, but is far from ideal. Certainly accurate force measurements at small separations are not possible. We investigated the deposition temperature of the layers on the surface roughness and found that it had no significant effect.

The roughness can be reduced by producing thinner films. Thin films of these material have low roughness, however, the van der Waals properties of such films is not representative of the properties of the bulk materials; the effective Hamaker constants
being low due to the influence of the silicon substrate. To produce surfaces with higher effective Hamaker constants, yet still smooth, we decided to deposit titania films overlaid with either hafnia or zirconia. Such layered structures will possess similar van der Waals properties to those of the bulk hafnia or zirconia while remaining smooth enough to provide accurate force measurements at small separations. To prepare such surfaces, 800-cycle titania layers were deposited at 80 °C then a 121-cycle layer of hafnia or a 141-cycle layer of zirconia was deposited over the titania layer. AFM images of these surfaces are shown in Figure 3.15.

Figure 3.15: AFM images of hafnia (top) and zirconia (bottom) grown onto titania films
The roughness of these surfaces are 0.53 nm and 0.8 nm for hafnia and zirconia respectively. The roughness of these is sufficiently low to be viable model surface for force measurements.

3.2.3.1.2 Film thickness

Due to the layered structure of these surfaces, it is important that the thickness of each layer is known accurately so that the calculations of the van der Waals force can be performed. XRR was used to measure these layer thicknesses. An example of the measurement of the titania/hafnia surface is shown in Figure 3.16

![Graph](image)

**Figure 3.16:** XRR measurement of 121 deposition cycles of hafnia grown onto 800 cycles of titania on a silicon wafer. The hafnia layer was found to be 12.16 nm thick.

Analysis of the fringes of the XRR measurement determined that the hafnia layer is 12.16 ± 0.02 nm using an SLD of 5.70 ± 0.13×10^{-5} Å^{-2} and a surface roughness of 0.77 ± 0.01 nm. The titania layer is 28.93 ± 0.02 nm thick, which was modeled with a SLD of 2.56 ± 0.06×10^{-5} Å^{-2} and an interface roughness between the titania and hafnia layers of 0.76 ± 0.01 nm. The SLDs used in the model indicates that the titania and hafnia films have an electron density similar to that for the bulk materials (SLD of titania = 3.08×10^{-5} Å^{-2} and SLD of hafnia = 6.40×10^{-5} Å^{-2})^{99}. 

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Similar measurements on zirconia/titania surfaces determined the zirconia layer was 1.45±0.04 nm thick, using a SLD of 3.60±0.09×10⁻⁵ Å⁻² and a roughness of 0.84±0.01 nm. The titania layer was 30.05±0.01 nm thick using a SLD of 2.57±0.04×10⁻⁵ Å⁻² and a boundary roughness of 0.54±0.02 nm. Again, the electron densities of these layers are similar to that of the bulk materials (SLD zirconia: 4.37×10⁻⁵ Å⁻²).³⁹

### 3.2.3.1.3 Crystal structure

The crystal structures of the hafnia and zirconia surfaces were examined using XRD. These measurements are presented in Figure 3.17.

Figure 3.17: XRD measurements of hafnia and zirconia films that have been grown onto a smooth titania film which was deposited onto a silicon wafer substrate with a native oxide layer.

The diffraction peaks observed in the XRD measurements are all consistent with the diffraction peaks for the silicon wafer substrate. The titania layers that were deposited at low temperature are amorphous and therefore present no diffraction peaks (see §3.2.2.1). The lack of diffraction peaks for the hafnia and zirconia layers is unexpected as studies of these materials prepared using ALD in the past have been seen to be crystalline.⁵⁷ The lack of diffraction peaks for the hafnia and zirconia layers is likely the result of the layer being very thin and being trapped in an amorphous state; the films described by Kukli et al.⁵⁷ were much thicker >100 nm.
3.2.3.1.4 Film stability

The stability of the hafnia and zirconia surfaces in an aqueous environment was determined using OR. Surfaces were prepared by depositing a 10 nm film of hafnia or zirconia onto silicon wafer with a 320 nm silica layer. Upon immersion into an aqueous environment, a stable baseline was achieved over a wide range of pH for both hafnia and zirconia surface. Therefore, these surfaces were deemed stable for surface force measurements.

3.2.3.2 Summary

Thick layers of hafnia and zirconia, which have bulk van der Waals properties are far too rough to be used for force measurements. However, by depositing these materials onto a titania layer, it is possible to produce smooth surfaces with similar properties to the bulk materials. These surfaces are stable in aqueous environments and therefore are suitable to use as model surfaces of hafnia and zirconia. The thickness of these layers needs to be measured accurately to enable the effective Hamaker constant between two surfaces or the sensitivity parameter for OR measurements to be accurately calculated.

3.2.4 ALD of particles

To produce coated colloids for surface force measurements, films of mineral oxides were deposited onto smooth borosilicate spherical colloids. In order to perform the deposition of the film without a significant loss of material, the particles were contained in an opened ended glass tube. This allowed the precursor gases access to the colloid surfaces while confining the colloids to prevent them from being blown around the chamber by the pressure changes that occur during the deposition process. Examination of flat silicon wafers that were placed in the in the ALD chamber with the colloids during deposition allowed the thickness of the film deposited onto the colloids to be determined.

3.3 Summary

A selection of mineral oxide surfaces was produced using ALD, then characterized using a variety of techniques to produce model surfaces for use in the study of surface properties relevant to colloidal systems. Alumina surfaces produced using ALD are smooth enough for accurate force measurement. However, they are unstable in water, except in the presence of a strongly adsorbing additive. As such, alumina surfaces
produced in this manner are unsuitable for many investigations. Titania films produced at 250 °C that are thick enough to have comparable properties to the bulk material, were far too rough for accurate force measurements. Titania layers deposited at 80 °C were smooth, even when thick layers are deposited (>50 nm), and stable in water. This makes them ideal for use as model surfaces. Hafnia and zirconia were too rough at the thickness necessary to provide bulk like dispersion forces. By depositing these materials onto titania, smooth surfaces could be produced that have dispersion forces representative of bulk materials. These hafnia and zirconia surfaces are stable in water and can be used as model surfaces for colloidal systems.
Chapter 4: Direct Measurement of Surface Forces between Titania Surfaces Prepared by ALD in Electrolyte Solutions

4.1 Introduction

Understanding the fundamental forces between matter has long been recognised as an important scientific endeavour and elucidating the relationship between the properties of materials and surface forces by direct force measurement is an ongoing pursuit. Direct force measurements have been conducted between Mica, Silica, Gold, Cellulose, Polystyrene and Polypropylene surfaces both pristine and modified. Notably, very few direct surface force investigations of mineral oxide surfaces have been reported despite strong interest in these materials, as they previously were not able to be prepared in a suitable form. For precise quantitative force measurements the surfaces must be prepared in a suitable geometry (typically a cylinder, flat or sphere) with minimal surface roughness. For this reason, a large number of earlier investigations have been performed using mica or silica.

This chapter describes surface force measurements that were performed using ALD deposited titania surfaces, the preparation and characterization of which is described in §3.2.2. Titania was chosen for the force measurements due to it being a stable, non-toxic, non-soluble material that has a readily accessible isoelectric point (IEP). This allows the force between titania surfaces to be examined where the surfaces are positively charged, negatively charged and neutral.

Three types of titania surfaces were studied in this work. Force measurements between 80 nm thick anatase surfaces that were produced at 250 °C are described in section §4.2.1. The measurements described here were performed near the IEP in order to examine the van der Waals interaction between these rough surfaces. The measurements using 5 nm thick anatase films deposited at 250 °C described in section §4.2.1 were made to determine whether these surfaces are comparable to those of pure titania across a range of pH. Finally, measurements between 100 nm thick amorphous titania films...
deposited at 80 °C are described in §4.2.2 for a range of electrolyte concentrations, pH, and electrolyte types.

4.2 Results and Discussion

4.2.1 80 nm Anatase Films

Surface forces between 80 nm thick anatase titania layers were measured in the presence of $10^{-3}$ M NaCl, near the IEP (pH 4.6). An example of these measurements, along with a retarded van der Waals calculation and a non-retarded van der Waals fit using a Hamaker constant of 60 zJ are presented in Figure 4.1.

![Figure 4.1: Surface forces measured between 80 nm anatase titania layers in the presence of $10^{-3}$ M NaCl at pH 4.6. The experimental data (dots) has been fitted with a van der Waals force using a non-retarded Hamaker constant of 60 zJ (solid line).](image)

An attraction is evident at a surface separation of less than 30 nm. At first glance, this attraction appears to be the van der Waals attraction between the surfaces and it even has a similar magnitude. However plotting the data on a semi-log plot, as shown in Figure 4.2, reveals a straight line showing that the attraction increases exponentially as the separation decreases. An un-retarded van der Waals attraction between surfaces across a medium is expected to have the form of an inverse power law. Thus the data is of the wrong mathematical form to be a van der Waals attraction. An exponentially
increasing force is indicative of an electrostatic type interaction. Such a force is typically repulsive for two identical surfaces but here an attractive force is observed.

Figure 4.2: Surface forces measured between 80 nm anatase titania layers in the presence of $10^{-3}$ M NaCl at pH 4.6. The experimental data (dots) and the van der Waals force, using a non-retarded Hamaker constant of 60 zJ (solid line) are shown on a log-linear plot.

In order to explain these forces the heterogeneous surface charge model of Miklavic et al.\textsuperscript{32} can be applied. This force is a result of the attraction between patches of opposite charge on each surface. With the surface being composed of anatase crystals (see §3.2.2.1) the different crystal faces of the rough anatase surface could charge to differing degrees, resulting in the formation of patches of charge over the surface. The theory of Miklavic et al., which is described in more detail in §1.1.2.3, describes the force between the surfaces using

$$\frac{F}{R} = Be^{-2q_{\text{min}}L}$$

[1.37]

where $B$ is a constant, $L$ is the separation between the surfaces and

$$q_{\text{min}} = \left[\left(\frac{n}{d}\right)^2 + \kappa^2\right]^{1/2}$$

[1.38]
where $a$ is the size of the areas of charge and $\kappa^{-1}$ is the Debye length. This model predicts that the maximum decay length of the force should be half the Debye length of the system. A fit of this theory to the experimental measurements, by adjusting the values of $B$ and $q_{min}$, is presented in Figure 4.3.

![Figure 4.3](image-url)

Figure 4.3: Surface forces measured between type A titania surfaces in the presence of $10^{-3}$ M NaCl at pH 4.6. The experimental data (dots) has been fitted with a heterogeneous charged surfaces model (line) with fitting parameter $B$ being 0.32 N/m and a $q_{min}$ of 8.3 nm.

The experimental data was fitted with $A = 0.32$ N/m and a $q_{min}$ of 8.3 nm, but the Debye length of the solution is nominally 9.4 nm therefore the maximum decay length allowed by the theory is only 4.7 nm. Parson et al. describe an amplification of the electrostatic force due to the surface roughness. However, the amplification factor takes the form of $\exp(\sigma_m^2 / 2\lambda^2)$, where $\sigma_m$ is the mean roughness and $\lambda$ is the decay length. This amplification will affect the magnitude of the force but not the decay length, which suggests that heterogeneously charged surfaces are not the origin of the attraction.

We therefore considered other explanations. An attempt was made to apply DLVO theory to the experimental data where the surface potentials used are of equal magnitude but opposite sign, generating an attraction between the surfaces. For such a scenario to apply, the titania, coated sphere and flat surface would need to have different IEPs.
Given that the surfaces were prepared using different substrates, it is possible that the substrate influences the deposition behavior of the layer and therefore the surface properties. A fit of the experimental data using a force of this type is presented in Figure 4.4.

![Diagram](Image)

Figure 4.4: Surface forces measured between 80 nm anatase titania surfaces in the presence of $10^{-3}$ M NaCl at pH 4.6. The experimental data (dots) has been fitted with a DLVO fit (line) using the a Hamaker constant of 60 zJ and surface potentials of equal magnitude but opposite sign; the magnitudes of the potentials used were +8 mV and -8 mV.

The surface potentials used in this DLVO fit were +8 mV and -8 mV with a non-retarded Hamaker constant of 60 zJ. Due to the low surface potentials and the strong van der Waals interaction, the DLVO fit does not have an exponential form and so does not match the experimental measurements.

In order to model the interaction, this data was fitted with an electrostatic double layer (EDL) with surfaces that have an equal magnitude of surface potential but opposite sign with no van der Waals force, see Figure 4.5.
Figure 4.5: Surface forces measured between type A titania surfaces in the presence of $10^{-3}$ M NaCl at pH 4.6. The experimental data (dots) has been fitted with a fit using only an electrostatic double layer (line) where the surfaces have surface potential of equal magnitude but opposite sign; the magnitude of the potentials used were +15 mV and -15 mV and the Debye length was 8.1 nm.

