Surface and Hydrodynamic Forces in Wetting Film

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ABSTRACT

The process of froth flotation relies on using air bubbles to collect desired mineral particles dispersed in aqueous media on the surface, while leaving undesirous mineral particles behind. For a particle to be collected on the surface of a bubble, the thin liquid films (or wetting films) of water formed in between must rupture. According to the Frumkin-Derjaguin isotherm, it is necessary that wetting films can rupture when the disjoining pressures are negative. However, the negative disjoining pressures are difficult to measure due to the instability and short lifetimes of the films.

In the present work, two new methods of determining negative disjoining pressures have been developed. One is to use the modified thin film pressure balance (TFPB) technique, and the other is to directly determine the interaction forces using the force apparatus for deformable surfaces (FADS) developed in the present work. The former is designed to obtain spatiotemporal profiles of unstable wetting films by recording the optical interference patterns. The kinetic information derived from the spatiotemporal profiles were then used to determine the disjoining pressures using an analytical expression derived in the present work on the basis of the Reynolds lubrication theory. The technique has been used to study the effects of surface hydrophobicity, electrolyte (Al$^{3+}$ ions) concentration, and bubble size on the stability of wetting films. Further, the geometric mean combining rule has been tested to see if the disjoining pressures of the wetting films can be predicted from the disjoining pressures of the colloid films formed between two hydrophobic surfaces and the disjoining pressures of the foam films formed between two air bubbles.

The FADS is capable of directly measuring the interaction forces between air bubble and solid surface, and simultaneously monitoring the bubble deformation. The results were analyzed using the Reynolds lubrication theory and the extended DLVO theory to determine both the hydrodynamic and disjoining pressures. The FADS was used to study the effects of surface hydrophobicity and approach speeds. The results show that hydrophobic force is the major driving force for the bubble-particle interactions occurring in flotation.
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Chapter 1. Introduction

1.1 General

A wetting film is formed when a vapor condenses on a surface, a liquid spreads on a surface, or when a gas bubble is pressed against a surface in a liquid. Thus, wetting films are ubiquitous in our daily lives and play vital roles in a variety of industrial and medical applications, e.g., flotation [1-3], enhanced oil recovery [4-6], surface cleaning [7, 8], heat transfer [9, 10], microfluidics [11, 12], and optoelectronics [13, 14].

In the minerals industry, flotation has been widely used to separate valuable minerals from valueless gangue minerals for more than a century. The process may appear simple, but is capable of separating a variety of minerals by control of the surface chemistries of the minerals involved. In a flotation cell, air bubbles collide with mineral particles, during the course of which wetting films are formed between the bubbles and particles. Initially, the water in the film drains due to the surface tension pressure (or Laplace pressure) created by the curvature change. The film will continue to drain until the excess pressure becomes equal to the disjoining pressure ($\Pi$) created by the surface forces acting between the bubble and the mineral surfaces. In most cases, the disjoining pressure is repulsive, because both the electrical double-layer and van der Waals forces are repulsive. Therefore, the disjoining pressure provides a resistance to film thinning. When the Laplace pressure is equal to the disjoining pressure, the wetting film is stable and the film drainage stops at an equilibrium thickness.

Thermodynamically, disjoining pressure is defined as the change in excess Gibbs free energy ($G$) per unit area of a flat film with film thickness ($h$) [15, 16],

$$\Pi(h) = -\left(\frac{\partial G}{\partial h}\right)_{p, T, \mu_s}$$

(1.1)

at a constant pressure ($p$), temperature ($T$), and chemical potentials of the solutes ($\mu_s$). According to eq. (1.1), the disjoining pressure becomes positive when $\partial G/\partial h < 0$, which is the case when both the double-layer and van der Waals forces are repulsive. For a wetting film to rupture, $\Pi$
should be negative, which is the case when \( \frac{\partial G}{\partial h} > 0 \). This condition is realized when the surface forces in the thin liquid film (TLF) of water in the wetting film are net negative.

According to the classical DLVO theory [17, 18], the stability of a TLF confined between two surfaces, e.g., between two colloidal particles, is determined by two surface forces, namely, electrical double-layer force and the van der Waals force. Depending on the relative magnitudes of the two forces, the disjoining pressure of film can be positive or negative. The film (or the colloidal suspension) is stable when \( \Pi > 0 \) and unstable when \( \Pi < 0 \). Likewise, the stability of the TLF confined between an air bubble and a mineral surface should be determined by the disjoining pressure in the wetting film. A problem with this logic is that in most flotation systems, \( \Pi > 0 \) according to the DLVO theory, as both the double-layer and the van der Waals forces are repulsive. In 1969, Laskowski and Kitchener [19] recognized this problem and suggested that for the wetting film to rupture, the disjoining pressure must be negative and that the negative pressure may be due to a long-range hydrophobic effect. In 1972, Blake and Kitchener [20] conducted a series of disjoining pressure measurement in the wetting films of water formed on the surface of methylated silica. The experimental results showed that \( \Pi > 0 \) but the wetting film ruptures at \( h = 64 \) nm, which led the authors to suggest that the film rupture observed at long separation distance was due to the hydrophobic force.

In 1982, Pashley and Israelachvili [21] reported the measurement of the hydrophobic force in the TLFs of water confined between mica surfaces hydrophobized by the cetylammomium bromide (CTAB). Since then, numerous other investigators confirmed the presence of the hydrophobic force in the TLFs confined between hydrophobic surfaces using the surface force apparatus (SFA) and atomic force microscope (AFM) [22-31]. Eriksson, et al. [25] suggested that the hydrophobic force may be due to the structuring of the water in the TLFs. The structuring has something to do with the structure of the solid. Many other investigators had a difficulty with the suggestion that the structure of a solid can influence the structure of water as far as \( h = 80 \) nm or more [32-35]. As an alternative explanation, Attard and others showed evidences that the long-range attractive hydrophobic forces may be due to the nanobubbles preexisting on hydrophobic surfaces [36-41].

More recently, Yoon and his coworkers [42] conducted surface force measurements at several different temperatures to show that hydrophobic interactions entail entropy decrease, which is
contrary to the hydrophobic interactions at molecular scale. As is well known, the self-assembly of surfactants and lipids entails entropy increase [43]. The authors attributed the entropy decrease associated with the macroscopic hydrophobic interaction to the formation of H-bonded structures of water in the TLFs confined between hydrophobic surfaces. The formation of H-bonded structures, which is also referred to as partial clathrates, may be a way to minimize the free energy of the water molecules that cannot be H-bonded to the confining surfaces. In this regard, the hydrophobic force may be considered a thermodynamic force. More recently, Yoon and his coworkers [44] reported the measurement of long-range attractive forces in the TLFs of ethanol and methanol confined between hydrophobic surfaces. It appears, therefore, that the hydrophobic force is a solvophobic force arising from the structuring of H-bonding liquids.

It is the main objective of the present work to explore the possibility that hydrophobic forces are present in the wetting films of water confined between air bubbles and hydrophobic surfaces. The first measurement of disjoining pressures were reported by Derjaguin and his co-workers in 1939 [45] using the bubble-against-plate technique. The initial measurements were conducted on hydrophilic surfaces such as mica and silica. The disjoining pressures were positive and, hence, the TLFs were stable, which made it possible to do the measurement. The experimental technique involves the measurement of the excess pressure ($p$) in the film while monitoring the film thicknesses ($h$) using an optical interference technique. However, it is difficult to do the measurement when the wetting films are unstable. Typically, the lifetimes of the wetting films formed hydrophobic surfaces are fractions of a second. In the present work, the optical interference patterns (Newton rings) generated during the film thinning process is recorded on a high-speed camera; and the results were used to reconstruct the spatial and temporal film profiles and calculate the disjoining pressure using a model developed in the present work on the basis of the Reynolds lubrication theory. The results show that the disjoining pressure is negative in the wetting films of water formed on hydrophobic surfaces.

Many investigators [46-50] reported the measurement of the surfaces forces involved in bubble-particle interactions. Typically, they used AFM and SFA for this purpose. A challenge with this approach has been that it is difficult to determine the film thicknesses accurately as bubbles deform during the measurement. It is, therefore, another objective of the present work to develop a new instrument that can directly measure not only the forces involved in bubble-particle interactions but also the distances between the bubble and the surface. The new
instrument and the numerical methods developed for the analysis of the experimental data allows one to visualize the dynamic process in the form of nano-scale thickness profiles, while monitoring the hydrodynamic, surface tension, and surface forces. The results show that the hydrophobic force is the major driving force for flotation. The new instrument developed in the present work can also be used to study the interactions between biological membranes.

1.2 Literature Review

The presence of the disjoining pressure (\( \Pi \)) in a thin liquid film (TLFs) has been known since 1939 when its first measurement was reported by Derjaguin and Kussakov [45]. It is now well recognized that disjoining pressures are present in the TLFs of liquids confined between two colloidal particles, liquid droplets, or gas bubbles, and its magnitude and sign determines the stability of the TLFs. In general, a film is stable when \( \Pi > 0 \) and is unstable when \( \Pi < 0 \). The classical DLVO theory has been used to predict the disjoining pressures of in the TLFs formed between colloidal particles and between bubbles in foams.

Attempts have also been made to measure or predict the disjoining pressures in the wetting films formed between air bubbles and mineral particles [51]. When the disjoining pressure is positive, the measurement is easy. However, the measurement is difficult when the disjoining pressure is negative. Laskowski and Kitchener [19] was the first to recognize that the disjoining pressure must be negative for a contact angle to form or for bubble-particle attachment to occur. When \( \Pi < 0 \), however, the film is so unstable that no one has been able to directly measure the negative disjoining pressures for more than 70 years, nor has anyone developed an analytical expression for the negative disjoining pressures in wetting films. What follows below is the review of the experimental techniques that has been developed to date for the measurement disjoining pressures in wetting films.

The techniques that have been develop for the determination of the disjoining pressure isotherms in wetting films can be classified into two categories: static and dynamic methods. The static methods are based upon measuring the film thickness at equilibrium in a well-controlled environment, when the disjoining pressure in a wetting film is balanced by the pressures across the film. The dynamic methods involve monitoring of the temporal changes in film thickness, or directly measuring the interaction force between an air bubble and a solid surface across a thin
layer of liquid. Both methods have been intensively used to study the wetting films of various liquids on solid surfaces. Each method has unique features and advantages over the others in view of thickness range, nature, and magnitude. Both techniques have been used interchangeably over the years.

1.2.1 Static measurement of determining the disjoining pressure isotherm

The first study of the disjoining pressure in a wetting film was carried out by Derjaguin and Kussakov in 1939 [52]. In their experimental set-up, gas bubbles with sizes from 0.1 mm to 1 mm in radius were slowly pressed against a horizontal glass plate in aqueous solutions. Given sufficient time, a liquid film of water between the air bubble and the solid surface was stabilized and reached an equilibrium. The thickness of the thin wetting film between an air bubble and a solid surface was monitored using the interferometry technique. A thick film, known as β-film, was formed in equilibrium with a bulk liquid surrounding the air bubble. At equilibrium, the disjoining pressure in the wetting film is balanced by the Laplace pressure ($\Delta P$) inside the air bubble. Thus,

$$\Pi = \Delta P = 2\sigma / R$$

(1.2)

where $\sigma$ is the surface tension of the liquid and $R$ is the radius of the bubble. Given an inverse linear relationship between the disjoining pressure and the bubble size, the disjoining pressure was determined by measuring the thicknesses of the equilibrium wetting films using the bubbles with varying sizes. This work was the first experimental evidence supporting the DLVO theory.

In 1968, Read and Kitchener [53] also took advantage of eq. (1.2) while developing a refined experimental cell for studying the wetting film formed on polished silica plates. Air bubble was generated in-situ by the electrolysis of a platinum wire and manually placed under a small inverted silica cup. The thin liquid film was created afterwards by slowly lowering the air bubble towards a silica plate until an equilibrium film was formed. The intensity of light reflected from the wetting film was determined by means of a cadmium sulfide photoconductive cell. The thickness of the thin liquid film was determined from the intensity of the reflected light in accordance to the Raleigh equations,
\[
\frac{I_r}{I_0} = \frac{\alpha^2 + \beta^2 + 2\alpha\beta \cos \delta}{1 + \alpha^2 + \beta^2 + 2\alpha\beta \cos \delta}
\]

\[
\alpha = \frac{(n_1 - n)}{(n_1 + n)}
\]

\[
\beta = \frac{(n_2 - n)}{(n_2 + n)}
\]

\[
\delta = \frac{(4\pi nd \cos \phi)}{\lambda}
\]

where \(n_1, n\) and \(n_2\) are the refractive indices for solid, water and vapor, respectively, \(\phi\) is the angle of refraction in the film, \(d\) the film thickness and \(\lambda\) is the wavelength of the light. From a normalized light intensity \((I_r/I_0)\), equilibrium film thicknesses obtained in an aqueous solutions of electrolytes were compared with the theoretical values predicted using the DLVO theory.