In order to optimize the agreement between the experimental data and the calculation, surface potentials of +15mV and -15mV were used with a Debye length of 8.1 nm. This model fits the experimental data better than those describe above. In addition, the form of the model is exponential and values of the variables in the model are reasonable for the conditions of the experiment. However, this model requires an explanation for the absence of a van der Waals attraction. The significant surface roughness, 8.2 nm RMS (see Figure 3.7 of §3.2.2.1) is a likely cause, as it will reduce the van der Waals interaction as the interface becomes diffuse. Roughness will also affect the electrostatic attraction but the form of the interaction will remain exponential.\textsuperscript{118}

### 4.2.1 5 nm Anatase Films

The 5 nm titania layers produced at 250 °C are much smoother than the thicker 80 nm surfaces (see Figure 3.7 of §3.2.2.1), so the roughness issues will be significantly reduced. Surface force measurements were performed in $10^{-4}$ M NaCl at three pHs: pH 10 where the surfaces are negatively charged, pH 6.5 where the surfaces are negative...
but the magnitude is lower than that at pH 10 and pH 3.4 where the surfaces are positively charged. These measurements are presented in Figure 4.6

![Figure 4.6: Surface Force measurement between 5 nm titania surfaces, produced using ALD at 250 °C, in the presence of $10^{-4}$ M NaCl, at the following pHs: 3.4, 6.5 and 10. The data was fitted using DLVO theory (curves not shown) with the following parameters: at pH 3.4, Debye length 12 nm, surface potential +19 mV, surface charge +0.086 Cm$^{-2}$; at pH 6.5 Debye length 18 nm, surface potential -33 mV, surface charge -0.16 Cm$^{-2}$; and at pH 10 Debye length 13 nm, surface potential -32 mV, surface charge -0.15 Cm$^{-2}$. In all DLVO fits, a non-retarded Hamaker constant of 60 zJ was used.

At pH 10, the negative charge of the surfaces gives rise to a long-range diffuse double layer repulsive force. Reducing the pH to 6.5 results in a reduced surface potential and an increase in the Debye length as the ionic strength of the solution at pH 6 is less than at pH 10. Upon further decreasing the pH to 3.4, the surfaces are now positively charged (as evident from the zeta potential data in Figure 3.13) and a diffuse double layer repulsion again results. What is apparent in all these measurements is that the diffuse double layer repulsion continues up to contact, unaffected by the expected van der Waals attraction. In all cases, upon separation there is no hysteresis or adhesion, as the forces follow those of the approach curves.
Similar behavior has been seen between silica surfaces\textsuperscript{113, 119} and is attributed to the short-range repulsive hydration force overcoming the attractive van der Waals component. This explanation is not easily applied to titania as the expected van der Waals attraction of titania is $\sim 10$ times larger than that of silica and therefore would be measurable at a far greater range. The measurable range of the van der Waals force is therefore expected to be beyond the range of any reasonable hydration force in the case of titania surfaces. Roughness is not the cause either, as the surfaces are extremely smooth (see Figure 3.8 of §3.2.1.1). However, these surfaces consist of a number of layers (silicon, silica and titania), with the titania surfaces making up only the outermost 5 nm on each surface. It should therefore be considered that the dispersion interaction between these layered surfaces may be reduced from that of bulk titania, requiring that the dispersion interaction forces between the layered surfaces be theoretically evaluated.

A program to calculate such dispersion interactions was developed by Drew Parsons of the Department of the Applied Mathematics at The Australian National University, which is described in the journal paper: Direct Measurement of van der Waals and Diffuse Double-Layer Forces between Titanium Dioxide Surfaces Produced by Atomic Layer Deposition by Walsh et al.\textsuperscript{94}. This calculation is described briefly below.

4.2.1.1 Van der Waals Interaction between Layered Surfaces

The Hamaker van der Waals interaction energy between a titania coated flat surface and a similarly coated silica probe, separated by distance $L$, is given (for flat surfaces) by

$$F_{\text{Hamaker}}(L) = \frac{-A(L)R}{6L^2}$$

[4.1]

The separation-dependent Hamaker coefficient $A(L)$ is calculated with retardation using the multilayer formula of Parsegian and Ninham\textsuperscript{120}. For two multilayer surfaces, one on the left and one on the right of an intervening medium $m$ of thickness $L$, the Hamaker coefficient is given by,

$$A(L) = \frac{2k_BT}{3} \sum_{n=0}^{\infty} \int \int \text{d}x \text{d}y \left[ \ln \left( 1 - \frac{\Delta_{mL}(i\omega_n)\Delta_{mR}(i\omega_n)e^{-x}}{\Delta_{mR}(i\omega_n)e^{-x}} \right) \right]$$

$$+ \ln \left[ 1 - \Delta_{mL}(i\omega_n)\Delta_{mR}(i\omega_n)e^{-x} \right]$$

[4.2]

83
where $\omega_n$ are the so-called Matsubara frequencies ($\omega_n = 2\pi k_B T n / \hbar$), $r_n = 2L \omega_n \sqrt{\varepsilon_m (i\omega_n)} / c$, $\varepsilon_m$ is the dielectric function of the intervening medium between the two multilayers and $c$ is the speed of light. $\Delta$ describes the reflection of the magnetic component of a photon passing across an interface and $\overline{\Delta}$ describes the reflection of the electric component. Here $\Delta_{mL}$ and $\overline{\Delta}_{mL}$ refer to the reflection coefficients between the medium and the left multilayer structure, $\Delta_{mR}$ and $\overline{\Delta}_{mR}$ are the reflection coefficients between the medium and the right multilayer. For two materials $j$ and $k$, the retarded diamagnetic reflection coefficient is defined at an imaginary frequency $i\omega$ as

$$\Delta_{jk}(i\omega) = \frac{s_j \mu_j - s_j \mu_k}{s_j \mu_j + s_j \mu_k}$$

where $\mu$ is the magnetic permeability of each material. The dielectric reflection coefficient is

$$\overline{\Delta}_{jk}(i\omega) = \frac{s_j \varepsilon_j - s_j \varepsilon_k}{s_j \varepsilon_j + s_j \varepsilon_k}$$

where $\varepsilon$ is the electric permittivity or frequency dependent dielectric function of each material. The variable $s$ is a retardation coefficient,

$$s_j(i\omega) = \sqrt{p^2 - 1 + \frac{\varepsilon_j(i\omega)}{\varepsilon_m(i\omega)}}$$

where

$$p = \frac{xc}{2\omega L \sqrt{\varepsilon_m(i\omega)}}$$

In the non-retarded limit (i.e. taking the limit $c \to \infty$), the retardation coefficients $s_i \to \infty$, and therefore the reflection coefficients cancel, leaving $\Delta_{jk} \to 0$ (when $\mu = 1$) and $\overline{\Delta}_{jk}(i\omega) = (\varepsilon_j - \varepsilon_k) / (\varepsilon_j + \varepsilon_k)$.

A recursion formula leads from the multilayer reflection coefficients $\Delta_{mL}$, $\overline{\Delta}_{mL}$, $\Delta_{mR}$ and $\overline{\Delta}_{mR}$ to the coefficients $\Delta_{jk}$, $\overline{\Delta}_{jk}$ between neighbouring layers of materials

$$\Delta_{mL} = \frac{\Delta_{m,1} + \Delta_{1,L} e^{-x s_1 l_1 / p L}}{1 + \Delta_{m,1} \Delta_{1,L} e^{-x s_1 l_1 / p L}}$$
where \( l_N \) is the thickness of the layer \( N \) adjacent to the central medium, and \( \Delta_{j,L} \) the reflection coefficient of each layer \( j \). \( j \) becomes larger with increasing distance from the central medium such that,

\[
\Delta_{jL} = \frac{\Delta_{j,j+1} + \Delta_{j+1,L} e^{-xS_{j,j+1}/p_{j+1}}}{1 + \Delta_{j,j+1} \Delta_{j+1,L} e^{-xS_{j,j+1}/p_{j+1}}}
\]

In the non-retarded limit, the exponential term reduces to \( e^{-xL_{j-1}/l_{j}} \). This means that in the non-retarded limit the Hamaker coefficient of the multilayer system has a dependence on separation \( L \), depending on the relative thickness of the layers that make up the multilayer surfaces. This means that the van der Waals interaction of a multilayered system cannot generally be reduced to a single Hamaker constant independent of surface separation.

4.2.1.1.1 Van Der Waals Interaction of ALD Prepared Titania Surfaces

The titania surfaces used here were prepared by forming a titania film on a substrate, the goal of which was to produce smooth surfaces with the force properties of bulk titania. The above algorithm for layered systems was applied, by Drew Parsons, to calculate the retarded van der Waals force for titania surfaces that were prepared using a range of titania layer thicknesses.

The dielectric functions for each material were taken from the literature. Single UV oscillator models were applied to titania,\(^{64}\) silica\(^{113}\) and silicon\(^{121}\); a numerical dielectric function is used for water.\(^{122}\) In all cases, these models were derived from experimental data.

For these titania surfaces, the sub-layers (substrate) were fixed for a given experiment between surfaces. The flat substrate is a layer of titania on a 2 nm layer of silica on a semi-infinite silicon substrate. The spherical probe is a silica colloid with the titania layer deposited over the surface. The van der Waals energy for the retarded case is presented in Figure 4.7 for surfaces with titania layers of various thicknesses.
Figure 4.7: Flat plate retarded van der Waals interaction energies for various thicknesses of the titania layer are shown on a semi-log plot. This interaction describes the interaction between a titania layer on a 1.7 nm silica layer on a silicon wafer and a titania surface on a silica substrate in an aqueous medium. The negative interaction energy means that the force between the surfaces is attractive.

It was found that once the thickness of the titania layer exceeded 100 nm, the Hamaker coefficient of the multilayered titania surface was within 4% of that of pure titania surfaces at separations of less than 50 nm. As a result of this determination, from this point forward, all force measurements described were performed using 102 nm thick amorphous titania layers as the surfaces.

In order to simplify the calculation of the DLVO interaction, an effective non-retarded Hamaker constant that best fitted the full calculation was determined. The error introduced using this approach was small as can be seen from the comparison in Figure 4.8.
4.2.2 102 nm Amorphous Films

The amorphous titania surfaces produced at 80°C are very smooth even when the deposited layer is >100 nm (see Figure 3.8 of §3.2.2.1). As a result, they are ideal to use in surface force measurements, as the Van der Waals properties will be comparable to those of a pure titania surface without roughness dominating the forces measured between the surfaces.

4.2.2.1 10⁻⁴ M NaCl Solutions

Surface force measurements between 102 nm amorphous titania surfaces were performed over a range of pH in 10⁻⁴ M NaCl. It is expected that near the IEP (~pH 5), the diffuse double layer force should be negligible and the interactions between the surfaces will be dominated by the van der Waals force. Force curve measurements between titania surfaces at pH 5.2 are presented in Figure 4.9. On approach, an attractive force of increasing magnitude is evident from a separation of 35 nm, leading to a spring instability at a separation of ~18 nm where the gradient of the force exceeds the spring constant of the cantilever and the surfaces jump together. A comparison of
this interaction with the theoretical non-retarded van der Waals interaction between titania surfaces, leads to the conclusion that the observed attraction is due to dispersion forces and that the Hamaker constant employed (60.5 zJ) is appropriate.

Figure 4.9: The normalized force vs. separation measurement between a borosilicate sphere and silica flat coated with 102 nm of titania using ALD. The measurements were performed in the presence of $10^{-4}$ M NaCl with the pH adjusted to 5.2. The data is compared to the van der Waals equation for a sphere-flat system, with a Hamaker constant of 60.5 zJ.

Reducing the pH below the IEP should result in the titania developing a positive charge at the surface. Therefore, the interaction between the surfaces should exhibit a diffuse double layer repulsion. Figure 4.10 shows data acquired just below the IEP at pH 4.25.
Figure 4.10: The forces measured in the presence of $10^{-4}$ M NaCl, pH adjusted to 4.25. The data has been fitted using DLVO theory using a value of 60.5 zJ for the non-retarded Hamaker constant. The two theoretical fits represent the boundary conditions of constant charge and constant potential. The data was fitted using a surface potential of +12 mV, a surface charge of $+0.053 \text{ C m}^{-2}$ and a Debye length of 26 nm.

Compared to data acquired at the IEP, the attraction is observed at a smaller separation (25 nm compared with 40 nm); the spring instability also occurs at a smaller separation (12 nm compared to 18 nm) and the magnitude of the adhesion upon separation is less than half. This is all consistent with the surfaces acquiring a small positive charge. The data has been fitted using DLVO theory with a surface potential of +12 mV, surface charge of $+0.053 \text{ C m}^{-2}$ and the same Hamaker constant as in Figure 4.9.