Later, Blake and Kitchener [20] further modified the experimental set-up for an extended study of a wetting film on a hydrophobic methylated silica surface. Unlike the previous work done by Read and Kitchener [53], the interference patterns were directly observed under an inverted microscope by means of a 35 mm camera. The film thickness was determined from a photo of the ‘Newton rings’ by scanning with a microdensitometer. In their experimental set-up, an air bubble of nitrogen was formed at the bottom of a capillary tube. The position of the air bubble was controlled by means of a micrometer. Blake and Kitchener showed variances in the thickness of the wetting films formed on hydrophobic surfaces in aqueous solutions containing different concentrations of electrolytes. Similar approach was also applied to study the equilibrium wetting films of alkanes on alumina surfaces [54].

Aronson and Princen [55, 56] followed the approach developed by Blake and Kitchener, and studied the wetting films formed on the silica surfaces of surfactant solutions. The sizes of the air bubbles varied from 0.75 mm to 6 mm with the internal hydrostatic pressures ranging from 2000 to 200 dyne/cm\(^2\). The equilibrium film thicknesses were determined at varying hydrostatic pressures in the thin liquid films by changing the sizes of the air bubbles. The disjoining pressure isotherm was plotted in the hydrostatic pressures as a function of the film thicknesses.

The methods developed by both Derjaguin’s group and Kitchener’s group were based upon varying the sizes of the air bubbles. Knowing the sizes of the air bubbles, the disjoining pressure isotherm was plotted using the Laplace pressure as a function of the equilibrium film thickness, \(i.e., \) disjoining pressure \(vs.\) film thickness. In order to visualize the equilibrium wetting films, the
sizes of the air bubbles practically used ranged from 1 mm up to 10 mm with the hydrostatic pressures inside the air bubbles up to 144 Pa. Thin liquid pressure balance (TFPB) technique, on the other hand, allows a measurement of the disjoining pressure isotherm at II above 1000 Pa. The design of TFPB technique was originally published by Mysels and Jones [57] for a study of the free film, i.e., a thin liquid film of water between two bubbles. In the TFPB technique, a meniscus of the liquid film between two air bubbles was formed in a porous porcelain disc by sucking the liquid out of the cell through a capillary tube. The cell was enclosed in a pressure chamber sealed by an O-ring. By varying the pressure inside the cell, one can obtain the equilibrium film thicknesses at the disjoining pressure measuring up to $10^4$ Pa. The film thickness in Mysels and Jones’s work was determined from an optical set-up by means of a photomultiplier tube.

The TFPB technique was later adapted for the disjoining pressure measurements in wetting films [58-60]. Klitzing and his co-workers [59, 60] used the TFPB technique to study the wetting films formed on silicon surfaces. In their experimental set-up, the substrate was sitting beneath the porous cell. By sucking the liquid out of a capillary inside the porous cell, a meniscus was formed between a solid surface and the vapor phase with the liquid wetting the wall of the capillary hole. The film holder was enclosed in a sealed cell by regulating the pressure using a piston pump. The film thickness was monitored from the top using the interferometry technique by means of a photomultiplier tube. The morphologies of the solid surfaces across thin liquid films were simultaneously monitored by a video microscope.

The monochromatic interferometry technique has proven to be a powerful and feasible tool for determining the film thickness of the wetting film above 30 nm. However, use of the monochromatic interferometry technique was rather limited when determining the film thickness below 30 nm. Instead, the ellipsometry technique allows an accurate measurement of the film thickness below 30 nm [61-66]. Ellipsometry characterized the reflected light beams from a thin liquid film or an assembly of thin liquid films at varying incident angles [67, 68]. When the thicknesses of the thin liquid films vary, the reflectivity and phase of p-polarized and s-polarized light changes depending upon the reflective indices of the layers that the incident light beams passed through. Reflectivity and phase changes are related to the Frensel reflection coefficients $r_p$ and $r_s$ for p- and s-polarized light as $r_p/r_s = \tan \phi \ e^{i\Delta}$. By scanning the polarization of the reflected light beams at varying incident angles, the thickness of the thin liquid film can be
determined from the ellipsometrical angle ($\phi$) and the phase difference ($\Delta$) upon the reflection. Ellipsometry can also be operated in an imaging mode using a CCD camera as the detector [39]. It provides detailed, real-time information on 2D profiles of the film thicknesses and refractive indices across an entire field of view.

Eliseeva et al. [61, 62] combined both ellipsometry and TFPB techniques to determine the disjoining pressure in wetting films at varying hydrostatic pressures. The thickness of the wetting film was determined by means of the ellipsometry technique. Fukuzawa et al. [69] used an ellipsometry microscope to study the dewetting process of the lubricant films on magnetic plates. A lubricant film with a thickness less than 10 nm was obtained. The surface energy vs. the thickness was used to reconstruct the disjoining pressure isotherm in a lubricant film.

The methodologies discussed above were valid for the measurement of the disjoining pressures in the stable wetting films with $\Pi > 0$ and $d\Pi/dh > 0$. It was typically observed in wetting films of aqueous solutions formed on the hydrophilic surfaces, such as mica, silica, or alkanes on alumina and metal surfaces. As the surfaces became hydrophobic, the wetting film became less stable, leading to a formation of an $\alpha$-film. An $\alpha$-film was formed when a continuous $\beta$-film was ruptured at a critical point or by an adsorption of the volatile liquid on surfaces. In an $\alpha$-film, the disjoining pressure is equivalent to zero at constant chemical potential and pressure. In general, the thickness of $\alpha$-film is less than 10 nm varying with the pattern of the disjoining pressure isotherm in a wetting film.

Therefore, the measurement of the disjoining pressure in an unstable wetting film at a thickness below 30 nm was not possible by varying the size of the air bubbles. Shishin et al. [63, 64] developed a modified TFPB technique to determine the disjoining pressure in a liquid film of tetradecane on a solid surface. The film thickness was obtained by means of the ellipsometry technique. In their approach, the disjoining pressure was controlled by changing the hydrostatic pressure of the liquid. From a balance of the disjoining pressure with the hydrostatic pressure, the disjoining pressure is given by,

$$\Pi = \rho g H$$  \hspace{1cm} (1.4)

where $\rho$ is the density of the liquid, $g$ is the gravitational acceleration, and $H$ is the difference in liquid level between the liquid/vapor interface in a thin film and at bulk liquid.
Alternatively, the disjoining pressure of absorbed vapor on the solid surface was determined by controlling the chemical potential ($\mu$) of the thin liquid film. Here, the disjoining pressure was represented in terms of the chemical potential of molecules in the liquid phase ($\mu = \Pi \cdot V_m$) and the vapor phase ($\mu = RT \ln(P/P_s)$) from eq. (1.2) at constant pressure, namely

$$\Pi = -(RT/V_m) \ln(P/P_s)$$  \hspace{0.5cm} (1.5)

where $V_m$ is the molar volume of the liquid, $T$ is the temperature, $R$ is molar gas constant and $p/p_s$ is the relative vapor pressure. By controlling the relative vapor pressure of molecules in a liquid film, the disjoining pressure in an adsorbed liquid film could be determined. As calculated using eq. (1.5), the disjoining pressure can be varied by changing the ratio of $p/p_s$ up to saturation. Therefore, it is possible to study the property of the adsorbed vapor film over the entire region of positive $\Pi$.

Bangham et al. [70, 71] might be the first to apply the vapor adsorption method to study the properties of the adsorbed vapor film on a solid surface. They visualized an adsorbed film of the volatile liquid on a mica surface. Later, Derjaguin et al. [72, 73] investigated the adsorption of the liquid vapor onto a solid surface by measuring the film thickness ellipsometrically. The relative vapor pressure ($p/p_s$) was controlled by changing the temperatures of the solid surface and the volatile liquid separately in a closed chamber. Simultaneously, the thickness of the liquid film on the solid surface was monitored in-situ using the ellipsometry technique. Following a similar approach by Derjaguin et al., Hall studied the adsorption of the water vapor on a quartz surface by measuring the thickness of an adsorbed water film [65]. The closed chamber was degassed by a vacuum and refilled with helium repeatedly. The measurements were carried out at an atmospheric pressure in a helium environment. Hu and Adason [66] determined the adsorption isotherm (or disjoining pressure isotherm) ellipsometrically for a variety of volatile liquids, including water, bromobenzene, methane, methanol, and ethanol on a polished hydrophobic surface.

Instead of using the ellipsometry technique to obtain the thicknesses of the liquid films, Garbatski and Folman [74] determined the thickness of an absorbed liquid film of water and isopropanol on a glass plate by measuring the changes in capacity of a quartz crystal at varying relative vapor pressures. The electrical method was based using a crystal controlled oscillator, in which the capacity of the quartz crystal was measured at the anode circuit.
Slutsky and his co-workers [75-78] used a quartz crystal microbalance technique to determine the mass of the vapor molecules absorbed on the solid surface. The thickness of the adsorbed film was obtained by converting the changes in the mass into the thickness. The adsorption isotherms of the vapor molecules at varying relative vapor pressures were obtained on both quartz surfaces and metal surfaces. The quartz crystal functioned as a microbalance by measuring a shift in the resonance frequency of the crystal when the gas molecules were absorbed on the quartz surface. Sabisky and Anderson used the acoustic interferometry technique to measure the thickness of helium films on surfaces of fluoride at 1.38K [79].

1.2.2 Dynamic methods of determining the disjoining pressure isotherm

Above is a review of the static methods that have been used to determine the disjoining pressure isotherm ($\Pi(h)$) in a thin liquid film between the vapor phase and the solid surface. The static methods can be used for determining positive disjoining pressure isotherms in both stable ($\partial \Pi / \partial h > 0$) and unstable wetting films ($\partial \Pi / \partial h < 0$). A positive disjoining pressure was obtained by balancing the pressure in liquid with the pressure in vapor. In a stable wetting film with a continuous liquid phase, typically known as a $\beta$-film, the disjoining pressure isotherm could be obtained when the pressure in the thin liquid film was in equilibrium with the bulk liquid. In an unstable wetting film, the rupture of the $\beta$-film led to a formation of an $\alpha$-film, i.e., a liquid film of the adsorbed gas molecules in equilibrium with the vapor phase [80]. The disjoining pressure isotherm was obtained from the adsorption isotherm of the gas molecules on a solid surface.

As discussed above, the static methods only allow one to obtain a positive disjoining pressure in a wetting film. The negative pressure could not be determined directly, but only from a theoretical extrapolation of the DLVO theory. On the other hand, the dynamic methods show an ability of determining both a positive and a negative disjoining pressure in a wetting film. In the 1960s, Scheludko and his co-workers measured the disjoining pressure in a thin liquid film by monitoring the film drainage of a liquid film between two bubbles. It was designed to study symmetric free film, i.e., a foam film of a liquid between two vapor/liquid meniscuses [81-83]. With a modification of the liquid cell, the dynamic method was also adapted to study the drainage of a wetting film [84].
The dynamic method developed by Scheludko et al. [84] was based upon the Reynolds theory of a thin liquid film between two plane-parallel interfaces. The Reynolds equation yields an expression for the rate of film drainage by the pressure difference in the thin film relative to the adjacent bulk liquid [85]. The Reynolds approximation is given by

\[
\frac{d\left(1/h^2\right)}{dt} = \frac{4\Delta P}{3\eta r_0^2}
\]

where \(h\) is the film thickness, \(\eta\) is the viscosity of the liquid, \(r_0\) is the radius of the flat film, \(t\) is the time and \(\Delta P\) is the pressure difference in a thin film relative to the pressure in a bulk liquid. Equation (1.6) was derived assuming that two adjacent interfaces were parallel with zero slip velocity at the interfaces. In general, a zero slip velocity is referred to as the non-slip boundary condition. The pressure difference was given by subtracting the Laplace pressure from the disjoining pressure; namely,

\[
\Delta P = P_c - \Pi = \frac{2\sigma}{R} - \Pi
\]

where \(P_c\) is the Laplace pressure due to the changes in curvature in the flat film compared to the meniscus neighboring the flat film. In eq. (1.7), \(P_c\) is equal to \(2\sigma/R\), where \(R\) is the radius of the meniscus at the edge. As shown in eq. (1.6), the disjoining pressure can be determined when the rate of the film drainage \((dh/dt)\) is known.

Experimentally, the film thickness was determined using the microinterferometric methods by monitoring the interference of the light beams reflected from two adjacent interfaces of a wetting film. Instead of recording one photo of the interference fringe at equilibrium in the static method, continuous photos of the interference fringes were captured and analyzed to obtain the film thickness by means of either a photometer or a CCD camera [84, 86-92].

Platikanov [86] experimentally observed the dimpled film by monitoring the temporal changes in the film thickness between an air bubble and a glass plate in an aqueous solution. He captured a series of interference patterns when an air bubble was approaching a silica surface separated by a thin liquid film. The kinetics of the film drainage was compared with the Frankel-Mysels’ model [93]. It was found that a positive disjoining pressure was present in a wetting film of water formed on a glass surface. In a thin liquid film of benzene on a mercury surface, Scheludko and Platikanov [84] showed a negative disjoining pressure acting in a wetting film.
due to the van der Waals attractions. Later in 1972, Schulze [87] measured a negative disjoining pressure in a wetting film of octane on a quartz crystal surface. A negative disjoining pressure due to the van der Waals attraction was obtained with a maximum attraction at \( h = 33 \) nm.

Scheludko's method of determining the disjoining pressure in a wetting film was achieved by comparing the theoretical prediction with the experimental data. The disjoining pressure was determined by simulating the kinetics of the film drainage with the theoretical prediction based upon the Reynolds approximation. The approximation assumes that the drainage occurs between two plane-parallel surfaces with no thickness variances at the interfaces. It works for the smaller bubbles with less hydrodynamic resistance, while the theory overestimates the drainage rate when the deformation occurs due to a larger hydrodynamic resistance. In order to simulate the drainage process of the thin liquid film between a deformable air bubble and a rigid surface, many fluid models have been proposed and derived under these dynamic conditions [94-97], with a number of models considering the effect of the van der Waals force [98-100] and electrostatic double layers force [101].

Alternatively, Nakamura and Uchida [102] studied the wetting films by monitoring the interference fringes of a wetting film when an air bubble was freely rising towards a glass plate. Under the buoyancy of the air bubble, a film confined between a vapor/water interface and a solid/water interface was drained spontaneously until an equilibrium film was reached. The kinetics of the wetting film drainage was obtained to determine the disjoining pressure by monitoring the changes in the film thickness using the interference methods. Parkinson and Ralston [91] followed a method similar to Nakamura and Uchida by releasing a tiny air bubble towards a titania surface in an aqueous solution. The kinetics of the film drainage was captured from the interference fringes by means of a high-speed camera at 1000 hz. The film drainage kinetics were described by the Taylor equation [103],

\[
\frac{dh}{dt} = \frac{F_b h}{6\pi \mu R^2}
\]  

(1.8)

where \( F_b \) is a sum of forces acting on the air bubble. It contains both the hydrodynamic and surface forces. The surface force between an air bubble and a solid surface across a thin liquid film can be acquired when \( dh/dt \) is obtained.
A multi-wavelength interferometry technique offers an alternative solution for the thickness measurement of the thin liquid film between an air bubble and a solid surface. Pushkarova and Horn [104, 105] modified the surface force apparatus (SFA) to measure the interfacial profiles of the thin liquid films between an air bubble and a silver-coated mica surface by monitoring the reflected FECO (Fringes of Equal Chromatic Order). The air bubble was manually fixed on a customized Teflon block with a pin hole on the surface. The use of the multi-wavelength interferometry technique for the thickness measurement of the thin liquid film exhibits a high resolution of the film thickness below 30 nm.

With the invention of the atomic force microscopy (AFM), some investigators applied the AFM technique to measure the interaction directly between an air bubble and a solid particle in a liquid. Many attempts have been taken for a force measurement between an air bubble and a particle in water [46, 48, 106-108]. Ducker et al. [46] might be the first to measure the force between an air bubble and a spherical particle using AFM. The AFM force measurement was conducted by attaching a particle on the tip of a cantilever and fixing an air bubble on a hydrophobic surface. The interaction force was recorded by monitoring the deflection of the cantilever when the air bubble approached towards the particle. A follow-up experiment was conducted by Preuss and Butt [48], showing a repulsion due to the electrostatic double-layer force between the air bubble and the particle. When the bubble was driven against the hydrophobic sphere, the force jumped to an adhesion at a large separation distance.

However, the direct measurement of the interaction force between an air bubble and a solid particle was often accompanied with deformation of the air bubble under both the hydrodynamic and surface forces. Therefore, the force obtained directly using the AFM technique is composed of both the hydrodynamic and surface forces due to intermolecular interaction. A solution was proposed by Chan et al. [109-112], who derived a mathematical model to predict the dynamic interaction between an air bubble and a rigid solid surface in a liquid.

Manor et al. [113, 114] measured the interaction force between an air bubble and a solid surface directly using the AFM technique by attaching an air bubble on the surface of the cantilever. The disjoining pressure in a thin liquid (or the surface force between the bubble and the solid surface) was extracted by fitting the experimentally measured force with the theoretical prediction using Chan's model on the basis of the lubrication theory [109]. The lubrication model
quantitatively predicted the film profiles of the thin liquid film. However, the film profiles varied significantly when the interfacial boundary condition was slightly changed. Krasowska et al. [115] also applied the AFM technique to study the interaction force between an air bubble and a titania particle in a KCl solution. The particle was glued on the AFM tip, while the air bubble was fixed on the hydrophobic surface and positioned at the bottom of the fluid cell. Using Chan's model on the dynamic interaction between an air bubble and a particle, the raw AFM data for the bubble-particle interaction was interpreted to extract the disjoining pressure in the thin liquid film and the projected spatiotemporal profiles of the thin liquid films.

When comparing the dynamic methods with the static methods in determining the disjoining pressure in a wetting film, the dynamic methods exhibit the applicability in determining the disjoining pressures in wetting films with a variety of configurations. However, the dynamic methods are often influenced by the fluid stresses during the course of the interaction. Therefore, the determination of the disjoining pressure was not possible without an accurate fluid model for the dynamic methods. Additionally, the dynamic methods showed an ability of determining a negative disjoining pressure in an unstable wetting film, which played a significant role in understanding the fundamentals of the coagulation processes.

1.3 Dissertation Outline

The objective of the present study is to determine the interaction forces between air bubbles and solid surfaces in water. This work is aimed to measure the negative disjoining pressures in the wetting films of water formed on the hydrophobic solid surfaces and discuss the origin of the attractive pressure that cannot be predicted by the DLVO theory.

The present work is focused on studying both the surface and hydrodynamic forces operating between air bubbles and solid surfaces during the course of the bubble-particle interaction. In Chapter 2, a modified thin film pressure balance (TFPB) technique has been used to monitor the changes in the thickness profiles of the thin liquid film between an air bubble and a solid surface. A mathematical model based on the lubrication theory has been derived to determine the disjoining pressures (or surface forces) in wetting films.

In Chapters 3 and 4, the role of collectors and the effect of bubble size in the stability of wetting films have been studied by measuring the drainage rates of the wetting films formed on
the surface hydrophobic gold surfaces. The surface hydrophobicity was controlled by varying the collector concentration and the contact time for hydrophobization. The results will be useful for better understanding the factors affecting flotation efficiency.

In Chapter 5, the asymmetric hydrophobic interactions between bubble and gold are predicted from the symmetric hydrophobic interactions between two air bubbles and between two gold surfaces. It has been found that the asymmetric interactions can be predicted using the geometric mean combining rule, which is used for molecular interactions such as van der Waals interaction.

In Chapter 6, the Frumkin-Derjaguin isotherm is used to predict the stability of wetting films due to electrical double-layer interactions. The results show that wetting films becomes stable when the double-layer forces are repulsive and unstable when the double-layer forces are attractive.

In Chapter 7, a new scientific instrument that can be used to directly measure for the first time the interaction forces between a deformable object such as air bubble and a solid surface. The instrument, which is referred to as force apparatus for deformable surfaces (FADS), consists of two optical systems: one for determining temporal and spatial film profiles, and the other for monitoring the deflection of a cantilever for direct surface force measurements.

In Chapter 8, the experimental results obtained using the FADS developed in Chapter 7 have been analyzed by the numerical methods. A model has been derived on the basis of the lubrication theory and the DLVO theory. The results presented in this chapter are for stable wetting films due to positive disjoining pressures.

Chapter 9 is the same as Chapter 8 except that the theoretical analysis has been made for the unstable wetting films of water formed on hydrophilic surfaces.

In Chapter 10, the FADS has been used to study the interaction between an air bubble and gold surfaces hydrophobized by potassium ethyl xanthate (KEX). The results show that the disjoining pressure is negative due to the presence of the hydrophobic force not considered in the DLVO theory.

In Chapter 11, the results obtained in the present work are summarized and conclusions are drawn, which suggestions for future research presented at the end.
1.4 Reference


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Chapter 2. Effect of Hydrophobicity on the Stability of the Wetting Films of Water Formed on Gold Surfaces

ABSTRACT

We have developed a methodology that can be used to determine disjoining pressures (Π) in both stable and unstable wetting films from the spatial and temporal profiles of dynamic wetting films. The results show that wetting films drain initially by the capillary pressure created by the changes in curvature at the air/water interface and subsequently by the disjoining pressure created by surface forces. The drainage rate of the film formed on a gold surface with a receding contact angle ($\theta_r$) of 17° decreases with film thickness due to a corresponding increase in positive Π, resulting in the formation of a stable film. The wetting film formed on a hydrophobic gold with $\theta_r = 81^\circ$ drains much faster due to the presence of negative Π in the film, resulting in film rupture. Analysis of the experimental data using the Frumkin-Derjaguin isotherm suggests that short-range hydrophobic forces are responsible for film rupture and long-range hydrophobic forces accelerate film thinning.
2.1 Introduction

Wetting films form on surfaces by vapor deposition or when particles and bubbles suspended in liquids encounter each other under dynamic conditions. Thus, wetting films are ubiquitous and play important roles in daily lives and many industrial processes, such as flotation, foam and emulsion destabilization, food processing, self-cleaning materials design, heat transfer, corrosion protection, etc. The liquid in a wetting film drains by gravity and/or capillary pressure initially. When the film thickness is sufficiently reduced, the drainage rate and the stability of the thin liquid film (TLF) are also controlled by the pressure created due to the surface forces acting between the walls confining the liquid. The pressure in a TLF is referred to as disjoining (or wedging apart) pressure ($\Pi$), which is defined as the change in excess Gibbs free energy per unit area of a flat film ($G$) with film thickness ($h$) [1, 2],

$$\Pi(h) = -(\partial G / \partial h)_{p,T,\mu_S}$$  \hspace{1cm} (2.1)

at constant pressure ($p$), temperature ($T$), and chemical potential of solutes ($\mu_S$) [1]. The TLF is stable when $\partial \Pi / \partial h < 0$. The concept of disjoining pressure, introduced by Derjaguin [3] in 1935, served as a basis for modeling the stability of not only the wetting films but also colloidal suspensions.

As is well known, TLFs are stable on hydrophilic surfaces if the liquid is water. On the surface of a well-cleaned hydrophilic quartz, thick wetting films known as $\beta$ films are formed [1, 4]. As the mineral substrate becomes less hydrophilic by heating or methylation, the film becomes thinner and ruptures spontaneously, forming lenses of water on the surface [5]. At equilibrium, the lenses form contact angles ($\theta_o$) on a partially hydrophobic surface, with the surface covered by a thinner film known as $\alpha$ film [6]. Thus, the rupture of wetting films represents a $\beta$ to $\alpha$ phase transition.

That $\beta$ films are substantially thicker than expected from the DLVO theory lead to a suggestion that the “structural forces” not considered in the theory may be present in the wetting films formed on hydrophilic surfaces. The term was first introduced by Derjaguin and Kussakov [4], who considered that the boundary layers of water have structures different from that of the bulk water. As two surfaces approach each other, the boundary layers overlap and give rise to short-range repulsive forces. The hydration forces measured between silica and glass surfaces in
water are regarded as structural forces [7-9], while others view that they are caused by the silica hairs formed on the surface [10].

Thermodynamically, a wetting film can rupture when the $\theta_o$ of water on a substrate is greater than zero. In view of the Frumkin-Derjaguin isotherm [11, 12], Laskowski and Kitchener [13] wrote: “The criterion for a contact angle to develop is that films in a certain range of thickness would be subject to a negative disjoining pressure,” hinting the presence of a long-range attractive force in unstable wetting films. Derjaguin and Churaev [14] showed later that the Frumkin-Derjaguin isotherm can explain the increase in $\theta_o$ of quartz up to 15-16° with the decrease in the electrostatic component of disjoining pressure that can be controlled by pH and electrolyte (KCl) concentrations. The authors noted, however, that larger increases in $\theta_o$ cannot be explained without recognizing the actions of hydrophobic attraction forces [14-16].

Blake and Kitchener [17] found that the wetting films of water formed on methylated silica were meta-stable due to the large repulsive double-layer forces present in the films. In the presence of 8.6 x 10^{-3} M KCl, however, the film ruptured at 64 nm. This observation was attributed to a double-layer compression, which in turn brought the film to the domain of “hydrophobic force”. In this regard, Blake and Kitchener considered the hydrophobic force a shorter-range force than the double-layer force.