Increasing the pH above the IEP will result in the surfaces acquiring a negative charge, the interaction will therefore exhibit a diffuse double layer repulsion. Figure 4.11 shows the interaction forces at pH 8.9, well above the IEP. At this pH the surfaces have acquired a substantial surface potential and the diffuse double layer repulsion should be considerable.
Figure 4.11: Measured surface forces between titania in the presence of $10^{-4}$ M NaCl at pH 8.9. The data has been fitted using DLVO theory with a surface potential of -66 mV, a surface charge of -0.38 Cm$^{-2}$, a Debye length of 29 nm and a Hamaker constant of 60.5 zJ.

The repulsion between the surfaces is apparent at separations in excess of 100 nm and increases exponentially as the separation is reduced up to contact. The data can be fitted at separations beyond 20 nm using the DLVO theory with a surface potential of -66 mV and a surface charge of -0.38 Cm$^{-2}$. However the DLVO theory predicts that at separations below 20 nm the attractive van der Waals component should become evident and the interaction forces should become attractive at a separation of ~10 nm. No evidence of a van der Waals attraction is seen in the measurement. Rather the repulsive force continues to increase up to contact and no adhesion is observed upon separation. This observation is surprising given the large magnitude of van der Waals forces observed at the IEP.

An investigation of the interaction forces over a range of pH values found evidence that the van der Waals attractive forces are only seen at pH values near the IEP. Figure 4.12 shows a family of force curves in $10^{-4}$ M NaCl over a range of pH values ranging from 4.3 to 8.9 on both approach and separation.
Figure 4.12: The measured surface forces on approach (top) and separation (bottom) between 102 nm titania layer surfaces in the presence of $10^{-4}$ M NaCl. At pH values close to the IEP an attraction is seen at small separations indicative of van der Waals attraction, however at pH values well above the IEP no attraction is seen between the surfaces even at small separations. Similarly upon separation an adhesion is observed near the IEP, whereas no adhesion is observed well above the IEP.
At the IEP, an attractive van der Waals curve is observed on approach while on retraction a large adhesion between the surfaces is seen. At pHs near the IEP, the forces follow that of the DLVO paradigm where the electrostatic repulsion dominates at large separations and the van der Waals attraction dominates at small separations. As the pH is increased well above the IEP, no van der Waals attraction is evident and no adhesion is observed.

4.2.2.2 $10^{-3} \text{ M NaCl}$

The interaction forces between titania surfaces were also measured at higher salt concentrations. A family of force curves is shown in Figure 4.13, for a NaCl concentration of $10^{-3} \text{ M}$, where the pH has been varied between 3.2 and 8.3.
Figure 4.13: The measured surface forces on approach (top) and separation (bottom) between titania surfaces in the presence of $10^{-3}$ M NaCl. At pH values close to the IEP an attraction is seen at small separations indicative of van der Waals attraction, however at pH values well above the IEP no attraction is seen between the surfaces even at small separations. Similarly, upon separation, an adhesion is observed near the IEP, whereas no adhesion is observed well above the IEP.
In this case it was found that the IEP is shifted to a lower value (pH 4.14) suggesting specific adsorption of chloride to the surface\textsuperscript{123}. A similar trend was observed as pH was varied. Near the IEP, the forces are described well by the DLVO paradigm, however, when the pH is raised substantially above the IEP the van der Waals force is no longer observed and the profile is repulsive at all separations.

4.2.2.3 High pH

What is the explanation for the absence of a van der Waals attraction at pHs far above the IEP? In this case, a direct effect of pH or electrolyte concentration on the van der Waals attraction can be ruled out because, whilst electrolyte can influence the magnitude of the dispersion forces, the changes in solution are insufficient to substantially reduce the attraction.

Force curves of this nature are commonly seen between silica surfaces\textsuperscript{113, 119} for which the widely accepted explanation is that the surfaces are strongly hydrated. The repulsion is thought to be the result of dehydrating the surfaces of water (hydration force) or ions adsorbed to the surface (secondary hydration force), which leads to an extra repulsion not accounted for in the DLVO theory that overcomes the van der Waals attraction at short range. While these hydration forces are strong, they decay exponentially with a decay length of ~0.25 nm\textsuperscript{124, 125}. As a result, such forces do not provide a reasonable explanation for the data obtained for titania surfaces, as the magnitude of the van der Waals attraction for titania surfaces across an aqueous environment is about 10 times larger than that between silica surfaces, evident by a comparison of the magnitude of the Hamaker constants for titania (~60 zJ) and silica (~10 zJ\textsuperscript{113}). Therefore, at separations beyond 5 nm, hydration forces are absent but the van der Waals attraction for titania is still substantial and should still be evident in force measurements. The masking of the van der Waals forces by surface roughness is unlikely, due to the extremely smooth ALD titania surfaces that have been used here. In addition, at the IEP, an attraction consistent with the full van der Waals interaction is observed. It should also be noted that the van der Waals interaction measured at the IEP, and the lack thereof at high pH, was measured regardless of the pH history of the surface. Therefore, two options remain: either an additional force that balances the van der Waals attraction arises when the surfaces acquire a charge or the van der Waals force is ‘switched off’ when the surfaces acquire a charge. No reasonable candidate for an additional force is known, therefore it should be considered how the interaction may be ‘switched off’.
As described above, changes in solution conditions cannot achieve the “switching off” of the van der Waals force. Another possibility is that the surfaces swell as they acquire a charge. This would effectively reduce the density of the titania surfaces and thus reduce the magnitude of the van der Waals attraction. Additionally, such swelling has the potential to extend the range of the hydration force.

For such swelling to explain the experimental data, it must be reversible, as the measurements are independent of the pH history of the surface. It would also occur rapidly as force data can be captured within a few minutes of exchanging the solutions, with no evidence of further changes in the data occurring after the initial measurements. Therefore, the swelling would have to be complete in a matter of minutes. If swelling does occur, it might be expected that the concentration of electrolyte in solution may influence the behavior of the surface through the adsorption of counter-ions. To investigate this, the forces at high pH were measured as a function of electrolyte concentration; this data is shown in Figure 4.14.

![Figure 4.14: Surface forces between ALD titania surfaces at high pH (8.8±0.8) as a function of electrolyte concentration. Only the approach data are shown, as the retraction force curves were identical to the approach data. As the concentration of the electrolyte is increased, the decay length of the forces decreases and the magnitude of the surface potential decreases. It is also noticeable that at this pH in all cases there is no significant van der Waals attraction in the force curves. This data was fitted with DLVO theory and the parameters are presented in Table 4.1.](image-url)
Table 4.1: DLVO fitting parameters of the force measurements between titania surfaces at a pH of (8.8±0.8) over a range of NaCl concentrations

<table>
<thead>
<tr>
<th>Electrolyte Concentration (M)</th>
<th>Surface Potential (mV)</th>
<th>Surface Charge (Cm⁻²)</th>
<th>Debye Length (nm)</th>
<th>Hamaker Constant (zJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-2}$</td>
<td>-27</td>
<td>-0.13</td>
<td>3.3</td>
<td>60.5</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>-22</td>
<td>-0.10</td>
<td>10.5</td>
<td>60.5</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>-60</td>
<td>-0.33</td>
<td>29</td>
<td>60.5</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>-71</td>
<td>-0.43</td>
<td>38</td>
<td>60.5</td>
</tr>
</tbody>
</table>

From these measurements it can be determined that, while the electrolyte concentration influences the Debye length and therefore the decay length of the diffuse double layer repulsion, no van der Waals interaction is evident across any of the concentrations studied.

4.2.2.3.1 Properties of ALD Titania

The titania surfaces employed are amorphous; this may promote swelling. While it would be interesting to examine crystalline films for comparison, they are insufficiently smooth for these kinds of measurements. In order to evaluate the swelling of the amorphous surfaces, nano-indentation was employed across a range of pH values. An example of these measurements is shown in Figure 4.15.
Figure 4.15: Nano-indentation measurements of load vs. penetration distance. Measurements were performed in $10^{-4}$ M at pH 4, 5, and 9. Each data point here represents the mean measurement of 25 separate indentation measurements with the error being one standard deviation. There is no discernable change in the measurements as the pH is changed.

An analysis of these measurements yields the reduced modulus ($E_r$) of the system, which is related to the Young’s modulus of the film ($E_f$) by

$$
\frac{1}{E_r} = \frac{(1 - \nu_f^2)}{E_f} + \frac{(1 - \nu_i^2)}{E_i}
$$

[2.6]

where, $E_i$ is the Young’s modulus of the indenter, $\nu_i$ is Poisson’s ratio for the indenter and $\nu_f$ is Poisson’s ratio for the film.76

In these experiments the indenter stiffness ($E_i = 1140$ GPa) is very much larger than the film stiffness, thus the reduced modulus will be only slightly less than the Young’s modulus of the film. From the experimental data a reduced modulus of 152 ± 15 GPa was determined which equates to a Young’s modulus for the film of $E_f = 159 ± 16$ GPa ($\nu_i = 0.07$, $\nu_f = 0.28$). No discernible difference in the Young’s modulus was observed over the pH range and this value agrees with literature values of the Young’s modulus.
for titania films.\textsuperscript{126} This can be taken as further evidence that the titania ALD films used in these experiments have typical material properties. So, while surface swelling is a possible explanation for the absence of a detectable van der Waals interaction between the surfaces at high pH, there is currently no evidence that this is the case. Neutron scattering experiments could possibly be performed in the future, to investigate whether the films swell. Such experiments should have the necessary sensitivity.

4.2.2.4 $0.1 \text{M NaCl}$

At high electrolyte concentrations (<0.1 M), the range of the repulsive diffuse double layer force becomes very short (Debye length is <1 nm), which results in this force being absent or unobservable. Two types of forces therefore dominate the interactions of these systems: the van der Waals force and the hydration forces. The van der Waals force will be present between the surfaces but the dispersion forces will also influence the ions near the surfaces and how they interact with the surfaces. These dispersion forces between surface and ion will depend strongly on the nature of the ion. Therefore, different ions would be expected to adsorb to the surfaces to different extents. The primary hydration force is the result of the hydration layer associated with the surface and the secondary hydration force is associated with the adsorption of ions to the surface. This means that the strength of the hydration forces will be strongly influenced by the nature of the ions present.

The very short range of these forces means that they cannot be distinguished by a typical force measurement. However, the combined influence of these forces should be evident in the measurements when the surfaces are pulled apart, as the net interaction will influence the strength of the adhesion between the surfaces. For example, a very strong hydration force counters the van der Waals force, which will result in a small adhesion. To examine what effect ions have on the interaction force, measurements were performed for a wide range of electrolytes. Both the force on approach and the adhesion upon separation were measured.

The force on approach was measured for a number of sodium electrolytes (Na\textsuperscript{+}) where the anion was varied. Some examples of these forces at pH 3 are shown in Figure 4.16.
Figure 4.16: Forces measured on approach between two ALD Titania surfaces in 0.1 M electrolyte solutions at pH 3.0. The anion was varied. Na$^+$ was the cation.

The forces shown here on approach are reproducible and are observed for a range of electrolytes and at both pH 3 and pH 9. It is apparent from these measurements, that at high electrolyte concentration there is a small attraction between the surfaces that appears to be mildly influenced by the type of anion or cation and the pH. For all of these systems, no repulsion is observed and the force is attractive at separations below 20 nm. These results indicate that a colloidal suspension of titania at these concentrations using these electrolytes will be unstable and flocculate regardless of the electrolyte present.

Examples of the adhesion between the titania surfaces after contact are shown in Figure 4.17 for a number of sodium electrolytes at pH 3.
Figure 4.17: Forces measured upon separation between two ALD Titania surfaces in 0.1 M electrolyte solutions at pH 3.0. The anion was varied. Na⁺ was the cation.

In all cases, a significant adhesion is observed between the surfaces, the magnitude of which is influenced by the type of anion present and the pH. For the measurements shown for pH 3, the strength of the adhesion from weakest to strongest is Cl⁻, I⁻, ClO₄⁻, Br⁻ then SCN⁻. This implies that at pH 3 the hydration forces is strongest for Cl⁻ and weakest for SCN⁻ as the hydration force will oppose the van der Waals attraction. However, the adhesion measurements are not as repeatable as the measurements upon approach. This is partly due to minor variations in the surface having an influence on the adhesion and partly because adhesion measurements are very susceptible to small amounts of contamination. For this reason many measurements were made on each system in order to obtain statistically significant results. In Figure 4.18, a histogram of the adhesion values for 0.1 M NaCl at pH 3 is shown as an example of the variation of the adhesive force between the surfaces over many measurements. The data reported in these histograms was obtained within a single experiment using the same surfaces.
Figure 4.18: Histograms of the adhesion force measured at pH 3 and pH 9 for a range of electrolytes. It is evident from the histograms that there is a substantial variation in adhesion from one measurement to the next even within a single set of experiments. Note that the result of one experiment is shown for illustration; repeat experiments gave different adhesion measurements.