Israelachvili and Pashley [18] were the first to directly measure the short-range hydrophobic force between two curved mica surfaces using the surface force apparatus (SFA). Since then, many other investigators reported the measurement of both short- and long-range hydrophobic forces using SFA and atomic force microscope (AFM). The measured forces are often represented in the following form [19],

$$F/R = C_1 \exp(-h/D_1) + C_2 \exp(-h/D_2)$$  \hspace{1cm} (2.2)

where $F/R$ is the force normalized by the radius of curvature of the macroscopic surface(s) used for the measurement, $h$ the closest separation distance between the macroscopic surfaces, and $C_1$, $C_2$, $D_1$ and $D_2$ are fitting parameters. The first and second exponential terms of Eq. (2.2) represent the short- and long-range hydrophobic forces, respectively, with $D_1$ being in the ranges of 1-2.8 nm at $h < 10$ nm and $D_2$ in the range of 4.5-50 nm at longer separations [19-21]. Some of the experimental data show two distinct regions where short- and long-range forces are
predominant, while other data can be fitted to a single-exponential function. Still other investigators used a power law to represent hydrophobic forces [22, 23],

$$F / R = K / 6h^2$$

Eq. (2.3) is of the same form as the van der Waals-dispersion force, with $K$ being the only adjustable parameter.

Eriksson et al. [24] derived a theoretical model for hydrophobic force based on the idea that the intervening water between two surfaces is progressively more ordered with decreasing $h$, which is consistent with the concept of the structural force. The model suggests an increase in order parameter with decreasing $h$ and corresponding decreases in enthalpy and free energy per unit area. The authors related the free energy changes to surface forces using the Derjaguin approximation [25] and modeled hydrophobic surface forces in the middle and long ranges at $h > 2$ nm. Other investigators attributed the long-range attractive forces to the electrostatic attractions between charged [26-28] and uncharged [29] domains, pre-existing nano-bubbles [30, 31], cavitation [32], and others. It appeared for a while that the long-range attractions are indeed due to the nano-bubbles and/or cavitation. Typical evidences for this possibility included the discontinuities (or ‘steps’) in force vs. distance curves, disappearance of attractive forces in degassed water, and actual observation of nano-bubbles on hydrophobic surfaces. More recent studies showed, however, that long-range attractions can still be observed in degassed solutions [33, 34], and that the steps can be avoided by modifying the conditions and procedures involved in force measurement [35].

Another difficulty for accepting the hydrophobic force as a structural force is that molecular dynamic (MD) simulations invariably showed that structuring of water is limited to only a few layers of solvent molecules, while the long-range attractions are observed in experiment at $h \approx 80$ nm. It should be noted, however, that the excess free energies per molecule related to the long-range attractions are in the range of $10^{-5}$ to $10^{-3}$ kT, while the energy of a hydrogen bond is about 7 kT [24]. Therefore, it would be a challenge to detect the structural changes responsible for the long-range attractions using the MD simulations, which would have difficulties in detecting changes in energy below approximately 0.1 kT per molecule due to limitations in accuracy.
The most recent view on the origin of hydrophobic forces has been presented by Hammer et al. [36]. According to these authors, the attractive forces measured in the range of 1.5-15 nm are ‘pure’ but still not well-understood long-range forces possibly due to the enhanced Hamaker constant, while the attractions below 1.5 nm may be due to ‘pure’ short-range hydrophobic forces related to water structuring effect. On the other hand, the long-range forces observed at $h > 15$-20 nm may be due to the electrostatic attractions between charged patches and/or bridging vapor cavities.

Studies of wetting films provided useful information for better understanding the surface forces present in TLFs. It was found that the repulsive structural forces measured in the wetting films of water on silica and glass surfaces are similar to the hydration forces measured in direct surface force measurements [7, 8]. Also, Churaev [16, 37] suggested that the attractive structural forces found in the wetting films on partially hydrophobic silica surface are short-range hydrophobic forces. It should be pointed out, however, that this conclusion was drawn by extrapolating the positive disjoining pressures measured on metastable films rather than from the negative disjoining pressures measured directly in experiment. The bubble-against-plate technique developed originally by Derjaguin and Kussakov can be used to measure $\Pi > 0$ [38]. However, it has been a challenge to directly measure $\Pi < 0$ due to several reasons, including fast kinetics of film thinning, deformation of air/water interface, and complex interactions between hydrodynamic and surface forces. In 1969, Laskowski and Kitchener [13] wrote: “There is no theory leading to even approximate calculation of negative disjoining pressures on hydrophobic surfaces.” More recently, many investigators reported the measurement of the surface forces involved in bubble-particle interactions using SFA and AFM, with inconsistent results [39-42].

Horn and his co-workers [43, 44] studied the interactions between mica surface and mercury drop in a 0.1 mM KCl solution by recording the spatial and temporal profiles of the intervening films using a modified SFA and a video camera. The authors compared the results with the profiles obtained from the theoretical predictions made using the Reynolds lubrication theory, with excellent agreements. The predictions involved the use of the disjoining pressures calculated using the DLVO theory from the known potentials at the mercury/solution and mica/solution interfaces. In the mica-mercury system studied, the attractive van der Waals force was minimal as compared to the double layer forces.
In the present work, we used the bubble-against-plate technique to directly measure both the positive and negative disjoining pressures in the wetting films of water formed on gold surfaces. Using a high-speed video camera, we recorded the Newton rings as a function of time to obtain spatial and temporal film profiles of the wetting films and extracted appropriate hydrodynamic information that can be used to obtain disjoining pressure isotherms, $\Pi(h)$, using an analytical expression derived in the present work. The expression was derived from the Reynolds lubrication theory and has a provision to study the effect of slip, which has been a topic of interest and debate in recent years. From the experimentally obtained $\Pi(h)$ isotherms, it was possible to obtain the information on hydrophobic disjoining pressure ($\Pi_h$), which plays a dominant role at contact angles above approximately $40^\circ$ [16]. The methodology developed here is a step forward from an earlier approach, in which the Reynolds lubrication approximation [45] was used to determine the hydrophobic disjoining pressures at different contact angles [46].

2.2 Model Derivation for Disjoining Pressure

When an air bubble is pressed against a plate lying horizontally in water, a thin liquid film is formed in between. The pressure of the liquid in the film becomes higher than that of the bulk liquid due to the curvature difference, causing the film to thin. As the film thinning continues, disjoining pressure ($\Pi$) in the film also begins to play a role. If it is positive (or repulsive), the film thinning is retarded. In the present system, the repulsive disjoining pressure arises from double-layer interaction and increases exponentially with decreasing $h$. Thus, there can be a point where the excess pressure due to curvature change ($p_{\text{cur}}$) becomes equal to $\Pi$, when the film thinning stops at an equilibrium thickness ($h_e$). If a water film is formed on a substantially hydrophobic surface, the disjoining pressure can be negative (or attractive) and can facilitate the film thinning process. In this case, the film ruptures catastrophically at a critical thickness ($h_c$). Thermodynamically, the rupture occurs when contact angle is greater than zero. Thus, the process of film thinning is controlled initially by $p_{\text{cur}}$ (or capillary pressure), while $\Pi$ plays a significant role during later stages.

The film thinning process can be described by considering the force balance in the fluid using the Navier-Stokes equation, which is highly nonlinear and difficult to solve analytically. For TLFs and at low fluid velocities, it can be reduced to the linear Stokes' equation,
\[ \nabla p = \mu \nabla^2 u \]  

(2.4)

where \( p \) is the excess pressure in the film relative to the pressure in the far field, \( u \) the fluid velocity, and \( \mu \) the fluid viscosity.

By combining Eq. (2.4) with the continuity equation for film thinning, one obtains the Reynolds lubrication equation [47],

\[
\frac{1}{2} U_u \frac{\partial h}{\partial r} + \frac{\partial h}{\partial t} = \frac{1}{12 \mu r} \frac{\partial}{\partial r} \left( r h^3 \frac{\partial p}{\partial r} \right) 
\]

(2.5)

where \( h \) the film thickness, \( r \) the radial position, and \( U_u \) is the slip velocity at the interface. Eq. (2.5) can be reduced to an approximate form as follows [45],

\[
\frac{dh}{dt} = -\frac{2h^3 p}{3 \mu R^2} 
\]

(2.6)

under conditions of flat films and no slip at phase boundaries, i.e., \( U_u = 0 \). Eq. (2.6) has been used widely to explain the kinetics of film thinning [45, 48].

Eq. [5] can be integrated twice to obtain

\[
p = \int_{r=\infty}^{r} \frac{1}{r h^3} \left[ \int_{r=0}^{r} 12 \mu r \frac{\partial h}{\partial t} \, dr - \frac{\partial p}{\partial r} \right] \, dr - p(r = \infty) 
\]

(2.7)

By integrating Eq. (2.7) again under the boundary conditions that \( p(r = \infty) = 0 \) and \( \frac{\partial p}{\partial r} \bigg|_{r=0} = 0 \), one obtains

\[
p = 12 \mu \int_{r=\infty}^{r} \frac{1}{r h^3} \left[ \int_{r=0}^{r} r \frac{\partial h}{\partial t} \, dr \right] \, dr 
\]

(2.8)

A normal stress balance across the interface gives a relation between the excess pressure, disjoining pressure, and curvature pressures as

\[
p = p_{\text{cur}} - \Pi 
\]

(2.9)

For a weakly-changing fluid height, i.e., \( \partial h / \partial r \ll 1 \), the curvature pressure becomes,

\[
p_{\text{cur}} = \frac{2\gamma}{R} - \frac{\gamma}{r} \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) 
\]

(2.10)
where \( R \) is the radius of the bubble in the far field, and \( \gamma \) is the air/water interfacial tension.

Substituting Eqs. (2.8) and (2.10) into Eq. (2.9), one obtains an expression for the disjoining pressure

\[
\Pi = \frac{2\gamma}{R} - \frac{\gamma}{r} \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) - 12\mu \int_{r=R}^{r=\infty} \frac{1}{r^3} \left[ \int_{r=0}^{r} r \frac{\partial h}{\partial r} \, dr \right] \, dr
\]

(2.11)

which is a function of \( h(r,t) \) only. Thus, a disjoining pressure isotherm, \( \Pi(h) \), can be numerically determined if the spatial and temporal profiles of a wetting film can be obtained in experiment.

2.3 Experiment

2.3.1 Materials

Gold-coated glass plates (CA134, EMF) were used as substrates for wetting films. They were cleaned in a boiling piranha solution (7:3 by volume of \( \text{H}_2\text{SO}_4: \text{H}_2\text{O}_2 \)) for 1 hour, rinsed with Millipore water (>18.2 MΩ/cm), and then dried in a nitrogen gas stream [35]. The freshly-cleaned gold substrate exhibited r.m.s. roughness of 1-2 nm as determined from AFM images. The gold plate obtained in this manner exhibited an equilibrium contact angle (\( \theta_o \)) of 42° with receding (\( \theta_r \)) and advancing (\( \theta_a \)) angles of 17° and 60°, respectively, as measured by using the dynamic sessile drop technique.

A gold plate obtained in the manner described above was rendered hydrophobic by immersing it in a \( 10^{-5} \) M potassium amyl xanthate (KAX) solution for 10 min, followed by rinsing with Millipore water and drying in a nitrogen gas stream. The xanthate-treated gold exhibited contact angles of \( \theta_r = 81°, \theta_o = 91°, \text{and} \ \theta_a = 99° \). The hydrophobizing agent had been purified twice just before use by dissolving a technical grade KAX (>90%, TCI America) in acetone (HPLC grade, Fisher Sci.) and re-crystallizing in diethyl ether (99.999%, Sigma-Aldrich).

2.3.2 Procedure

Both the xanthate-treated and untreated gold plates were used as substrates for wetting films of water. The kinetics of film thinning was monitored using the thin film pressure balance (TFPB) technique described previously [46]. In each experiment, a gold plate was placed on a film...
holder with a 2-mm inner diameter as shown in Figure 2.1. The film holder was then placed in a vapor-saturated chamber (to avoid evaporation of the film), which in turn was placed on an inverted microscope (Olympus IX51) equipped with a tilting stage (M-044.00, Polytec PI). A monochromatic light source with a center wavelength of 526 nm was directed to the wetting film so that the reflected light can produce optical interference patterns (Newton rings) as curvature of the air/water interface changes with time.

Initially, the excess water in the film holder was removed by means of a piston pump until the first Newton ring appeared on the camera screen. The film was then allowed to thin spontaneously, while recording the interference patterns as a function of time using a CCD camera (Fastcam 512PCI, Photron) at 60 frames per second. The data recorded in this manner were used to obtain the temporal and spatial profiles of wetting films, which were then used to obtain the values of radial flow velocities and the values of \( \partial h / \partial r \) and \( \partial h / \partial t \) that are necessary to determine \( \Pi \) using Eq. (2.11).
Film thinning experiments were conducted with wetting films smaller than 20 μm in radius, so that dimple formation could be avoided. The film radii were controlled by means of the piston pump, while the tilting stage was used to ensure that the films were disposed horizontally. Dimples are formed when the liquid near the edge of a film drains substantially faster than at the center, which is the case with large films [49]. Eq. (2.11) can be used for the data obtained from both dimpled and flat films. With the former, only the data collected in the barrier rims can be used to calculate $\Pi$. With the latter, the data obtained in the whole area of a film can be used. It may be noteworthy that the images of the wetting films obtained in the present work were smooth and showed no irregularities.