After repeating this experiment multiple times at both pH 3 and pH 9 using new surfaces each time, it was not possible to obtain adhesion data that was consistent from one experiment to the next. The magnitude of the adhesion varied from one electrolyte to the next and there was no consistent order in the strength of the adhesion between electrolytes from one experiment to another. This variation is illustrated in the summary of the adhesive force obtained under the same conditions (0.1 M electrolyte) using different surfaces on different days shown in Figure 4.19. As a result, it is not possible to draw any conclusions about the effect the different electrolytes have on the hydration of the titania surfaces. This situation is attributed to extreme sensitivity of the measurements to low levels of contamination at the surfaces.
Figure 4.19: Comparison between mean adhesion values measured in 0.1 M electrolyte solution between ALD prepared titania surfaces in different experiments. Here the data point is the mean value and the error bars are set at one standard deviation. Note that the magnitude of the adhesion and the ordering of the electrolytes vary considerably between experiments. It should be noted that during these measurements, no obvious sign of contamination was observed in the experiment.
4.3 Summary

Force measurements between ALD prepared titania films have been performed in the presence of electrolyte solutions. Measurements between 80 nm thick anatase layers revealed that at the IEP, an attractive force is observed but it is not due to the van der Waals attraction. The origin of this force is unclear, however, it does not match the heterogeneous charge model and a DLVO fit would require the absence of dispersion forces.

Force measurements between 102 nm amorphous titania layers at the IEP revealed a van der Waals interaction well described by Lifshitz theory. At pHs near the IEP, the forces follow the DLVO paradigm, where an electrostatic repulsion occurs at large separation and the van der Waals attraction dominates at small separations. However, at high pH the forces are repulsive all the way into contact. There is no evidence of a van der Waals attraction. The explanations for these types of forces observed in the case of silica surfaces (roughness and surface hydration) are not applicable to the smooth titania surfaces employed here, which suggests that the earlier explanations for silica surfaces may be incorrect and that the phenomena may be applicable to a range of surfaces. Hence, a DLVO interpretation of the interaction forces between mineral surfaces may be profoundly incorrect at pH values well above the IEP. This apparent absence of the van der Waals interaction at high pH remains unresolved.

Surface force measurements in concentrated salt solutions revealed that as the surfaces approach, the force is attractive for a range of different electrolytes. The measurements of the adhesion upon separation were not reproducible from one experiment to the next, making it impossible to reach any conclusions about the specific effect of the ions on the interactions. This is attributed to the influence of very low levels of contamination on the surfaces and sensitivity of the measurements to the local roughness.
Chapter 5: Non-DLVO Interactions between Titania Surfaces: Influence of Water and Argon Plasma Cleaning

5.1 Introduction

In the previous chapter, surface force measurements between titania surfaces revealed that, at high pH, the van der Waals attraction is absent from the force profile. This chapter explores the hypothesis that the radio frequency discharge water plasma treatment that was employed to clean the surfaces prior to the measurements stimulates the formation of a gel layer at the surface and is therefore responsible for the non-DLVO repulsion seen at small separations. To study this possibility, surface force measurements between titania surfaces that have been treated using different techniques, were performed to determine the influence of the cleaning protocol on the interactions which occur between the surfaces.

Three cleaning treatments have been examined in this work: water plasma, argon plasma and ultra-violet irradiation. During water plasma treatment, the radio frequency field cleaves the bonds of the water molecule, forming hydrogen and hydroxyl radicals. Upon exposure to these radicals, organic contamination on the surface is decomposed and removed, cleaning the surface. Additionally, the reaction of the radicals with the surface will result in the modification of the chemical groups that terminate the surface, which may change the surface wettability and charging properties. The extent of the modification of the surface is dependent on the duration and intensity of the plasma exposure. When treated with water plasma the surface is exposed to hydroxyl radicals and therefore the number density of titanol groups on the surface is expected to increase. As these groups are acidic in aqueous solution this will lead to an increase in the magnitude of the negative charge when the surface is immersed in aqueous solution. If the modification of the surface by the radicals is responsible for the force profiles that has been observed, using argon plasma instead of the water plasma should change the force profile as the hydrogen/hydroxyl radicals will not be present during treatment. UV irradiation which has been observed to remove
organic contamination from titania surfaces and to produce hydrophilic surfaces,\textsuperscript{128} will also be investigated as well.

5.2 Results and Discussion

Water plasma treatment of the surfaces involved exposing them to plasma generated in an in-house RF plasma reactor. The reactor chamber was filled with water vapour at low pressure and the plasma was generated using 10 W of power and a frequency of 130 MHz for a period of 30 s. Argon plasma treatment used the same plasma reactor that was used for water plasma treatments. In order to ensure the exclusion of water during treatment the system was purged multiple times with argon gas prior to plasma generation. Surfaces were cleaned with a 10 W plasma, generated using a frequency of 130 MHz for 30 s.

Ultraviolet irradiation of the surface was achieved using a UV light box, containing 16 NEC FL8BL 8W lamps in a cylindrical formation. During treatment, surfaces were enclosed in a metal container with a quartz lid to prevent dust settling on the surfaces. The surfaces were exposed to the UV light for a period of 48 hours. The treatment was performed in a humid atmosphere, achieved by placing a drop of Milli-Q water (conductivity \(\sim 18.2\) M\(\Omega\)) inside the metal container during treatment.

5.2.1 Contact Angle Measurements

Titania surfaces exposed to air will quickly acquire a layer of contamination. Typically, this will lower the surface energy and lead to an increase in the contact angle of water with the surface. Therefore, the efficiency of the cleaning treatments can be monitored using contact angle measurements. The measured advancing and receding contact angles of water on titania surfaces treated with water plasma, argon plasma or UV irradiation are summarized in Table 5.1.
The advancing contact angle of an untreated titania surface was measured to be 74 ± 4°. The cleaning treatment caused a reduction in the advancing contact angle to a value of less than 10° in all cases, indicating that the surface contamination had been removed.

5.2.2 Determination of Roughness

Changes in the surface morphology due to the cleaning treatments were determined by performing tapping mode images of the argon plasma and water plasma treated surfaces. These images are presented in Figure 5.1. The argon plasma treated surfaces have a roughness of 0.62 nm RMS over a 1000 nm × 1000 nm area and the roughness of water plasma treated surfaces over the same area was 0.64 nm RMS. As the difference between these measures is not significant, the conclusion reached is that the surface roughness is not dependent on the type of plasma treatment. No attempts to image surfaces that had not been submitted to a cleaning treatment were made, as the presence of contaminants on the surface will influence the image obtained.

### Table 5.1: Measured contact angles of water of titania surfaces

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Power</th>
<th>Duration</th>
<th>Advancing Contact Angle (°)</th>
<th>Receding Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td></td>
<td></td>
<td>74 ± 4</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Argon plasma</td>
<td>10 W</td>
<td>30 s</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>H2O plasma</td>
<td>10 W</td>
<td>30 s</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>UV light</td>
<td></td>
<td>48 hours</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>
Figure 5.1: Tapping Mode AFM images of argon plasma cleaned (top) and water plasma cleaned (bottom) ALD titania surfaces. The surface roughness over an area of 1000 nm × 1000 nm was determined to be 0.62 nm RMS for the argon plasma treated surface and 0.64 nm RMS for the water plasma treated surface. The scale bar in each image is 400 nm long.

To evaluate any influence that the solvent may have on the surface roughness such as causing the surface to swell, a water plasma treated surface was imaged under water at both neutral pH and at pH 9 where the repulsive forces were observed in the force measurements. These images are presented in Figure 5.2.
Figure 5.2: ScanAsyst Mode AFM image of a water plasma cleaned ALD titania surface immersed in water (top) and water adjusted to pH 9 (bottom). The RMS surface roughness over an area of 1000 nm × 1000 nm was determined to be 0.67 nm in water and 0.7 nm at pH 9. The same surface imaged in air gave an RMS roughness of 0.68 nm over the same area. The scale bar in the image is 400 nm long.

It was found that the image of the surface under water exhibited the same features as the image in air and that the surface roughness was unchanged. This suggests that the solvent does not significantly alter the surface morphology. Upon increasing the pH to 9, there was no significant change to the surface, indicating that increasing the pH does not change the surface morphology.
5.2.3 Surface force measurements

Force measurements made between surfaces cleaned with argon plasma are presented in Figure 5.3. The measurements were obtained in $10^{-4}$ M NaCl and the pH was adjusted by addition HCl or NaOH.

![Figure 5.3](image_url)

Figure 5.3: Surface Force measurements between titania surfaces cleaned with argon plasma. Measurements were made in an aqueous solution of $10^{-4}$ M NaCl with pH adjustment. Force measurements obtained on approach are presented at the top and upon separation are on the bottom.
At pH 6.0 a repulsion is observed from a separation of ~70 nm, which increases exponentially up to ~10 nm where the force begins to become attractive. Upon separation, the surfaces adhere. Increasing the pH to 7 leads to an increase in the magnitude of the diffuse double layer repulsion. The repulsion is apparent at separations of 80 nm and increases exponentially as separation is reduced. A small adhesion is observed when the surfaces are separated. When the pH is increased to 9, the magnitude of the diffuse double layer repulsion increases further while the decay length of the force decreases. This decrease is caused by the increased ionic strength of the pH 9 solution compared with pH 7, associated with the increased quantity of NaOH required to adjust the pH to 9. No adhesion occurs at pH 9. These measurements were fitted using DLVO theory. Examples of the fits for pH 5.5 and pH 9 are shown in Figure 5.4.
Figure 5.4: Surface force measurements between titania surfaces cleaned using argon plasma. Measurements were performed in an aqueous solution of $10^{-4}$ M NaCl with the pH adjusted to pH 5.5 (top) and pH 9 (bottom). The data measured on approach was fitted with the DLVO theory, for the constant charge (solid line) and constant potential (dotted line) boundary conditions, using a Debye length of 29 nm, a surface potential of -34 mV or a surface charge of -0.16 C/m$^2$ for pH 5.5 and a Debye length of 29 nm, a surface potential of -61 mV or a surface charge of -0.34 C/m$^2$ for pH 9. In both cases, a non-retarded Hamaker constant of 60.5 zJ$^{94}$ was used.
Under the DLVO theory paradigm the van der Waals attraction should be observed at small separation at all values of the pH studied here. In the case of measurements near the IEP, the measured force is well described by DLVO theory at all separations, where the limits are defined by the constant charge and constant potential boundary conditions. At a pH of 7 or higher, the surface interaction can be described by the diffuse double layer force alone, as the attractive component of the DLVO theory is not observed; instead the force remains repulsive up until contact. For comparison, an example of the surface force measurements between water plasma cleaned titania surfaces in aqueous $10^{-4}$ M NaCl adjusted for pH, is presented in Figure 5.5.

![Figure 5.5: Surface Force measurements between titania surfaces cleaned with water plasma (data from §4.2.2.1). Measurements were made in a solution of $10^{-4}$ M NaCl with the pH adjusted to 5.5 and 9. The data measured on approach was fitted with the DLVO theory, for the constant charge (solid) and constant potential (dotted) boundary conditions. Debye lengths of 29 nm and 24 nm were used in the DLVO fits for pH 5.5 and 9 respectively.](image)

The same general features are observed in the force measurements of the water plasma treated surfaces as those seen in the argon plasma treated case, though the magnitude of the electrostatic double layer repulsion differs. For water plasma cleaned surfaces at pH 5.5 the force is attractive from a separation of 15 nm which leads to a spring instability at ~10 nm, where the gradient of the force exceeds the spring constant of the cantilever and the surfaces jump into contact. This attraction was fitted by a van der Waals
interaction with a Hamaker constant of 60.5 zJ. Upon separation, the surfaces adhere. At high pH the force is repulsive at all separations, no attraction is observed and there is no adhesion. In both cases, an additional repulsion occurs once the pH is greater than 7, preventing the van der Waals attraction from being seen. Since the additional repulsion occurs for both water plasma and argon plasma cleaned surfaces, the conclusion reached is that the water plasma treatment of the surface is not the cause of the observed repulsion at short range.

A summary of the surface charge and surface potential parameters for DLVO fits are provided in Table 5.2. In all cases, the fitted Debye length was between 19 nm and 31 nm and a Hamaker constant of 60.5 zJ was used. The surface charge and surface potential is greater in magnitude for the surfaces treated with water plasma.