2.4 Result

Figure 2.2 compares the temporal profiles of the wetting films formed on the gold surfaces with and without hydrophobization by KAX. The untreated substrate exhibited $\theta_r = 17^\circ$, while the treated one exhibited $\theta_r = 81^\circ$. Other investigators also reported non-zero contact angles for gold surfaces cleaned using various methods [50]. This may be attributed to the abstraction of impurities from the air owing to the large Hamaker constant of gold. Note that the wetting film formed on the hydrophobized gold surface thinned much faster than that formed on the untreated surface. With the latter, an equilibrium film thickness ($h_e$) of 105 nm was reached in 11 s, while with the former the film thinned to a thickness of 29 nm in 0.8 s and ruptured. The values of $h_e$ and the critical rupture thickness ($h_c$) obtained in the present work are within the range of values reported in the literature [51, 52].
Figure 2.2  Spatial and temporal profiles of the wetting films formed on a) a freshly cleaned gold surface with $\theta_r=17^\circ$, and b) a gold surface hydrophobized with potassium amyl xanthate with $\theta_r=81^\circ$. $h_e$ represents the equilibrium film thickness, and $h_c$ represents the critical rupture thickness.
Figure 2.3  Radial velocities of the liquid in a) a wetting film formed on gold surfaces with $\theta_r = 17^\circ$, and b) with $\theta_r = 81^\circ$ as obtained from the data given in Figure 2.2. The acceleration of film thinning at $r < 0.02$ mm is due to the presence of the negative disjoining pressure.
Figure 2.4  Shear rates at the solid/water interface in the wetting films formed on the gold surface with a) $\theta_r = 17^\circ$ and b) $\theta_r = 81^\circ$ as obtained from the data in Figure 2 under non-slip boundary conditions at the air/water and solid/water interfaces. The high shear rates observed in b) are due to the negative disjoining pressure in the wetting film.
Figure 2.3 shows the temporal changes in the average radial velocity, \( u(r,t) \), of the liquid in the wetting films. The values were obtained using the continuity equation,

\[
\frac{\partial h}{\partial t} = - \frac{1}{r} \frac{\partial (rhu)}{\partial r}
\]  

(2.12)

under nonslip boundary conditions on both interfaces. Eq. (2.12) was used to determine \( u(r,t) \) from the velocities of film thinning (\( \partial h/\partial t \)) obtained from the temporal profiles (\( h(r,t) \)) of the films presented in Figure 2.2. Since the profiles are axial-symmetric, the radial velocity, \( u(0,t) \), at the center of the film is zero.

During film thinning, \( u \) increased with \( r \), reached a maximum, and then decreased as \( r \) increased further. In the film formed on the untreated gold surface, \( u \) decreased steadily as the film became thinner, which can be attributed to the increase in positive (or repulsive) disjoining pressure and, hence, a decrease in \( p \) with decreasing film thickness. At \( t = 11 \) s, \( u \) was almost zero, indicating that the film reached an equilibrium thickness, at which disjoining pressure was equal to the capillary pressure and \( p \approx 0 \).

In the wetting film formed on the KAX-treated hydrophobic gold, \( u \) increased with time at \( r < 0.02\text{-}0.03 \) mm. The acceleration of the film thinning kinetics observed in this region may be due to the presence of a negative (attractive) disjoining pressure in the film. Note here that the acceleration increased with decreasing film thickness particularly at \( h \) below approximately 100 nm. At the radial distances above approximately 0.03 mm, the film behaved similarly as that formed on the untreated gold surface. In this region, the films were too thick for the negative disjoining pressure to play a role in film thinning, particularly during the initial stages of the film thinning process.

From the radial velocity gradients in the vertical (\( z \)) direction, the shear rates, \( \partial u(z)/\partial z \), at the solid/liquid interface were obtained, with the results plotted in Figure 2.4. The calculations were made under the nonslip boundary condition at both the air/water and solid/water interfaces. On the untreated gold surface (Fig. 2.4a), the shear rate decreased steadily with decreasing film thickness and reached zero at the equilibrium film thickness.

The shear rates calculated for the film formed on the hydrophobic gold (Fig. 2.4b) were much higher. However, the shear rates obtained during the initial stages of the film thinning process were about the same as those calculated for the film formed on the hydrophilic gold (Fig. 2.4a).
For example, the shear rate was $300 \text{ s}^{-1}$ at $t = 0\text{ s}$, which was the same as obtained for the film formed on the untreated gold. This finding suggests that the initial film thinning process is controlled by the excess pressure created due to curvature change ($p_{\text{cur}}$). As the film thinning continued, the shear rate increased with time and reached a maximum of $5500 \text{ s}^{-1}$ at $t = 0.8\text{ s}$. The increase in shear rate may be attributed to the increase in the negative disjoining pressure with decreasing film thickness.

Eqs. (2.5) and (2.6) show that under the nonslip condition, $i.e., U_u = 0$, the kinetics of film thinning varies with the excess pressure ($p$) in a wetting film. Figure 2.5 shows the values of $p$ plotted vs. the radial distance ($r$) as obtained using Eq. (2.8). At $t = 0\text{ s}$, the $p$ in the wetting film formed on the surface of untreated gold was $50 \text{ N/m}^2$ at the center, which is close to the value of

![Figure 2.5](image)

Comparison of the excess pressures ($p$) in the thin films of water formed on the gold surfaces with a) $\theta_r = 17^\circ$ and b) $\theta_r = 81^\circ$. The large values of $p$ in b) are due to the negative disjoining pressure in the film and are responsible for the high drainage rates.
60 N/m² obtained with the KAX-treated gold surface. This is not surprising because the initial film thinning process is controlled by $p_{\text{cur}}$. As the film thinning continues, however, the $p$ in the former decreased gradually with time and became zero at $t = 11$ s, when the film thickness reached $h_e$. In the film formed on the KAX-treated gold, the excess pressure increased...
dramatically to 2000 N/m² at t = 0.7 s, when the local film thickness at the center reached 44 nm. It can be stated, therefore, that the large value of $p$ and the high pressure gradient were responsible for the fast film thinning kinetics observed in Figure 2.2.

The driving force for film thinning is the excess hydrodynamic pressure ($p$) in the film, which in turn varies with the pressure change due to curvature ($p_{\text{cur}}$) and the disjoining pressure in the film ($\Pi$), as shown in Eq. (2.9). Figure 6 shows the changes in $p$, $p_{\text{cur}}$ and $\Pi$ with film thickness ($h$), as obtained using Eqs. (2.8), (2.10) and (2.11), respectively. In these calculations, the values of $\gamma = 72$ mN/m and $R = 2$ mm were used. In the wetting films formed on both the untreated and treated gold surfaces, $p_{\text{cur}}$ increased with decreasing film thickness and reached a plateau value of 72 N/m². In the film formed on the untreated surface with $\theta_r = 17^\circ$, the $p$ at the center of the film increased slightly as the film thinned from approximately 300 to 200 nm, where $p$ was dominated by $p_{\text{cur}}$. As the film drained further, $p$ decreased sharply due to the corresponding increase in the positive disjoining pressure. In the wetting film formed on the KAX-treated gold surface with $\theta_r = 81^\circ$, however, $p$ increased sharply with decreasing film thickness due to the increase in the negative disjoining pressure. Obviously, the sharp increase in $p$ was responsible for the fast kinetics of film thinning shown in Fig. 2.2b. Note here that at $h < 100$ nm, $p_{\text{cur}}$ is negligibly small in magnitude as compared to $\Pi$. Thus, film thinning is controlled initially by the curvature pressure and subsequently by the negative disjoining pressure.

### 2.5 Discussion

The results presented in the foregoing section show that the driving force for the drainage of wetting films is the excess pressure ($p$) in the films. Initially, $p$ is dominated by the pressure associated with the changes in curvature ($p_{\text{cur}}$) of the air/water interface and then by the disjoining pressure ($\Pi$) created by the surface forces in the film.

Figure 2.7 shows the changes in these parameters with the thickness ($h$) of the wetting films formed on the untreated gold surfaces with $\theta_r = 17^\circ$ and the KAX-treated gold with $\theta_r = 81^\circ$. In the former, $\Pi$ may consist of two components in accordance to the DLVO theory

$$\Pi = \Pi_d + \Pi_e$$  \hspace{1cm} (2.13)

i.e., the dispersion force component,
\[ \Pi_d = -\frac{A_{132}}{6\pi h^3} \]  

(2.14)

and the electrostatic force component due to double-layer interaction,

\[ \Pi_e = -\frac{\varepsilon \varepsilon_0 \kappa^2}{2\sinh(\kappa h)} \left[ (\psi_1^2 + \psi_2^2) \cothh(\kappa h) - 2\psi_1 \psi_2 \coth(\kappa h) \right] \]  

(2.15)

In Eq. [14], \( A_{132} \) is the Hamaker constant for the wetting film of water formed on gold. Eq. [15] is the Hogg–Healey–Fuerstenau (HHF) approximation [53], in which \( \varepsilon_0 \) is the permittivity in vacuum, \( \varepsilon \) dielectric constant of water, \( \psi_1 \) and \( \psi_2 \) the double-layer potentials at the solid/water and air/water interfaces, respectively, and \( \kappa \) is the reciprocal Debye length. In this communication, the subscripts 1, 2, and 3 represent solid, gas, and water phases, respectively. Other investigators also used the HHF approximation to study bubble-particle interactions [42, 54, 55].

In using Eq. [14], the value of \( A_{132} = -14.8 \times 10^{-20} \) J was used as reported by Tabor et al. [56]. These investigators used an AFM to directly measure the repulsive van der Waals force between air bubble and bare gold surface in water. The \( A_{132} \) value was close to those that can be calculated using the geometric mean combining rule with the Hamaker constants for gold (10-40 \( \times 10^{-20} \) J) from the full Lifshitz equation and for air bubbles (3.7 \( \times 10^{-20} \) J) in water [57].

In using Eq. [15], \( \psi_1 \) was taken to be the same as the \( \zeta \)-potential of the micro-spheres of gold in distilled water, which was reported to be -40 mV [46]. On the other hand, the values of \( \psi_2 = -29 \) mV and \( \kappa^1 = 42 \) nm were obtained by fitting the \( \Pi \) values (circles), obtained from the temporal film profiles shown in Figure 2a using Eq. (2.11), to Eqs. (2.13)-(2.15). As shown in Fig. 2.7a, the fit is reasonable. The value of -29 mV obtained for the air/water interface from the fitting procedure is close to the \( \zeta \)-potentials of argon bubbles in distilled water as reported by Usui et al. [58]. These authors calculated the \( \zeta \)-potentials from the Dorn potentials measured using bubble columns. They found that unlike the case with glass beads, the \( \zeta \)-potentials of bubbles become less negative with increasing size, which was attributed to the likelihood that the surface charges are displaced backward resulting in a weaker electric dipole and hence a reduced Dorn potential [59]. Likewise, the charges at the air/water interface of a wetting film may traverse toward the edge of the film and give rise to the same effect. Note here that the Debye
length obtained from the curve fitting exercise was relatively small for the interactions in Millipore water. In a previous work, one of us fitted the force curves obtained between glass
sphere and silica plate in Nanopure water using AFM with $\kappa^1 = 42$ nm [22].

Note in Figure 2.7a that both the electrostatic and van der Waals force components of the disjoining pressure were repulsive, with the former being much larger. Also shown in the figure are the changes in curvature pressure ($p_{\text{cur}}$) with $h$. At the crossover point between the $p_{\text{cur}}$ vs. $h$ and the $\Pi$ vs. $h$ curves, $\Pi$ is equal to $p_{\text{cur}}$. At this point, the excess pressure in the film ($p$) becomes zero according to Eq. (2.6), when the film thinning process stops, resulting in the formation of a stable film at an equilibrium thickness ($h_e$). As shown, the value of $h_e = 105$ nm obtained in experiment agrees well with the predictions from the DLVO theory.

Figure 2.7b shows the results obtained with the KAX-treated gold with $\theta_r = 81^\circ$. The triangles represent the $\Pi$ values obtained from the temporal and spatial film profiles obtained in experiment using Eq. (2.11). As shown, $\Pi$ is negative and becomes increasingly so with decreasing film thickness. Also shown are the isotherms of $\Pi_e$ and $\Pi_d$ drawn by assuming that both $\psi_1$ and $A_{131}$ do not change due to xanthate adsorption. Several investigators showed indeed that the $\zeta$-potentials of sulfide minerals do not change significantly upon xanthate adsorption [60]. That $\Pi < 0$ while both $\Pi_e$ and $\Pi_d$ are positive show that there should be an attractive force, i.e., hydrophobic force, in the wetting film under consideration. Thus, one may write the extended [61] (or modified [62]) DLVO theory

$$\Pi = \Pi_d + \Pi_e + \Pi_h$$

(2.16)

in which $\Pi_h$ represents the contribution from the hydrophobic force. Since the values of $\Pi$, $\Pi_d$, and $\Pi_e$ are known, one can back-calculate the values of $\Pi_h$ using Eq. (2.16). In the present work, we represent the hydrophobic disjoining pressure as follows,

$$\Pi_h = \frac{C}{2\pi D} \exp\left(-\frac{h}{D}\right)$$

(2.17)

where $C$ and $D$ (decay length) are constants for the surface forces measured between two cylinders or between sphere and flat surfaces. We adjusted these two parameters to obtain the values of $\Pi_h$ that can best fit the $\Pi$ values obtained from the film profiles. It was found that $C = -1.55$ mN/m and $D = 36$ nm can best fit the experimental data. The $\Pi$ and $\Pi_h$ isotherms obtained in this manner are given as dotted and solid lines, respectively, in Figure 2.7b. Owing to the large negative $\Pi$, $p$ increases beyond $p_{\text{cur}}$ according to Eq. (2.9), and hence the film thinning process
accelerates until the film ruptures. The large decay length obtained in the present work might be partly due to the fact that we did not consider the capillary wave mechanism [63, 64]. Manica et al. [43] showed, however, that it is not necessary to invoke capillary waves to predict the time at which the aqueous film between mica and mercury collapses. The $C$ and $D$ values obtained from the data presented in Figure 2.7b are comparable to those reported in the literature for the hydrophobic interactions between two macroscopic surfaces [35, 65, 66].

Thermodynamically, wetting films rupture when contact angle ($\theta$) is greater than zero, or the wetting tension ($\gamma_{12}-\gamma_{13}$) is less than the surface tension of water ($\gamma_{23}$). For the process of bubble-particle attachment, receding angle ($\theta_r$) would be more relevant than the equilibrium ($\theta_o$) or advancing ($\theta_a$) angles. In the present work, two gold surfaces with $\theta_o = 42^\circ$ and $91^\circ$ have been studied. Only with the latter, we observed film rupture, which can be explained in view of the Frumkin and Derjaguin isotherm [11, 12],

$$\cos \theta_o = 1 - (1/\gamma_{23}) \int_0^{h_0} \Pi(h)dh$$

(2.18)

where $h_0$ is the thickness of the film in equilibrium with the meniscus of water. From Eq. (2.2), we can obtain an expression for the hydrophobic disjoining pressure as follows,

$$\Pi_o = \frac{1}{2\pi} \left[ \frac{C_1}{D_1} \exp\left(-\frac{h}{D_1}\right) + \frac{C_2}{D_2} \exp\left(-\frac{h}{D_2}\right) \right]$$

(2.19)

where the parameters with subscripts 1 and 2 represent those for the short- and long-range hydrophobic forces, respectively. One can substitute Eq (2.19) into Eq. (2.16) along with Eqs. (2.14) and (2.15) to obtain $\Pi(h)$, which can then be substituted into Eq. (2.18) for integration. By integrating it from infinity to $h_0$, one obtains the following

$$\cos \theta_o = 1 + \frac{\Delta G}{\gamma_{23}}$$

(2.20)

From Eq. (2.1),
\[ \Delta G = -\int_{h_0}^{h} \Pi(h) \, dh \]

\[ = \gamma_{23}(\cos \theta_o - 1) \]

(2.21)

where \( \Delta G \) is the Gibbs free energy change per unit area associated with thinning of a wetting film from infinity to a distance \( h_0 \).

For the KAX-treated gold surface, \( A_{132} \) is negative; therefore, the first term in the bracket representing the free energy change per unit area due to van der Waals interaction (\( \Delta G_d \)) is positive and hence is not conducive to film thinning and rupture. The second term in the bracket represents the free energy change due to electrostatic interaction (\( \Delta G_e \)). It can be negative, and its magnitude can be larger than that of \( \Delta G_d \) if \( \psi_1 \) and \( \psi_2 \) have opposite signs or have the same sign but of large difference in magnitudes. The fourth term represents the free energy change due to the long-range hydrophobic force (\( \Delta G_h \)), which is negative as \( C_2 < 0 \). However, its magnitude is smaller than that of \( \Delta G_d > 0 \); therefore, the film remains stable. Only the short-range hydrophobic pressure can become large enough at smaller film thickness to overcome the repulsive van der Waals pressure and cause the film to rupture. At \( h < h_c \), the magnitude of \( \Delta G_h \) becomes larger than that of \( \Delta G_d \).

In the present work, we used Eq. (2.20) to determine the \( C_1 \) and \( D_1 \) parameters for the short-range hydrophobic force. We know the values of \( C_2 \) and \( D_2 \) from curve fitting the data presented in Figure 2.7b to Eq. (2.17). (The \( C \) and \( D \) parameters of this equation can be considered equal to \( C_2 \) and \( D_2 \), respectively, as the experimental data show only the long-range part of \( \Pi_h \).) We also know the values of \( A_{132} \), \( \psi_1 \), \( \psi_2 \), \( \kappa \), \( \theta_o \), and \( \gamma_{23} \). Although we do not have the value of \( h_0 \), we know that it is the film thickness at \( \Pi = 0 \). Thus, we have two equations and three unknowns. In the present work, we estimated the values of \( C_1 \) and \( D_1 \) to be -0.642 N/m and 2.3 nm, respectively, under the assumption that \( h_0 < 1 \) nm. The value of \( h_0 \) is found to be 0.56 nm, which is equivalent to approximately two layers of water molecules adsorbed on the hydrophobic surface of \( \theta_o = 91^\circ \) at equilibrium.

In the present work, it was possible to measure only the long-range part of the hydrophobic disjoining pressure as shown in Figure 2.7b. The reason is that the wetting film has already ruptured catastrophically by the time the attractive short-range hydrophobic pressure becomes strong enough to overcome the repulsive van der Waals pressure. It would, therefore, be
impossible to measure the short range hydrophobic force in the wetting film formed on strongly hydrophobic surface. On the other hand, the theoretical analysis carried out in view of the Frumkin-Derjaguin theory of wetting suggests that short-range hydrophobic force should exist in wetting films if the film is to rupture.

As shown in Figure 2.7b, $\Pi_h$ extends to $h \approx 150$ nm, which is beyond the range of hydrophobic forces observed between hydrophobic surfaces of solids. On the other hand, the studies conducted on foam films (or between two bubbles) showed that hydrophobic force affects drainage rates at film thickness as large as 250 nm [67]. This observation was given an explanation that the air-side of the air/water interface is more hydrophobic than the best-known hydrophobic substances known to date in view of the interfacial tensions involved [68]. Note in Figure 2.6b that the excess pressure ($p$) in the wetting film on the hydrophobized gold surface begins to increase at $h \approx 150$ nm where $\Pi_h$ begins to appear. Recognizing that it is the excess pressure $p$ that is the driving force for film drainage, it would be reasonable to suggest that the long-range hydrophobic force is responsible for the accelerated film drainage observed in the present work, while the short-range hydrophobic force is responsible for the film rupture at $h_c = 29$ nm.

Above discussions suggest that hydrophobic force can affect both film drainage and rupture. However, the accelerated drainage rate observed with the KAX-treated hydrophobic gold could also be explained by the slip at the solid/liquid interface [69, 70]. It has already been shown that the no-slip boundary condition can be used for the air/water interface of the wetting film formed in pure water [46, 49, 71, 72]. In this regard, we may need to consider the slip only at the solid/water interface. In general, slip velocity varies with shear rate, i.e., $U_u = b\dot{\gamma}$, where $b$ is the slip length and $\dot{\gamma}$ is the shear rate. Assuming that the horizontal liquid flow velocity, $u(z)$, is the sum of pressure-driven flow, $u_p(z)$, and slip-driven flow, $u_s(z)$, one can readily derive the following relation

$$u(z) = u_p(z) + u_s(z) = \frac{1}{2\mu} \frac{\partial p}{\partial r}(z^2 - zh) + U_u \left( \frac{h - z}{h} \right)$$

(2.22)

where $U_u$ is the slip velocity at the solid/water interface. It can be readily shown that

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\[ U_v = -\frac{b}{2\mu} \frac{\partial p}{\partial r} \frac{h^2}{b+h} \]  

(2.23)

Eqs. (2.22) and (2.23) were used to calculate the ratios between \( u_p \) and \( u_u \) at \( t = 0.7 \) s and \( h = 44 \) nm, which are plotted in Figure 2.8. The calculations were made at three arbitrarily chosen slip lengths at the solid/liquid interface: \( b = 10, 20 \) and \( 40 \) nm. The ratio becomes smaller at the center than near the edge, indicating that slip becomes more important as film becomes thinner. At \( b = 10 \) nm, the ratio is approximately 2 at the center, indicating that the pressure-driven flow \( (u_p) \) is more important than the slip-driven flow \( (u_u) \) in this region. The slip plays as important a role as the excess pressure \( (p) \) at \( b = 40 \) nm, in which case the ratio becomes 1.

Assuming that the slip at the solid/water interface affects the flow velocities in thin films, Eq.

![Figure 2.8](image)

Figure 2.8 The ratios between the pressure-driven velocities \( (u_p) \) and the slip-driven velocities \( (u_u) \) along the radial direction at \( t = 0.7 \) s and \( h = 44 \) nm as measured at the center of the film \( (r = 0) \). The number on each curve represents the arbitrary slip lengths in nm used in the calculation.
(2.11) can be modified using the continuity equation to obtain,

\[
\Pi = \frac{2\gamma}{R} - \frac{\gamma}{r} \left( \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) \right) - \int_{r=0}^{r=\infty} \frac{12\mu(b+h)}{r h^3 (4b+h)} \left[ \int_{r=0}^{r} r \frac{\partial h}{\partial t} dr \right] dr
\]

which can be used to predict \( \Pi \) from slip length and the vertical thinning velocity \( (\partial h/\partial t) \). With Eq. (2.24), we calculated \( \Pi \) vs. \( h \) curves at \( b = 0, 20, 40, \) and 1000 nm, which were then used to obtain the \( \Pi_h \) vs. \( h \) curves shown in Figure 9 in the same manner as employed for obtaining the \( \Pi_h \) vs. \( h \) curves given in Figure 7b. Under the no-slip boundary condition, the decay length \( (D) \) of \( \Pi_h \) was 36 nm. As \( b \) increased to 20 nm, \( D \) decreased to 35 nm. Doubling \( b \) to 40 nm caused a decrease in \( D \) to 34 nm. Even at \( b = 1000 \) nm, \( D \) decreased only to 28 nm. These findings suggest that it is difficult to explain the accelerated film drainage with slip alone. It is necessary to recognize the presence of the long-range hydrophobic force in wetting films.

Even if slip can explain increased drainage rate to some extent, it would be difficult to explain the rupture of the wetting films formed on hydrophobic surfaces. As has already been noted in a foregoing paragraph, wetting films can rupture when there is a short-range hydrophobic force that can overcome the repulsive van der Waals force. Knowing that the rupture can occur when \( \theta > 0 \), it may be reasonable to expect to see a short-range hydrophobic force as long as contact angle is greater than zero. At high contact angles, a long-range hydrophobic force may also be present and help expedite the kinetics of film thinning. The solid/water interface may slip at high contact angle, but the data obtained in the present work show that its effect is small as compared with the effect of the long-range hydrophobic force. As shown in Figure 2.6b, the negative disjoining pressure causes the excess pressure \( (p) \) to increase. If the disjoining pressure is positive, on the other hand, the \( p \) decreases with decreasing film thickness. It is possible, nevertheless, that slip can be an important factor at contact angles much higher than studied in the present work and when a surface has a much higher degree of roughness that would help trap vapor phase. Further investigation is needed to study the effects of contact angles in greater detail.

In the present work, we assumed that there is no slip at the air/water interfaces of the wetting films studied in the present work. This assumption was based on the observation that the thinning kinetics of the wetting films formed in the absence of surfactant can be modeled using the Reynolds lubrication theory under the no-slip boundary condition [46, 49, 71, 72]. It is well
known, on the other hand, that the surface of an air bubble rising in surfactant-free water is mobile [73]. Apparently, the air/water interface in the confined space of a wetting film behaves differently from the same in free space. Parkinson and Ralston [71] reported an interesting observation that a bubble rising toward a particle goes through a transition from the full-slip to no-slip boundary conditions.