Table 5.2: Fitted DLVO surface potential and surface change values for treated titania surfaces

<table>
<thead>
<tr>
<th>pH</th>
<th>Argon Plasma Cleaned</th>
<th>Water Plasma Cleaned</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface Potential (mV)</td>
<td>Surface Charge (C/m²)</td>
</tr>
<tr>
<td>5.5</td>
<td>-34</td>
<td>-0.16</td>
</tr>
<tr>
<td>6.5</td>
<td>-57</td>
<td>-0.30</td>
</tr>
<tr>
<td>9</td>
<td>-61</td>
<td>-0.34</td>
</tr>
</tbody>
</table>
Figure 5.6: A comparison of surface force measurements between titania surfaces which have been cleaned using argon plasma or water plasma. The solution was $10^{-4}$ M NaCl with the pH adjusted to a value of 4.

Measurements of the surface force at pH 4 were also undertaken; these are presented in Figure 5.6. For the argon plasma treated surface, a repulsion is observed from a separation of ~80 nm, which increases exponentially up to ~15 nm where the force begins to become attractive, which leads to a spring instability at ~8 nm. As the surfaces are separated, the surfaces adhere. This force measurement was fitted using the DLVO theory, with a Hamaker constant of 60.5 zJ, a surface potential of 22 mV and a Debye length of 21 nm.

After the surface has been cleaned with water plasma, the forces are quite different. An attractive force is observed from a separation of 150 nm, which leads to a spring instability at 25 nm. The magnitude of this force is much larger than the predicted van der Waals attraction and a large magnitude adhesion is measured upon separation, see Figure 5.7. It was also found that this attraction did not follow an inverse power law such as that seen for the van der Waals force. Instead, the attraction increases exponentially, which is indicative of an electrostatic type force (see Figure 5.8).
Figure 5.7: Force measurement between water plasma cleaned titania surfaces in $10^{-4}$ M NaCl at pH 4 and the prediction of the van der Waals force for titania surfaces across water.

Figure 5.8: Force measurement between water plasma cleaned titania surfaces in $10^{-4}$ M NaCl at pH 4 and a fit of heterogeneously charged surface interaction. Decay length of the attraction was determined to be 52 nm.

Attempts to describe the interaction with a double layer force, where the surfaces have equal but opposite charges, results in a fitted surface potential of $\sim$60 mV, which is not
credible. Another possible theory which could explain the experimental measurements is the heterogeneously charged surfaces model, such as those described by Miklavic et al.\textsuperscript{129} and Kékicheff et al.\textsuperscript{12}. Both of these models predict an exponential form with an upper limit for the decay length of half the Debye length. The decay lengths observed in these measurements exceed this, being close to the actual Debye length of the solution; therefore the attraction cannot be explained using these models.

Normally an attractive force of this range would be explained using a hydrophobic force. However, this explanation seems unlikely in this case, as the surfaces are hydrophilic, as demonstrated by the contact angle measurements. The surprising range and strength of the observed attraction between hydrophilic surfaces remains unexplained. Upon cycling the pH, between pH 4 and higher pH values, the forces were repeatable. That is, they did not exhibit any of the variability one might expect if bubbles are present on the surface, as sometimes occurs for hydrophobic surfaces.

5.2.3.1 \textit{UV Irradiation}

In the case of surfaces treated with UV irradiation, an attraction between the surfaces was observed on approach and upon separation a large adhesion was observed. The adhesion was large enough that the range of the piezoelectric drive (3.5 $\mu$m) of the E-type scanner used in the AFM was not sufficient to separate the surfaces. The magnitude of this force made the observation of any other forces impossible. The force measurements indicate that the UV treatment of the surface failed to completely clean the surface, as the forces found were characteristic of some reports of the long-range hydrophobic attraction which occurs between hydrophobic surfaces\textsuperscript{11, 23, 24, 27, 28} and can be attributed to nanobubbles on the surfaces.\textsuperscript{130, 131}

5.2.4 \textit{X-Ray Photoelectron Spectroscopy Measurements (XPS)}

Comparison of the magnitude of the surface charge obtained from the fitting of the force data indicates that the water plasma cleaned surface is more highly charged. XPS was used to investigate differences in the elemental composition of the surfaces following argon and water plasma cleaning. These measurements, along with the analysis, were performed by Dr Drew Evans of the Mawson Institute at the University of South Australia in Mawson Lakes, Australia.
The surfaces were determined to contain titanium, oxygen and carbon atoms. A better understanding of the species present at the surface was gained by studying the oxygen peak in more detail. Fine scans of the O 1s peaks for argon plasma and water plasma treated surfaces (see Figure 5.9) were studied to determine which oxygen species are present on the surface. Deconvolution of the fine scans of the O 1s show the presence of O$^2-$, OH$^-$ and H$_2$O on both surfaces.

Figure 5.9: Fine scans of XPS measurements of oxygen peaks for argon plasma (top) and water plasma (bottom) treated titania surfaces.
Table 5.3: Percentage of elements in titania film determined using XPS for argon and water treated titania surfaces.

<table>
<thead>
<tr>
<th>Element</th>
<th>% Present after Argon Plasma Treatment</th>
<th>% Present after water Plasma Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>20.1</td>
<td>18.4</td>
</tr>
<tr>
<td>C</td>
<td>20.8</td>
<td>24.8</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>56.2</td>
<td>38.6</td>
</tr>
<tr>
<td>OH$^{-}$</td>
<td>1.5</td>
<td>14.8</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.3</td>
<td>3.4</td>
</tr>
</tbody>
</table>

For water plasma treated surfaces, the ratio of Ti and O$^{2-}$ indicates that the film contains nearly stoichiometric TiO$_2$, while argon plasma treated surfaces are O$^{2-}$ rich. A summary of the XPS analysis can be found in Table 5.3. Argon plasma cleaned titania surfaces have been examined before by Jun et al.$^{132}$ using anatase powder produced in a sol-gel process. While they determined that argon plasma treatment can change the oxidation states of both Ti and O, it does not explain the O$^{2-}$ rich surface that is observed these ALD titania surfaces. This suggests that the excess O$^{2-}$ may be due to unreacted propoxide remaining in the surface following the ALD process. A significant amount of propoxide left in the titania would diminish the dispersion forces, but in the surface force measurements good agreement is achieved with the theoretical calculated van der Waals attraction at the IEP. In fact, analysis of the XPS fine scans for titanium 2p and carbon 1s reveal that the titanium exists solely as Ti$^{4+}$, while approximately 12% of the observed carbon is bonded to oxygen. Taking into account that propoxide contains 3 carbon atoms per molecule and the total carbon atomic percentage in the ALD films is of the order of 20 to 25%, the unreacted propoxide makes up less than 10% of the final film composition (based on atomic percentages). Our conclusion is that if the excess O$^{2-}$ is due to propoxide it is confined near the surface, which would explain the observed van der Waals forces and the O$^{2-}$ rich XPS measurements. Given that the total amount of oxygen in the surface is approximately the same for either plasma treatment, it is possible that the oxygen groups on the surface are converted by the plasma treatment. The conclusion is that the water plasma converts O$^{2-}$ into OH$^{-}$ via reaction with hydrogen radicals, while argon plasma converts OH$^{-}$ groups to O$^{2-}$. The XPS measurements show that water plasma treated surfaces have a greater
concentration of OH groups. This is consistent with the higher magnitude surface charge for water plasma treated surfaces obtained from DLVO fits of the forces.

The surface forces measured between titania surfaces are consistent with the surface forces measured between silica surfaces, meaning that in both cases the van der Waals attraction is not apparent. This implies an additional non-DLVO repulsion at small separations. Hydration forces are an obvious candidate, but they are of insufficient range to explain the results for the titania system.\textsuperscript{17,21,133} When combined with surface roughness this could explain the results for silica surfaces as the magnitude of the van der Waals force is relatively small.\textsuperscript{93} However, this is not the case for titania surfaces, which have a large van der Waals attraction; thus the nature of the interaction at high pH remains unexplained. The possibility remains that the additional repulsion present between silica surfaces and titania surfaces has the same origin.

It is still left to determine if this additional non-DLVO repulsion is a unique feature of titania and silica surfaces or if the same phenomena is observed for other oxide surfaces and therefore requires reconsideration of the application of DLVO theory to the understanding of surface forces between mineral oxide surfaces at high pH.

### 5.3 Summary

It was determined that the measured forces between both water plasma and argon plasma treated surfaces can be fitted by DLVO theory at pH values near the IEP. XPS analysis reveals that the use of water plasma generates a surface with greater relative levels of surface hydroxyl groups than argon plasma treatment. The relatively titanol rich surface provides a greater number of surface charge sites leading to an increase in the magnitude of the electrostatic double-layer repulsive surface forces. For both cleaning methods, no van der Waals attraction is observed at high pH, due to the presence of an additional non-DLVO repulsive force. The conclusion reached is that the non-DLVO repulsion does not arise as an artifact of water plasma treatment; the range of the additional repulsion is too large to be attributed to surface roughness or hydration forces and therefore its origin remains unresolved.
Chapter 6: Force Measurements between Titania Surfaces in the presence of Surfactants

6.1 Introduction

Surfactants adsorb to surfaces and in doing so alter their properties. Therefore the adsorption of surfactants at the solid-water interface finds important application in flotation,\textsuperscript{134} detergency,\textsuperscript{135} wettability and surface passivation.\textsuperscript{136} The surface properties are critically dependent upon the amount of surfactant adsorbed to the surface. Similarly, the surface concentration of surfactant influences the interaction forces. Indeed, depending on the concentration, the forces between surfaces can change from attractive to repulsive.\textsuperscript{82} Therefore, surfactants can act as either a stabilizing or destabilizing influence on colloidal systems, depending on the type and amount of surfactant present.

Charged sites present on the surface influence the adsorption of an ionic surfactant to a hydrophilic surface. Ionic surfactants are electrostatically attracted to charged sites of the opposite sign. The adsorption of surfactants and their influence on the surface forces between silica\textsuperscript{82, 137} and mica\textsuperscript{138, 139} surfaces has been investigated previously. At low levels of surfactant adsorption, adsorbed surfactant molecules neutralize surface charge and produce hydrophobic surfaces. This leads to attractive hydrophobic forces between surfaces. At higher levels of adsorption, surfactant molecules form aggregates and bilayered structures on the surfaces\textsuperscript{140} that lead to surfaces of like charge and a repulsion between the surfaces. It is notable that in previous studies of the surface forces measured between silica surfaces\textsuperscript{82} or between mica surfaces\textsuperscript{138} the dispersion forces observed are less than expected from Lifshitz theory.

An examination of the forces between titania surfaces in the presence of surfactant provides a means to assess whether they are described well by DLVO theory. The readily accessible isoelectric point (IEP) of titania allows the investigation of the adsorption of surfactant and surface forces to both the positively charged titania surface at low pH as well as the negatively charged titania surface at high pH. Therefore it is informative to investigate the adsorption of both anionic and cationic surfactants to
titania surfaces. Using titania prepared using Atomic Layer Deposition (ALD) provides the benefit of employing surfaces with near identical properties for both surface force measurements and adsorption studies, allowing direct comparison of the results.

In this chapter, optical reflectometry (OR) was used to measure the adsorption isotherms of surfactants to titania surfaces. The OR technique requires control of the optical properties of the surfaces which is achieved by controlling the thickness of the oxide layers on the surface. ALD allows the thickness of a titania layer to be controlled in order to produce the required optical properties for the OR instrument. The two surfactants used in this work are the cationic surfactant cetyltrimethylammonium bromide (CTAB) and the anionic surfactant sodium dodecyl sulphate (SDS). These were chosen as they are often chosen as model cationic \textsuperscript{80, 141-143} and anionic \textsuperscript{78, 144-146} surfactants.

The adsorption of CTAB to ALD prepared titania surfaces is examined in §6.2.1. The adsorption isotherms were measured and are used to inform the interpretation of surface forces measurements between titania surfaces immersed in CTAB solutions and assess whether the forces are well described by DLVO theory. Attempts were made to examine the adsorption of the anionic surfactant SDS to the titania surfaces; these are described in §6.2.2.

**6.2 Results and Discussion**

**6.2.1 Cetyltrimethylammonium Bromide (CTAB)**

**6.2.1.1 Surfactant Adsorption**

Typical Optical Reflectometry (OR) data for the adsorption of CTAB in the presence of an electrolyte is presented in Figure 6.1. For the arrangement employed in these experiments the sensitivity parameter to convert the p/s intensity ratio to surface excess was $-0.024 \text{ m}^2/\text{mg}$. This parameter is calculated using a Fresnel Optical model of the surface with a $\text{dn}/\text{dC}$ value for CTAB of 0.134 $\text{ cm}^3/\text{g}$, an incidence angle of 71° and a refractive index for amorphous titania of 2.493. The solvent used was aqueous $10^{-2} \text{ M NaBr}$, with the pH adjusted to 10. The CTAB concentration was $5\times10^{-3} \text{ M}$. The general form of the data was consistent for all pH, surfactant and electrolyte concentrations.
Figure 6.1: An example of typical data showing adsorption and desorption of CTAB to titania, measured by optical reflectometry. CTAB solution ($5 \times 10^{-3}$ M) is passed into the cell at approximately 600 s. The equilibrium surface excess is obtained before rinsing the cell with the solvent ($10^{-2}$ M NaBr) at approximately 2350 s.