In the present work, we used two gold surfaces, one with \( \theta_r = 17^\circ \) and the other with \( \theta_r = 81^\circ \). A question to be raised here may be why the former behaved as if it was a hydrophilic surface. An easy answer may be that the substrate was not hydrophobic enough to create a significant hydrophobic force. According to Churaev [16], the DLVO theory is applicable for colloids with contact angles in a narrow range of contact angles, \( i.e., \) between \( 20^\circ \) to \( 40^\circ \). One should include
the contributions from the structural forces, \textit{i.e.}, hydration force at $\theta < 20^\circ$ and the hydrophobic force at $\theta > 40^\circ$. Further, Derjaguin and Churaev [14] noted that “The formation of large contact angles cannot be explained without including the structural forces in the calculation of wetting.”

The methodology developed in the present work allows direct measurement of disjoining pressures on flat surfaces without a need to use curved surfaces. For many biological and mineral materials, it is difficult to prepare curved surfaces. The methodology should also be useful for studying the surface chemistry of deformable materials such as oil, bitumen, foam films, \textit{etc.} Furthermore, it can measure the disjoining pressures of unstable films, which has been a challenge for a long time. It is the information on the negative disjoining pressure that is useful for designing new materials with super-hydrophobic, self-cleaning, corrosion resistant, and high-efficiency heat transfer surfaces. In addition, one can readily convert measured disjoining pressures to surface forces using the Derjaguin approximation [25].

### 2.6 Summary and Conclusion

The stability of wetting films of water formed on gold surfaces was studied by monitoring the spatial and temporal profiles ($h(r,t)$) of the film. The film radii were kept small ($<20 \mu m$) to avoid dimple formation, so that the data obtained across the film can be used to determine the disjoining pressure isotherms ($\Pi(h)$) in the thin liquid film (TLF) between a flat substrate and an air bubble. The hydrodynamic information derived from the profiles and arbitrary slip lengths ($b$) were then used as input to an analytical expression for disjoining pressure ($\Pi$) derived from the Reynolds lubrication theory. The disjoining pressures in the water film formed on a gold surface with a receding contact angle ($\theta_r$) of 17$^\circ$ showed repulsive disjoining pressures, while those in the film formed on a gold with $\theta_r = 81^\circ$ showed negative disjoining pressures. The results were analyzed to determine the electrostatic ($\Pi_e$) and hydrophobic ($\Pi_h$) components of $\Pi$. The hydrophobic disjoining pressure is represented as a double-exponential function, with decay lengths ($D$) of 2.3 and 36 nm under the no-slip boundary condition. The experimental data obtained in the present work suggest that the short-range hydrophobic force is responsible for the rupture of wetting films formed on the hydrophobic surface, while the long-range hydrophobic force is responsible for the accelerated film thinning. It was found that the slip length has minimal impact on the decay length.
2.7 References


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Chapter 3.  A Fundamental Study on the Role of Collector in the Kinetics of Bubble-Particle Interaction

ABSTRACT

As an air bubble approaches a gold surface, a thin liquid film (TLF) is formed in between. The excess pressure \( p \) of the liquid in the film determines the rate of film thinning, which is of critical importance in flotation. In the present work, we have measured the kinetics of film thinning using a modified thin film pressure balance (TFPB) technique by monitoring the interference patterns using a high speed camera. The results were analyzed using the Reynolds lubrication theory. It has been found that initially a TLF thins by the curvature pressure \( p_{\text{cur}} \) created due to the bubble deformation and subsequently by the disjoining pressure \( \Pi \) created by the surface forces in a wetting film. The results show that \( \Pi > 0 \) on a hydrophilic surface and \( \Pi < 0 \) on a surface hydrophobized by xanthate. Thus, the role of xanthate in flotation is to create the hydrophobic force that can overcome the repulsive force present in wetting films. It has been found also that the use of small bubbles is more effective for increasing the kinetics of film thinning and hence flotation rate.
3.1 Introduction

In flotation, bubbles and particles collide with each other before hydrophobic particles are selectively collected on the surface of air bubbles. During the initial stages of collision, a bubble deforms and produces a thin liquid film (TLF) between the bubble and particle, which is referred to as wetting film. The curvature change associated with the deformation creates a capillary pressure and hence causes the film to drain. As the film thins due to drainage to a thickness below ~200 nm, surface forces begin to control the drainage process. On a hydrophobic surface, the film becomes unstable and ruptures, allowing bubble-particle adhesion to occur. On a hydrophilic surface, the film remains stable, denying bubble-particle adhesion.

Many investigators studied the mechanisms by which wetting films become unstable when mineral particles are hydrophobized by collector coating. It has been suggested that the films are destabilized by the negative disjoining pressure \( \Pi \) \[1\] caused by the hydrophobic force present in the film \[2\]. In 1982, Israelachvili and Pashley \[3\] reported the first direct measurement of the hydrophobic force, albeit in the TLFs between two hydrophobic surfaces rather than in wetting films, using the surface force apparatus (SFA). It was shown later that hydrophobic forces can also be measured using the atomic force microscope (AFM) \[4\]. More recently, we have measured the negative disjoining pressures in wetting films using a modified thin film pressure balance (TFPB) technique, in which the spatial and temporal profiles of an air bubble approaching a flat hydrophobic surface was monitored by means of a high-speed camera \[5\].

Disjoining pressure is defined as the change in excess Gibbs free energy per unit area of a flat TLF \( G \) with thickness \( h \) \[6, 7\],

\[
\Pi(h) = -(\partial G/\partial h)_{p, T, \mu_s}
\] (3.1)

at constant pressure \( p \), temperature \( T \), and chemical potential of solutes \( \mu_s \). Thus, a TLF should be stable thermodynamically when \( \partial \Pi/\partial h < 0 \). The concept of disjoining pressure is useful for analyzing the stability of colloids, foams and wetting films. According to the DLVO theory,

\[
\Pi = \Pi_e + \Pi_d
\] (3.2)
where $\Pi_e$ is the disjoining pressure due to electrostatic interaction between overlapping electrical double layers and $\Pi_d$ is the disjoining pressure due to the van der Waals dispersion force present in a TLF. Eq. (3.2) is applicable when there are no other forces in the film, which may be the case when the contact angles ($\theta$) of interacting surfaces are in the range of $20^\circ$ to $40^\circ$ [8].

At higher contact angles, Eq. (3.2) may be extended to include the contribution from the hydrophobic force ($\Pi_h$) as follow,

$$\Pi = \Pi_e + \Pi_d + \Pi_h$$  \hspace{1cm} (3.3)

In flotation, both $\Pi_e$ and $\Pi_d$ are usually positive (or repulsive); therefore, the use of Eq. (3.2) would not give a negative disjoining pressure that is required for bubble-particle adhesion. Eq. (3.3), on the other hand, allows $\Pi$ to become negative when $\Pi_h$, which is negative, can override the effects of $\Pi_e$ and $\Pi_d$. For bubble-particle interactions, $\Pi_d$ is always positive and $\Pi_e$ can vary with pH and the type and the amount of a collector used for flotation. In most cases, the surface charges of the bubbles and particles are of the same sign (usually negative at alkaline pH); therefore, both $\Pi_e$ and $\Pi_d$ are repulsive. Under these conditions, it is necessary that $\Pi_h < 0$ for bubble-particle adhesion to occur.

The Derjaguin approximation [9] relates $\Pi_h$ to the hydrophobic force ($F_h$) as follows,

$$\frac{F_h}{R} = 2\pi \int_0^\infty \Pi_h dh$$  \hspace{1cm} (3.4)

where $R$ is the radius of curvature of the hydrophobic surfaces interacting with each other. The hydrophobic forces measured in experiment are commonly represented using the following relation,

$$\frac{F_h}{R} = C \exp\left(-\frac{h}{D}\right)$$  \hspace{1cm} (3.5)

where $C$ and $D$ (decay length) are fitting parameters. Form Eqs. (4) and (5), one can obtain the following relation,

$$\Pi_h = \frac{C}{2\pi D} \exp\left(-\frac{h}{D}\right)$$  \hspace{1cm} (3.6)
While the electrical double-layer and van der Waals forces are well understood, there is no consensus on the origin of the hydrophobic force. Thus, one can determine $\Pi_e$ and $\Pi_d$ using well-defined theoretical expressions, while Eq. (3.6) is empirical. According to Rabinovich and Derjaguin [10], hydrophobic force originates from the structural changes in the overlapping boundary layers of water as two hydrophobic surfaces approach each other. Eriksson et al. [11] derived an exponential force law based on the basis of the same concept. However, other investigators showed evidences that the ‘hydrophobic force’ is an artifact due to the bubbles or cavities present in TFLs. A recent view on the subject is that while the short-range attractions observed at separations below $\sim$20 nm are ‘true’ hydrophobic force, longer-range attractions may not be related to surface hydrophobicity [12]. It has been shown, on the other hand, that the range of hydrophobic force increases with increasing chain length of $n$-alkane homologues [13] and water contact angle [14, 15].

As is well known, hydrocarbon chains of collector molecules associate with each other to form self-assembled monolayers or hemi-micelles [16, 17]. The driving force for the molecular-scale hydrophobic interaction is due to the configurational rearrangement of water molecules as two hydrophobic species come into contact, which entails entropy increase. It has been shown, however, that the hydrophobic interaction at macroscopic scale involves a decrease in both entropy and enthalpy, with the enthalpy change ($\Delta H$) being slightly larger in magnitude than the change in the entropy term ($T\Delta S$) [18]. These findings suggest that some type of structure may be forming in the vicinity of hydrophobic surfaces in support of the structural theory of the hydrophobic force as originally proposed by Derjaguin and his colleagues [19, 20].

In the present work, we have measured the negative disjoining pressures ($\Pi_h$) present in the wetting films formed on hydrophobic gold surfaces using the modified TFPB technique described above. Potassium amyl xanthate (KAX) was used for the hydrophobization of gold. The results will be used to discuss the basic role of collectors in flotation.
3.2 Experiment

3.2.1 Materials

Gold-coated glass plates (CA134, EMF) were used as substrates for wetting films. They were cleaned in a piranha solution (7:3 by volume of H$_2$SO$_4$:H$_2$O$_2$) for 10 minutes at 120 °C, rinsed with Millipore water (>18.2 MΩ/cm), and then dried in a nitrogen gas stream. The freshly-cleaned gold substrate exhibited rms roughness of 1-2 nm as determined from AFM images. The gold plate obtained in this manner exhibited an equilibrium contact angle ($\theta_o$) of 42° with receding ($\theta_r$) and advancing ($\theta_a$) angles of 17° and 60°, respectively, as measured by using the dynamic sessile drop technique.

A gold plate obtained in the manner described above was rendered hydrophobic by immersing it in a 10$^{-5}$ M potassium amyl xanthate (KAX) solution, followed by rinsing with Millipore water and drying in a nitrogen gas stream. The hydrophobizing agent had been purified twice just before use by dissolving a technical grade KAX (>90%, TCI America) in acetone (HPLC grade, Fisher Sci.) and re-crystallizing in diethyl ether (99.999%, Sigma-Aldrich). KAX solution is prepared freshly just before use.

3.2.2 Thin Film Pressure Balance

Both the xanthate-treated and untreated gold plates were used as substrates for wetting films of water. The kinetics of film thinning was monitored using the modified thin film pressure balance (TFPB) technique [21]. The interference patterns (or Newton rings) are recorded using a high-speed CCD camera (Fastcam 512PCI, Photron) at 120 frames per second. A monochromatic light with a center wavelength of 546 nm was obtained by passing the light source from a mercury short-arc lamp through a basspass interference filter (10 nm Bandwidth, Edmund Optics).

Initially, the excess water in the film holder was removed by means of a piston pump until the Newton ring was appeared on the camera screen. The film was then allowed to thin spontaneously, while recording the interference patterns as a function of time. The interference fringes behaved perfectly in axial-symmetric manner; therefore, we analyzed the data in
cylindrical coordinates. All the images were smooth and showed no irregularities. The spatial and temporal profiles of the wetting films were obtained by analyzing the changes in gray levels of the interference patterns using the Scheludko’s method [22]. The temporal and spatial profiles of the non-dimpled wetting films formed on (a) a freshly cleaned gold surface with $\theta_r = 17^\circ$, and (b) a gold surface hydrophobized with potassium amyl xanthate with $\theta_r = 81^\circ$. $h_e$ represents the equilibrium film thickness. The film formed on the gold surface with $\theta_r = 81^\circ$ ruptures at $h_e = 40$ nm at 0.80 s.  

![Image of spatial and temporal profile](image.png)

Figure 3.1 Spatial and temporal profile of the non-dimpled wetting films formed on (a) a freshly cleaned gold surface with $\theta_r = 17^\circ$, and (b) a gold surface hydrophobized with potassium amyl xanthate with $\theta_r = 81^\circ$. $h_e$ represents the equilibrium film thickness. The film formed on the gold surface with $\theta_r = 81^\circ$ ruptures at $h_e = 40$ nm at 0.80 s.
were used to obtain the information on the rate of film drainage and determine the disjoining pressure ($\Pi$) in the thin film.

Film thinning experiments were conducted using both small and large films of radii ($r_f$) in the range of 10-20 $\mu$m and 60-70 $\mu$m, respectively. In general, larger films thin with dimples and smaller films do so without dimples. The film radii were controlled by means of a piston pump.