In the first stage of the experiment, a baseline was measured for the solvent. This was followed by introduction of the surfactant at approximately 600 s, which results in a measurable surface excess. After equilibrium is achieved, the surface excess is stable while the flow of surfactant solution is maintained. When only the solvent is introduced into the cell (~2350s), desorption of the surfactant is rapid and complete.

6.2.1.2 Absorption Isotherms

Adsorption isotherms for CTAB in aqueous $10^{-2}$ M NaBr and $10^{-3}$ M NaBr solutions at a range of pH produced from data such as that shown in Figure 6.1 are presented in Figure 6.2. Presenting the isotherms together allows for the influence of electrolyte to be clearly seen. Dashed lines are presented only as a guide for the eye. The measurements for the $10^{-2}$ M NaBr isotherm were performed by Shaun Howard of the Department of Applied Mathematics at the ANU and the $10^{-3}$ M NaBr isotherm measurements were performed by Bo Wu of the Department of Chemical Physics at the University of Science and Technology of China. OR measurements were performed using an instrument that was custom built by Shaun Howard in the Department of Applied Mathematics.\textsuperscript{80}
Figure 6.2: Isotherms of CTAB on titania over a range of pH in $10^{-2}$ M NaBr, (filled symbols) and $10^{-3}$ M NaBr (open symbols), presented on a log-log scale. Where error bars are not visible, the error bars are less than the size of the symbol. The approximate value of the pH dependent common intersection points for pH 2, pH 4 and pH 6 are marked with grey squares. Dashed lines are provided as a guide to the eye only.

The general form of the isotherms in all cases is that adsorption increases with increasing concentration of CTAB up until the maximal coverage concentration (mcc) is reached, then adsorption becomes constant. The surface excess of CTAB increases with increasing pH. This reflects the increasing density of negatively charged sites on the titania surface with increasing pH. Titania has an isoelectric point (IEP) at a pH of 5. Above this pH, the surface is negatively charged, thus cationic CTA$^+$ will adsorb to the surface electrostatically. These electrostatically bound molecules then cooperatively interact with other CTAB molecules due to the hydrophobicity of the alkane chain, ultimately leading to a large adsorption of CTAB on the surface. Below the IEP, the
The surface is positively charged which will electrostatically repel CTA\(^+\). Thus below the IEP, negligible adsorption is expected. However, the isotherms (Figure 6.2) show that a significant amount of CTAB adsors to titania below the IEP. This may be due to dispersion forces between the hydrocarbon chain of the CTAB molecule and the surface, which will promote adsorption. For titania these forces will be larger than for silica or mica.

The titania surface has three different titanol groups. The infrared spectra reveals 3 bands at 3715 cm\(^{-1}\), 3675 cm\(^{-1}\) and 3640 cm\(^{-1}\) which are assigned to terminal (basic); terminal, (neutral/acidic); and bridging, (weakly acidic) functional groups respectively.\(^{148}\) The concentration of each type of bridging functional group varies with the degree and type of crystallinity and the surface preparation technique, therefore this will also influence the IEP. Overall, the surface will be positively charged below the IEP, but the CTAB will still bind to the negatively charged sites and these few bound molecules act as an anchor for further adsorption by hydrophobic interactions.

6.2.1.3 Common Intersection Point (CIP)

Adsorption is controlled by a combination of electrostatic interactions and hydrophobic interactions with some influence of dispersion forces. The electrostatic interactions are strongly influenced by the solution conditions. When the pH is below the IEP, the surface is positively charged as is the surfactant, so the electrostatics are repulsive; above the IEP the electrostatic interaction between the surface and the surfactant is attractive. The CIP or common intersection point is the point on an isotherm that does not change with electrolyte concentration.\(^{149}\) The CIP can be obtained by obtaining isotherms at different concentration of a particular electrolyte. For ionic surfactants at a given surfactant concentration, adsorption is higher at low salt concentrations below the CIP, whereas above the CIP, adsorption is higher at high salt concentrations. At surfactant concentrations below the CIP, electrostatics enhance adsorption and at surfactant concentrations above the CIP, electrostatic interactions oppose adsorption. Above the Common intersection Point (CIP) the surface coverage is sufficient to produce charge overcompensation.\(^{149}\) That is, the initially negatively charged surfaces acquire a net positive charge due to surfactant adsorption. This results from hydrophobic interactions dominating unfavorable electrostatic interactions between the like charged headgroups of the surfactant. It is the point where the surfactant begins to form bilayered aggregates on the surface.\(^{80}\) For CTAB adsorbing to titania surfaces in
NaBr we find that the CIP at pH 2 is \(6\times10^{-4}\) M, at pH 4 is \(4.2\times10^{-4}\) M and at pH 6 is \(3.6\times10^{-4}\) M. As the electrolyte concentration is increased, the maximal coverage concentration (mcc) is decreased. Electrolyte screens the repulsive head-group interactions between the surfactants in the admicelles. Therefore, an increase in electrolyte concentration leads to the maximal surface coverage being achieved at lower concentrations.

### 6.2.1.4 Comparison of the Adsorption Isotherm with Previous Studies

The adsorption isotherm obtained in this work at pH 10 and \(10^{-3}\) M NaBr is compared with the previous studies of Stratton et al.\(^{150}\) and Li et al.\(^{151}\) at pH 10 in Figure 6.3.

In Figure 6.3 we compare the adsorption isotherm obtained in our work at pH 10 and \(10^{-3}\) M NaBr with previous studies of Stratton et al.\(^{150}\) and Li et al.\(^{151}\) at pH 10. Stratton et al determined the surface excess spectroscopically at pH 10.5 and reported it in \(\mu\text{mol/m}^2\). Conversion was achieved by converting moles to mass using the molecular weight of CTAB. Li et al measured the surface concentration using ATR spectroscopy.

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Figure 6.3: A comparison of the CTAB adsorption Isotherm for the ALD prepared titania and examples from literature for a pH of \(\sim10.2\). Our Measurements are compared to those made by Stratton-Crawley et al.\(^{150}\) and Li et al.\(^{151}\)
looking at the 2850 cm$^{-1}$ absorption peak. Data was presented in units of molecules/nm$^2$. This was converted to moles using Avogadro’s number then to mass using the molecular weight of CTAB. Measurements were made at a pH of 10.3.

Excellent agreement is found with Li et al. over the whole concentration range. Below 4×10$^{-3}$ M CTAB there is agreement with Stratton et al, but at higher concentrations the values reported by Stratton et al are greater by up to 30%. This may be due to a difference in electrolyte concentration, the value of which was not reported by Stratton et al.

6.2.1.5 Slow Adsorption Kinetics

Previous studies of the adsorption kinetics of CTAB to silica surfaces found very slow adsorption kinetics at concentrations below the maximal coverage concentration (mcc)$^{152}$. Howard et al.$^{153}$ explored extremely slow adsorption by utilizing a series of sequentially increasing and decreasing concentrations of CTAB to create a “ziggurat” type plot of CTAB adsorption to a silica surface. Hysteresis in the ziggurat plot is evidence of kinetic trapping or jamming of the adsorption process. Shaun Howard performed a ziggurat experiment to examine slow adsorption on titania surfaces to test whether the phenomena is influenced by the nature of the substrate. The experiment was performed in 10$^{-2}$ M NaBr electrolyte at pH 9.5 and is presented in Figure 6.4.
Figure 6.4: A Ziggurat Type experiment to examine the slow adsorption of CTAB to titania in the presence of $10^{-2}$ M NaBr, at pH 9.5. A stable baseline is obtained before the surface excess of a series of increasing then decreasing concentrations of CTAB is measured. The concentration range of the CTAB solutions used was $10^{-5}$ M up to $10^{-4}$ M. Letters show solution concentration as indicated in the legend. Dashed lines are presented as visual guides to indicate the hysteresis of the adsorption of CTAB during the up and down cycles. The hysteresis is due to slow adsorption during the increasing concentration branch, (LHS) of the plot, which prevents equilibrium being reached within the timescale of the measurement.

During the experiment, CTAB solutions of $10^{-5}$ M, $3 \times 10^{-5}$ M, $5 \times 10^{-5}$ M, $7 \times 10^{-5}$ M and $10^{-4}$ M solutions were passed into the OR cell in order of increasing CTAB concentration, then the same solutions were introduced in order of decreasing concentration. Each concentration was maintained for more than 100 seconds, a period of time that would result in full equilibration above the critical micelle concentration (cmc). It is evident that the ziggurat plot shows significant hysteresis. This indicates that slow adsorption kinetics are observed when a titania surface is employed as previously seen for silica surfaces. This is consistent with the previous interpretation\textsuperscript{153, 154} whereby, slow adsorption kinetics results from the formation of aggregates at the surface, rather than any particular property of the surface. Below the cmc, these aggregates are necessarily formed by addition of a monomer one at a time to the aggregate structure. As adsorption progresses, this process becomes more hindered as a
greater number of adsorbed monomers must rearrange to accommodate an additional monomer. Above the cmc, fast kinetics are observed as micelles are now present in solution and they are able to adsorb directly to the surface (and then undergo rearrangements). This also supports the theory that equilibration of surfactant solutions in bulk proceeds to equilibrium via the collision of micelles rather than by the migration of monomers into micelles.\textsuperscript{155}

6.2.1.6 Surface Forces

The surface forces between titania surfaces in the presence of CTAB were measured. Our previous studies have shown that the kinetics of surfactant adsorption at concentrations below the mcc can be very slow unless achieved by dilution.\textsuperscript{153} In order to rapidly obtain equilibrium, solutions of CTAB were injected into the AFM fluid cell in decreasing order of concentration, ensuring that the first solution is above the mcc. Three concentrations of CTAB were chosen for each concentration of salt; one above the maximal coverage concentration (mcc); one just below the mcc; and one well below the mcc. For a NaBr concentration of $10^{-2}$ M the CTAB concentrations examined were $10^{-5}$ M, $10^{-4}$ M and $10^{-3}$ M. For $10^{-3}$ M NaBr, $10^{-5}$ M, $5\times10^{-4}$ M and $10^{-3}$ M CTAB concentrations were investigated.

In order to interpret the force data, an understanding of the nature of the surface in particular the level of surfactant adsorption, is needed. Therefore the OR data will be used in interpreting the data obtained in surface force measurements, however the surfaces used in these two studies are not identical. In the surface force studies titania films that were in excess of 100 nm thick were used, whereas films of only 5 nm thickness were employed in the OR measurements. There are technical reasons for the differences. The quality of the OR data is dependent upon the optical properties of the surface. Modeling the optical properties for a silicon wafer with various thicknesses of silicon oxide and titania films was performed in order to determine an arrangement that would provide high sensitivity, yet be robust to small inaccuracies in the incidence angle and film thickness. It was found that a thin layer of titania (~5 nm) was most suitable and moreover a thick layer such as that used in the force measurements would not work well. A thin titania layer could have been chosen for the force measurements, but Lifshitz calculations for a layered system show that this would reduce the dispersion interaction for the system from the value for a bulk phase by more than a factor of two\textsuperscript{94} and one of the interests of these experiments was in seeing the impact of a potentially...
large dispersion force. So is using the data from the OR measurements to interpret the force measurements justifiable? At low surfactant concentrations, where there is low surfactant coverage it is likely that an increased dispersion force would lead to an increase in surface excess, but at higher concentrations and higher levels of surfactant adsorption we expect that the dominance of hydrophobic interactions in the adsorption process\textsuperscript{140} will ensure that the difference in surfactant adsorption is minimal. Most of the measurements presented here relate to high surface coverage; as such, it is reasonable to use the OR data to interpret the force measurements.

On the basis of the electrostatics, the results of the surface force measurements can be divided into three groups: 1) below the IEP; 2) above the IEP and at low surfactant concentration – near or below the Common Intersection Point (CIP); and 3) above both the IEP and the CIP. Note that below the CIP, adsorption is promoted by electrostatic interactions and above the CIP adsorption is opposed by electrostatic interactions between the surfactant headgroups and driven by hydrophobic interactions\textsuperscript{156}.

6.2.1.7 Below the IEP

At a pH below the IEP (~pH 5\textsuperscript{94}) the titanium dioxide surface will have a positive charge. It is therefore expected that a negligible amount of the cationic surfactant CTAB would absorb to the surface. However, as discussed above, the OR data reveals that at both pH 2 and pH 4 significant amounts of surfactant are adsorbed to the surface.

1) Below the IEP (pH 2 and pH 4)

At pH 2 and 10\textsuperscript{-2} M NaBr, the force is repulsive all the way into contact at all concentrations of CTAB (10\textsuperscript{-5} M, 5\times10\textsuperscript{-4} M and 10\textsuperscript{-3} M) as shown in Figure 6.5. The same trend is observed for 10\textsuperscript{-3} M NaBr at pH 3 (Figure 6.6) and 4 for (Figure 6.7).
Figure 6.5: Force measurements between titania surfaces in the presence of $10^{-2}$ M NaBr pH 2, for a selection of CTAB concentrations. The forces are repulsive at all separations for all concentrations of CTAB.

Figure 6.6: Force measurements between titania surfaces in the presence of $10^{-3}$ M NaBr pH 3, for a selection of CTAB concentrations. The forces are repulsive at all separations for all concentrations of CTAB.
Figure 6.7: Force measurements between titania surfaces in the presence of $10^{-3}$ M NaBr pH 4, or a selection of CTAB concentrations. The forces are repulsive at all separations for all concentrations of CTAB.

The repulsion decays exponentially and is therefore attributed to an electrostatic repulsion. There is no significant observed van der Waals attraction. This is surprising as the van der Waals attraction between bare titania surfaces across water is large, being approximately 10 times that between silica surfaces across water, and the level of CTAB adsorption is very low. However, this is consistent with the previous observations of the surface forces between bare titania surfaces where, away from the IEP, the van der Waals force was not evident (see §4.2.1.1). While the cation CTA$^+$ is not expected to absorb to the positive titania surface, the isotherm reveals that significant adsorption does occur (Figure 6.2). When CTA$^+$ binds to a negatively charged site, this will result in the surface becoming more positively charged. However there is no change in surface charge with CTAB concentration observed in the force measurements. One possibility is that when the CTA$^+$ adsorbs to the surface a Br$^-$ counter-ion accompanies it, resulting in no net change in surface charge.

At pH 4 and $10^{-2}$ M NaBr, a small but not insignificant adsorption of CTA$^+$ to the surface is seen which increases with concentration. The corresponding forces are shown in Figure 6.8.
Figure 6.8: Force measurements between titania surfaces in the presence of $10^{-2}$ M NaBr pH 4, for a selection of CTAB concentrations. The forces are repulsive at all separations for all concentrations of CTAB.

At pH 4, $10^{-5}$ M CTAB a small degree of adsorption results in surfaces with no net charge. The lack of a significant electrostatic repulsion reveals an attraction due to the van der Waals force. At pH 4, $10^{-4}$ M CTAB, a DLVO type force is observed where an electrostatic repulsion dominates at large separation and a van der Waals attraction dominates at smaller separations. A DLVO type force is also observed at pH 4, $10^{-3}$ M CTAB where the magnitude of the electrostatic repulsion is greater than that seen at pH 4, $10^{-4}$ M CTAB. In all cases the magnitude of the attraction is small and is well fit using a Hamaker constant of only 3 zJ, not the expected 35 zJ for titania surfaces with adsorbed CTAB across water. The value of 35 zJ was determined using Lifshitz theory applied to a layered system as described in §4.2.1.1).

6.2.1.8 Above the IEP

Above the IEP the titanium dioxide surface is negatively charged, therefore the electrostatic interactions with the positive CTA$^+$ will promote adsorption. This is observed in the measurements of surface adsorption by OR where large surface excesses are obtained. The concentration of CTAB is therefore expected to have a large effect on the surface forces.
2) **Above the IEP (pH 6, 8 and 10) and low surfactant concentration (10^{-5} M CTAB)**

The forces in the presence of 10^{-5} M CTAB in 10^{-2} M NaBr at pH 6, 8 and 10 are presented in Figure 6.9.

![Figure 6.9: Force measurements between titania surfaces in 10^{-2} M NaBr and 10^{-5} M CTAB at pHs 6, 8 and 10.](image)

In all cases, an attractive force is seen from a separation of ~10 nm and the spring instability occurs at ~7 nm. The attraction is the result of adsorbed CTAB neutralizing most of the surface charge. These forces were compared with DLVO theory (see Figure 6.10). A non-retarded Hamaker constant of 60.5 zJ (the appropriate value for bare titania surfaces across water) was found to be too large as was 35 zJ, the expected value when adsorbed CTAB layers are included in the Lifshitz calculation.\(^9^4\) Rather a good fit was obtained using a Hamaker constant of only 3 zJ. Note the difference in form of the DLVO calculated curves is due to the higher potentials employed for the high Hamaker constant cases. When lower surface potentials were used the theoretical data was even further from the experimental data.
Figure 6.10: Comparison of DLVO fits of force measurements between titania surfaces in $10^{-2}$ M NaBr and $10^{-5}$ M CTAB at pH 10. Solid lines are constant charge boundary condition and dashed lines are the constant potential boundary condition. Parameters used in the DLVO fits are as follows; Hamaker constant = 3 zJ a surface potential = -4.8 mV; Hamaker constant = 35 zJ a surface potential = -20 mV; Hamaker constant = 60.5 zJ a surface potential = -27.8 mV. In all cases, a Debye length of 3 nm was used.

For $10^{-5}$ M CTAB in $10^{-3}$ M NaBr electrolyte, the forces are longer in range as the electrostatics are not as highly screened. At pH 6, 8 and 10 (Figure 6.11) a diffuse double layer force is seen at a separation of ~50 nm. As is the case for the $10^{-2}$ M NaBr solution, these forces are well described within the DLVO paradigm but only when a reduced dispersion force is employed. What is observed is that the electrostatic repulsion decreases with increasing pH, which is a result of an increase in the level of CTAB adsorbing to the surface, resulting in a drop in surface potential.
Figure 6.11: Force measurements between titania surfaces in $10^{-3}$ M NaBr and $10^{-5}$ M CTAB at pHs 6, 8 and 10.

3) **Above the IEP (pH 6, 8, 10) and above the CIP ($10^{-4}$ M, $5 \times 10^{-4}$ M and $10^{-3}$ M CTAB)**

In this case the surface is negatively charged which promotes adsorption of CTAB, but the final stages of adsorption of CTAB is driven by the hydrophobic attraction between the tail groups of the surfactant (and opposed by electrostatic interactions between the head groups). When the NaBr concentration is $10^{-2}$ M and the pH is 6 (Figure 6.13) a diffuse double layer repulsion is observed for $10^{-4}$ M and $10^{-3}$ M CTAB and an initial contact is seen at ~6 nm followed by a jump into contact. The jump into contact is attributed to displacement of the surface layers of surfactant from both surfaces. The thickness of two complete adsorbed bilayers of CTAB has been previously measured on mica surfaces to be 6.6±0.4 nm. The adsorption isotherms indicate the formation of incomplete bilayers, so it is reasonable to expect a slightly reduced thickness between titania surfaces as is observed.
Figure 6.12: Measurements in $10^{-2}$ M NaBr solutions of force curves between titania surfaces in the presence of CTAB at pH 6. For comparisons of the experimental data with the DLVO theory see Appendix 1.

Qualitatively similar forces are seen at pH 8 and pH 10 for $10^{-4}$ M and $10^{-3}$ M CTAB in $10^{-2}$ M NaBr (Figure 6.13). At these concentrations of CTAB in the presence of $10^{-2}$ M NaBr, aggregates of surfactant have formed on the surface, which results in the surfaces becoming positively charged and gives rise to a diffuse double layer repulsion between the surfaces. At small separations, when a sufficient force is applied, the aggregates of the surface are pushed out from between the surfaces, producing the push through into hard contact in the force measurements.
The forces in the presence of $10^{-3}$ M NaBr are quite different, as the range of the electrostatic repulsion is extended considerably. Again, the push through into contact arises from the removal of CTAB aggregates from the surfaces. At pH 6 (see Figure 6.14) and $5 \times 10^{-4}$ M CTAB the push through into contact occurs at a separation of 5-6
nm indicating the removal of both bilayers from the surfaces. While at $10^{-3}$ M CTAB the push through occurs at ~3 nm, indicating the removal of a single bilayer.

Figure 6.14: Measurements in $10^{-3}$ M NaBr solutions of force curves between titania surfaces in the presence of CTAB at pH 6. For comparisons of the experimental data with the DLVO theory see Appendix 1.

At pH 8, (Figure 6.15) a jump is observed at $5 \times 10^{-4}$ M but not at $10^{-3}$ M. This indicates that at $10^{-3}$ M none of the CTAB is removed from the surfaces by the applied force. At pH 10 (see Figure 6.16) no push through is observed for either concentration of CTAB. Again, the applied force is insufficient to displace any CTAB from the surfaces.
Figure 6.15: Measurements in $10^{-3}$ M NaBr solutions of force curves between titania surfaces in the presence of CTAB at pH. For comparisons of the experimental data with the DLVO theory, see Appendix 1.

Figure 6.16: Measurements in $10^{-3}$ M NaBr solutions of force curves between titania surfaces in the presence of CTAB at pH 10. For comparisons of the experimental data with the DLVO theory, see Appendix 1.

When examined as a group, a trend is apparent. As CTAB concentration is increased, less CTAB is removed indicating it is bound more strongly. The same trend is seen
when pH is increased. At high pH and high CTAB concentrations the adsorbed CTAB is bound so strongly that the applied force is not adequate to displace any CTAB layers from the surfaces.

6.2.1.9 Unexpectedly Small Dispersion Forces

A significant difference between titania surfaces when compared to mica or silica surfaces is that the expected dispersion forces are much larger for titania. For example, the effective Hamaker constant calculated using Lifshitz theory across water for titania surfaces is $60.5 \, \text{zJ}^{94}$ whereas silica that for is $7.7 \, \text{zJ}^{10}$ and that for mica is $22 \, \text{zJ}^{157}$. In all cases, the adsorption of CTAB to the surface will reduce the dispersion interactions. The dispersion forces for the layered system of Silicon/Titania/CTAB/water/CTAB/Titania/Silicon can also be calculated using Lifshitz theory$^{94}$ and for the titania surfaces of thickness $102 \, \text{nm}$ used here or greater, the value is not dependent on the thickness of the titania layer. Drew Parsons of the Department of Applied Mathematics, ANU calculated an effective Hamaker constant value to be $35 \, \text{zJ}$. Here, a selection of the force data is presented to illustrate how the magnitude of the dispersion forces influence the DLVO fit to the experimental data.

Figure 6.17 presents plots, which employ the dispersion force expected from Lifshitz calculations ($A = 35 \, \text{zJ}$) while Figure 6.18 depicts DLVO fits employing a much reduced dispersion force ($A = 3 \, \text{zJ}$).
Figure 6.17: Comparison of surface force measurements between titania surfaces in the presence of CTAB and NaBr with the DLVO theory. The CTAB concentration was $10^{-3}$ M and the pH 6. The top plot is for a NaBr concentration of $10^{-3}$ M and the bottom plot is for $10^{-2}$ M NaBr. A non-retarded Hamaker constant of 35 zJ was used. The fitting parameters of the DLVO fits for the upper plot are $\kappa^{-1}=8.2$ nm, $\psi_0=20.9$ mV and for the bottom are $\kappa^{-1}=3.1$ nm, $\psi_0=28.6$ mV.
Figure 6.18: Comparison of surface force measurements between titania surfaces in the presence of CTAB and NaBr with the DLVO theory. The CTAB concentration was $10^{-3}$ M and the pH 6. The top plot is for a NaBr concentration of $10^{-3}$ M and the bottom plot is for $10^{-2}$ M NaBr. A non-retarded Hamaker constant of 3 zJ was used. The fitting parameters of the DLVO fits for the upper plot are $\kappa = 8.2$ nm, $\psi_0 = 10.2$ mV and for the bottom are $\kappa = 3.6$ nm, $\psi_0 = 16.9$ mV.
What is apparent is that the experimental data is fit much better using the lower dispersion force. Whilst a limited data set is shown here to illustrate this, it was found that all the data that was obtained was best fit using the same low value of the effective Hamaker constant (A=3 zJ). Comparison of the experimental data with the DLVO theory using Hamaker constants of 35zJ and 3zJ is provided in Appendix 1. While an explanation for this has not yet been determined it should be noted that previous investigations of surface forces in the presence of CTAB using mica\textsuperscript{138} and silica\textsuperscript{82} surfaces are best fit using a dispersion force that is reduced from the expected value using Lifshitz theory. In addition, the dispersion forces are not evident between bare titania surfaces at a pH away from the IEP (see §4.2.2.3)

6.2.2 Sodium Dodecyl Sulphate (SDS)

The anionic surfactant sodium dodecyl sulphate (SDS) is often chosen for use as a model surfactant despite the difficulty in obtaining the material in high purity. So called pure commercial samples of SDS are contaminated with dodecanol, which has been observed to have a dramatic effect on the properties of SDS solutions\textsuperscript{66, 78, 144, 158, 159}. Even after purification SDS hydrolyzes producing dodecanol, meaning that SDS will decompose over time and self contaminate.

6.2.2.1 Purification

In order to trust any surface or colloid measurements involving SDS it is necessary to thoroughly purify the SDS. Here the purification process used by Casson and Bain\textsuperscript{66} was followed. The details of this process are described in §2.1.1.2. In addition, like Casson and Bain, after purification the solid SDS was stored in a freezer to minimize hydrolysis. Solutions prepared from this purified SDS were used as quickly as reasonably possible in the experiments to minimize the quantity of dodecanol contaminant present in the solutions.

6.2.2.2 Surface Tension Measurements

Historically the test to determine that SDS is free of contamination has been to measure the surface tension of SDS solutions over a range of concentrations near the CMC.\textsuperscript{66, 78, 158} Details of the surface tension instrument used in the this work are described in §2.4. Surface tension measurements performed using purified SDS solutions are shown in Figure 6.19.
These measurements show that the surface tension of the SDS solutions decreases as the concentration of SDS is increased up until 7.3 mM. Above this concentration, the surface tension remains constant despite changes in the SDS concentration. A minimum in the surface tension, which is evidence that the SDS is contaminated, is not observed.

6.2.2.3 Adsorption to a Titania Surface

Having purified the SDS, the adsorption to a titania surface was measured using OR. An example of this type of measurement for a 3.0 mM and a 7.3 mM solution at pH 4 is shown in Figure 6.20.
Figure 6.20: Optical reflectometry measurements of the change in surface excess of a titania surface exposed to 3.0 mM SDS solution at pH 4 followed by 7.3 mM solution. After washing the 3.0 mM SDS solution from the surface, the surface excess does not return to baseline. After exposure to the 7.3 mM solution the baseline is restored after the wash off phase.

In the first stage of the experiment, a baseline was established. Then at ~4 min 3.0 mM SDS was introduced into the OR cell. The adsorbed SDS was then washed off the surface at ~11 min however the surface excess does not return to the baseline. Repeats of the wash-on/wash-off cycle at 23 min and 42 min also fail to return to the baseline established before SDS was introduced into the cell. At ~62 min the 7.3 mM SDS solution is introduced to the cell then washed-off at 68 min. After exposing the surface to a concentrated SDS solution (above the CMC) the surface excess returns to zero. Subsequent exposure to the SDS solution with a concentration above the CMC also results in a return to the baseline after the wash off. This result indicates that the SDS is contaminated despite the purification process and that this contamination is solubilised by micelles of SDS.

This is curious as the surface tension measurements indicate the SDS is clean. After cleaning the SDS a second time using the same method the same result was obtained. Again the surface tension indicated the SDS is pure but the OR measurements reveal
that the SDS is contaminated. The conclusion is that the OR instrument is much more sensitive to trace levels of contamination. Since it was not possible to determine the surface excess of SDS on titania surfaces due to the presence of contamination and we were unable to purify the surfactant effectively, this area of study was not explored further.

6.3 Summary

The adsorption of CTAB to titanium dioxide surfaces prepared using Atomic Layer Deposition and the effect of CTAB on the surface forces were examined. Adsorption isotherms were measured in electrolyte concentrations of $10^{-2}$ M and $10^{-3}$ M NaBr. In both cases CTAB strongly adsorbs to the titania surface at high pH. Below the IEP, where CTAB and the surface have the same charge, there is a significant adsorption of CTAB to the surface. Slow adsorption kinetics of CTAB to titania surfaces were also observed, demonstrating that slow adsorption is not unique to the silica surface. Surface force measurements between titania surfaces with adsorbed CTAB were performed. In general the forces could be consistently described within the DLVO paradigm but only if a surprisingly low value of the Hamaker constant was employed ($3 \times 10^{-21}$ J). It is unclear why a larger dispersion force is not observed. At pH values $>2$ and high surfactant concentrations the forces at $<6$ nm separation reflected the presence of surfactant layers on the surface, which were displaced at high force.

Attempts to measure the adsorption of SDS to the titania surface were hampered by the presence of contamination. After an extensive purification process, the surface tension measurements indicated that the SDS was free of contaminants. However OR measurements revealed that the SDS still had trace amounts of contaminant which made accurate determination of the surface excess of SDS at the titania surface impossible.
Chapter 7: Conclusions and Future Work

This thesis describes an investigation into the surface forces between novel surfaces. Surfaces of appropriate geometry and the minimal roughness required for accurate force measurements were previously only available for a limited range of materials. The challenge of producing novel surfaces for this work was addressed by employing Atomic Layer Deposition (ALD) to produce smooth surfaces of alumina, titania, hafnia and zirconia. Whilst ALD had been used for decades in the electronics industry, this technique had not previously been applied to produce surfaces for the study of surface forces or surfactant adsorption before. Therefore, it was necessary to check the stability of the materials in aqueous environments. This was found to be prudent, as alumina was found to dissolve at a rate such that force measurements between pure alumina surfaces is unfeasible. However, the dissolution can be mitigated with a passivating molecule, such as a surfactant, which adsorbs to the surface and stabilizes it against dissolution. For this reason titania rather than alumina surfaces became the focus of this study.

Measurements between smooth ALD titania surfaces using the Atomic Force Microscope at the isoelectric point (IEP) revealed a monotonic attraction. The measured force was in good agreement with the calculated force using Lifshitz theory indicating that, in the absence of surface charge, the Van der Waals force was being measured. At pH near but not equal to the IEP, the surfaces acquired a charge and the measured forces followed the DLVO paradigm. However, at high pH, far from the IEP, the van der Waals attraction was not observed; instead the force is repulsive at small separations. The explanation that has been applied to observations of similar repulsive forces in the past, that it is due to a combination of surface roughness and surface hydration, cannot apply to the smooth titania surfaces employed here. Therefore we investigated other phenomena that may explain the measured forces. Swelling of the titania surface at high pH leading to a reduction in the van der Waals attraction was investigated. However there is currently no evidence for this and we show that the mechanical properties of the surface do not change with pH. It was also determined that the absence of the van der Waals attraction is not an artifact of the water plasma treatment used to clean the surfaces prior to measurement as the same trend was seen with argon plasma cleaned
surfaces. All other explanations considered were able to be ruled out. Thus, the absence of the van der Waals attraction remains an important unresolved issue.

The effect of adsorbed surfactant on the forces between titania surfaces was examined. Measurements of the surface excess of surfactant were used to inform the analysis of the force measurements. The adsorption of the surfactant CTAB to a titania surface was measured using optical reflectometry. Above the IEP (at high pH), CTAB strongly adsorbs to the surface. Below the IEP, where surface and surfactant have the same charge, significant adsorption was also observed, demonstrating the influence of dispersion and hydrophobic forces in the presence of electrostatic repulsion. Surface force measurements revealed that the forces consistently followed the DLVO paradigm but only if a surprisingly low value of the Hamaker constant was employed. It is unknown why a larger dispersion force is not observed, though this is likely to be closely related to the absence of the van der Waals force at high pH.

The absence of the van der Waals attraction between titania surfaces at high pH warrants further investigation. Swelling of the titania surfaces is a possible explanation despite nano-indentation measurements indicating there is no change in the mechanical properties of the surface. An alternative technique, Neutron Scattering, should have the necessary sensitivity to reveal changes in the surface properties if they are swelling at high pH. We note that cycling of the pH had no effect on the measured surface forces, therefore if the surfaces are swelling, this infers that they must collapse when the pH is reduced on a timescale of less than a few minutes.

The pervasiveness of the absence of the van der Waals attraction amongst different materials is also unknown. An investigation into the surface forces between a range of other materials, will provide insight into the prevalence of the repulsion and reveal whether this is a peculiar feature of titania surfaces or a more widespread phenomena. Using ALD, a wider range of materials is now available for these investigations. A student in the Department of Applied Mathematics has taken up this area of investigation and is currently examining the forces between hafnia and zirconia surfaces.
The reduced dispersion force observed between titania surfaces with adsorbed CTAB is likely caused by the same unknown phenomenon, which causes the absence of the van der Waals force at high pH detailed above. Similar observations of a reduction of the van der Waals force for surfaces with adsorbed surfactant have been made for silica and mica. Investigation of this effect from both a theoretical aspect, as well as experimentally will be needed to understand the interactions occurring in these systems. Further experiments examining both the effect of surfactants other than CTAB on the forces between titania, silica and mica along with an examination of the effect surfactants have on the force between other materials should provide a greater insight into the interactions that occur in these systems.
References


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Appendix 1

Figure A1 through to Figure A10 present DLVO fits of the surface forces for measurements made in electrolyte solutions of $10^{-3}$ M (Figure A1 through Figure A5) and $10^{-2}$ M (Figure A6 through Figure A10) NaBr. These DLVO fits were made used a non-retarded Hamaker constant of 35 zJ calculated using Lifshitz theory for the layered system, using the method described in §4.2.1.1. A summary of the fitting parameters used in the theoretical fits is presented in Table A1.

Figure A11 through to Figure A20 show DLVO fits for the same experimental data presented in Figure A1 through Figure A10 but in this case the DLVO fitting has used a non-retarded Hamaker constant of 3 zJ. This Hamaker value was determined by fitting the data set with the strongest attraction ($10^{-2}$ M NaBr, $10^{-5}$ M CTAB, pH 6: see Figure A18) to a dispersion force by adjusting the Hamaker constant. This value was then used for the Hamaker constant for all other fits of the DLVO forces. A summary of the fitting parameters used in the theoretical fits is presented in Table A2.
Figure A1: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-3}$ M NaBr over a range of CTAB concentrations at pH 3. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 35 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A1.

Figure A2: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-3}$ M NaBr over a range of CTAB concentrations at pH 4. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 35 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A1.
Figure A3: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-3}$ M NaBr over a range of CTAB concentrations at pH 6. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 35 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A1.

Figure A4: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-3}$ M NaBr over a range of CTAB concentrations at pH 8. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 35 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A1.
Figure A5: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-3}$ M NaBr over a range of CTAB concentrations at pH 10. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 35 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A1.
Figure A6: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-2}$ M NaBr over a range of CTAB concentrations at pH 2. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 35 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A1.

Figure A7: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-2}$ M NaBr over a range of CTAB concentrations at pH 4. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 35 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A1.
Figure A8: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-2}$ M NaBr over a range of CTAB concentrations at pH 6. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 35 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A1.

Figure A9: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-2}$ M NaBr over a range of CTAB concentrations at pH 8. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 35 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A1.
Figure A10: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-2}$ M NaBr over a range of CTAB concentrations at pH 10. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 35 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A1.
Table A1: A summary of the DLVO fitting Parameters for DLVO fitting curves, which use a non-retarded Hamaker constant of 35 zJ.

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Figure A11: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-3}$ M NaBr over a range of CTAB concentrations at pH 3. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 3 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A2.

Figure A12: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-3}$ M NaBr over a range of CTAB concentrations at pH 4. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 3 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A2.
Figure A13: Surface force measurements between TiO$_2$ surfaces in the presence of 10$^{-3}$ M NaBr over a range of CTAB concentrations at pH 6. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 3 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A2.

Figure A14: Surface force measurements between TiO$_2$ surfaces in the presence of 10$^{-3}$ M NaBr over a range of CTAB concentrations at pH 8. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 3 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A2.
Figure A15: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-3}$ M NaBr over a range of CTAB concentrations at pH 10. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 3 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A2.
Figure A16: Surface force measurements between TiO\textsubscript{2} surfaces in the presence of 10\textsuperscript{-2} M NaBr over a range of CTAB concentrations at pH 2. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 3 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A2.

Figure A17: Surface force measurements between TiO\textsubscript{2} surfaces in the presence of 10\textsuperscript{-2} M NaBr over a range of CTAB concentrations at pH 4. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 3 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A2.
Figure A18: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-2}$ M NaBr over a range of CTAB concentrations at pH 6. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 3 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A2.

Figure A19: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-2}$ M NaBr over a range of CTAB concentrations at pH 8. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 3 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A2.
Figure A20: Surface force measurements between TiO$_2$ surfaces in the presence of $10^{-2}$ M NaBr over a range of CTAB concentrations at pH 10. DLVO fits of force measurements were performed using a non-retarded Hamaker constant of 3 zJ. The upper solid line is for the constant charge boundary condition and the dashed lower line is for the constant potential boundary condition. A summary of fitting parameters is presented in Table A2.
Table A2: A summary of the DLVO fitting Parameters for DLVO fitting curves, which use a non-retarded Hamaker constant of 3 zJ.

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