### 3.3 Result and Discussion

Figure 3.1 compares the temporal profiles of the wetting film formed on (a) a freshly cleaned gold surface with a receding contact angle ($\theta_r$) of $17^\circ$ and (b) a gold surface hydrophobized with potassium amyl xanthate (KAX) with $\theta_r = 81^\circ$. The hydrophobic gold surface was prepared by immersing it in a $10^{-5}$ M KAX solution for 10 min. The xanthate-treated gold surface exhibited equilibrium, advancing and receding angles of $91^\circ$, $99^\circ$ and $81^\circ$, respectively. As shown, the film

![Figure 3.1](image)

**Figure 3.1** Minimum film thickness ($h_{\text{min}}$) vs. time ($t$) plots for the non-dimpled wetting films formed on the gold surfaces with and without KAX treatment. The number on each curve represents the receding contact angle ($\theta_r$). Untreated gold showed $\theta_r = 17^\circ$. 

![Figure 3.2](image)

**Figure 3.2** Minimum film thickness ($h_{\text{min}}$) vs. time ($t$) plots for the non-dimpled wetting films formed on the gold surfaces with and without KAX treatment. The number on each curve represents the receding contact angle ($\theta_r$). Untreated gold showed $\theta_r = 17^\circ$. 

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of water formed on the xanthate-treated hydrophobic gold surface was much faster than that on the bare gold surface. On the untreated bare gold surface, the film thinned gradually, and reached an equilibrium thickness \((h_e)\) of 103 nm in 12 s. The film formed on the xanthate-treated gold surface thinned much faster and ruptured within milliseconds at the critical rupture thickness \((h_c)\) of 40 nm.

Figure 3.2 shows a set of film thickness vs. time plots made for the wetting films formed on gold-coated plates immersed in a \(10^{-5}\) M KAX solution for different contact times. The film thicknesses used in these plots were the minimum thicknesses \((h_{\text{min}})\) of the films without dimples. The receding contact angles \((\theta_r)\) increased from 73° to 81° as the contact time was increased from 2 to 10 minutes. After the 60 minutes of contact time, \(\theta_r\) decreased to 78° most probably due to the adsorption of xanthate in multi-layers. As shown, the film thinning kinetics increased with increasing \(\theta_r\).

The liquid in a wetting film thins when the pressure of the liquid in the film is higher than that in the far field. A normal stress balance across a horizontal wetting film gives the following relation,

\[
p = p_{\text{cur}} - \Pi
\]  
(3.7)

where \(p\) is the excess pressure in the film, \(p_{\text{cur}}\) the pressure due to the changes in curvature, and \(\Pi\) is the disjoining pressure due to the surface forces acting between the air/liquid and solid/liquid interfaces of a wetting film.

The excess hydrodynamic pressure could be obtained from the linear Stoke’s equation with continuity equation assuming no slip boundary conditions at both the air/water and solid/water interfaces. It has already been shown that the no-slip boundary condition can be used for the air/water interface in the wetting film of pure water [23-25]. When the water wets a hydrophilic solid surface, there is no question that the no-slip condition can be used [26]. However, slip may occur when the water flows over a hydrophobic solid surface [27]. Also, the slip velocity (or slip length) correlates well with surface roughness and shear rate [28, 29]. The shear rates measured in the present work are much smaller than those employed for the measurement of slip lengths on hydrophobic surfaces using AFM or SFA. Therefore, we assume that the no slip boundary condition holds regardless of contact angle.
Under the boundary conditions that \( p(r = \infty) = 0 \) and \( \frac{\partial p}{\partial r} \bigg|_{r=0} = 0 \), one could obtain the excess hydrodynamic pressure [5],

\[
P = 12\mu \int_{r=0}^{r=\infty} \frac{1}{r h^2} \left[ \int_{s=0}^{r} r \frac{\partial h}{\partial t} \, dr \right] \, dr
\]  

(3.8)

where \( h \) is the film thickness, \( r \) the radial position, \( p \) the excess pressure in the film relative to the pressure in the far field, and \( \mu \) is the fluid viscosity.

The curvature pressure can be obtained from the following relation [5],
\[ p_{\text{cur}} = \frac{2\gamma}{R} - \frac{\gamma}{r} \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) \]  

(3.9)

where \( R \) is the radius of the bubble in the far field and \( \gamma \) is the air/water interfacial tension.

Substituting Eqs. (3.8) and (3.9) into Eq. (3.7), one obtains an expression for \( \Pi \)

\[ \Pi = \frac{2\gamma}{R} - \frac{\gamma}{r} \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) - 12\mu \int_{r=\infty}^{r=0} \frac{1}{r^3} \left[ \int_{r=0}^{r=\infty} r \frac{\partial h}{\partial t} dr \right] dr \]  

(3.10)

which is a function of \( h(r,t) \) only. Eq. (3.10) can be used to determine a disjoining pressure isotherm, \( \Pi(h) \), numerically if the spatial and temporal profiles of a wetting film can be determined experimentally using the method used in the present work.

\[
\begin{align*}
\theta_r &= 17^\circ & \theta_r &= 81^\circ \\
\text{(a)} & & \text{(b)} \\
0.7 & & 0.217 \\
0.2 & & 0.083 \\
0.083 & & \\
0 \text{ s} & & 0 \text{ s} \\
0 \text{ s} & & \text{11.8} \\
\end{align*}
\]

Figure 3.4 The excess pressure \( (p) \) in the thin wetting films of water formed on the gold surfaces with (a) \( \theta_r = 17^\circ \) and (b) \( \theta_r = 81^\circ \). The dramatic increase of \( p \) with increasing receding contact angle is responsible for the increased drainage rate observed at the higher contact angle as shown in Figures 3.1 and 3.2.
Figure 3.3 compares the time evolution of the curvature pressure ($p_{cur}$) vs. radial distance ($r$) plots in the thin wetting films of water formed on the gold surfaces with and without hydrophobization with KAX. As shown, $p_{cur}$ increases from the far field to the center. As the film thinning continues, the $p_{cur}$ at the center becomes larger, causing the film to become flatter with time. Note here that the values of $p_{cur}$ in the thin films formed on the xanthate-treated and -untreated gold surfaces are about the same. The slight differences observed are due to the difference in the size of the bubbles used in the measurements.

Figure 3.5 Comparison of the disjoining pressures ($\Pi$) in the thin wetting films of water formed on the gold surfaces with (a) $\theta_r = 17^\circ$ and (b) $\theta_r = 81^\circ$. The negative disjoining pressure observed at the higher contact angle is responsible for the high drainage rate observed at the higher contact angle. The negative disjoining pressure increases with time due to decreasing film thickness.
Figure 3.4 compares the values of $p$ in the thin wetting films formed on the gold surfaces with and without the hydrophobization with KAX. $p$ is the driving pressure for the thinning of TLFs. As shown, on the bare gold surface with $\theta_r = 17^\circ$, $p$ increased slightly as time elapses from $t = 0$.

Figure 3.6 Temporal profiles of the wetting films formed on the gold surfaces with (a) $\theta_r = 17^\circ$ and (b) $\theta_r = 81^\circ$. 

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to $t = 0.2$ s and then decreased to zero at $t = 15$ s. On the xanthate-treated gold surface with $\theta_r = 81^\circ$, $p$ continually increased with time. At $t = 0.583$ s, $p$ reached a value of 630 N/m$^2$ at the film center. At such a high pressure, the film ruptures catastrophically. The sharp increase in $p$ is due to the increase in the negative disjoining pressure (or attractive hydrophobic force), as will be shown below.

Figure 3.5 compares the disjoining pressure ($\Pi$) developed in the thin wetting film formed on the gold surfaces with and without hydrophobization with KAX. It shows that $\Pi > 0$ in the thin liquid film formed on the bare gold surface, while $\Pi < 0$ in the film formed on the hydrophobic surface. According to Eq. (3.7), $p$ becomes more positive and hence the liquid film thins faster when $\Pi < 0$. It is believed that, the negative disjoining pressure is due to the hydrophobic force. In wetting films, the disjoining pressure due to the van der Waals force is always positive. In the wetting films studied in the present work, both the air/water and solid/water interfaces are negatively charged [21]; therefore, disjoining pressure due to double-layer interaction is also repulsive. Therefore, the negative disjoining pressure can arise, i.e., $\Pi$ becomes less than zero, only in the presence of hydrophobic force in the wetting film. It is the role of collector (xanthate in the present system) to create the hydrophobic force.

As shown above, film drainage is controlled initially by $p_{cur}$ at $h > 200$ nm and then by the negative disjoining pressure at smaller film thicknesses. When $\Pi > 0$, the thin film of water formed between bubble and particle is stable and reaches an equilibrium film thickness ($h_{eq}$). Under this condition, no flotation is possible.

Above we have discussed the results of our drainage experiments conducted using wetting films of smaller radii. These films do not form dimples and remain approximately spherical even at the center of the film. Large diameter films ($r > 50 \mu m$), which can be formed by withdrawing the liquid quickly using the syringe pump, bounce up at the center and form convex-shaped dimples as shown in Figure 3.6a. The torus-shaped water film surrounding a dimple is referred to as barrier rim. In this case, $h_{\text{min}}$ occurs at the base of a barrier rim.

Figure 3.6 compares the temporal and spatial profiles of the dimpled wetting films formed on the gold surfaces with and without hydrophobization with KAX. On the hydrophilic surface, a dimple was formed initially at $h_{\text{min}} = 360$ nm on the barrier rim located at $r = 70$ $\mu$m. As the film thinning continued, the dimple disappeared gradually, forming a flat equilibrium film at $h_e = 103$
nm. On the gold surface with $\theta_r = 81^\circ$, however, the film was flat initially and then formed a dimple as the rate of film thinning accelerated due to the appearance of the negative disjoining pressure (or attractive hydrophobic force) with decreasing film thickness. A dimple began to form at 0.2 s, although the film remained close-to-flat. The dimple became more convex with time, forming a well-developed barrier rim. At $t = 0.916$ s, the film ruptured catastrophically at $h_{\text{min}}$ (or $h_c$) = 120 nm.

Figure 3.7 compares the $h_{\text{min}}$ vs. time plots for the dimpled and non-dimpled wetting films formed on gold surfaces. When the gold substrate was treated with $10^{-5}$ M KAX, the receding contact angle ($\theta_r$) increased from $17^\circ$ to $81^\circ$). $h_{\text{min}}$ represents the minimum film thickness in a wetting film.

Figure 3.7 compares the $h_{\text{min}}$ vs. time plots for the dimpled and non-dimpled wetting films formed on the gold surfaces with and without hydrophobization. As $\theta_r$ was increased from $17^\circ$ to $81^\circ$ due to xanthate coating, the wetting films thinned faster for both dimpled and non-dimpled cases. Note also that non-dimpled films thinned faster than dimpled films on both the hydrophilic and hydrophobic surfaces. In general, smaller bubbles are less likely to form dimples due to the higher Laplace pressures, which vary with the square of bubble radius. The results presented in Fig. 3.7 suggest, therefore, that smaller air bubbles should more readily attach themselves onto
hydrophobic surfaces and give rise to faster flotation kinetics. Of course, smaller bubbles also
give higher surface area flux ($S_b$), which is another benefit of using smaller bubbles for flotation [30, 31].

3.4 Conclusion

We have studied the kinetics of film thinning by monitoring the temporal and spatial profiles
of the wetting films formed on the gold surfaces treated with potassium amyl xanthate (KAX).
The results have been analyzed using the Reynolds lubrication theory to determine the excess
pressures ($p$) in the films. It has been found that the excess pressure is substantially higher in the
wetting films formed on hydrophobic surfaces, which explains the fast kinetics of film thinning
observed. The high excess pressure is largely due to the negative hydrophobic disjoining
pressure ($\Pi_h$) present in the film. On the hydrophilic surface, the excess pressure is low due to
the presence of the positive double-layer and van der Waals disjoining pressures. Thus, the role
of collector is to improve the kinetics of film thinning and to destabilize wetting films, so that
they can rupture expeditiously and form bubble particle aggregated. The results obtained in the
present work suggest also that smaller bubbles can attach on hydrophobic surfaces more readily
than larger bubbles.

3.5 References


Chapter 4. Effect of Bubble Size on the Rate of Wetting Film Drainage

ABSTRACT

The effect of bubble size on the drainage rate of wetting films has been studied by monitoring the spatiotemporal profiles of the fast-evolving wetting films. The study was conducted by recording the interference fringes of the wetting films by means of a high-speed camera, calculating film thicknesses from the fringes offline, and reconstructing the film profiles with a nano-scale resolution. The profiles were then analyzed on the basis of the Reynolds lubrication theory to determine the contributions from the hydrodynamic and surface forces to the film thinning process.

It was found that the rate of film drainage is controlled initially by the curvature pressure and subsequently by the disjoining pressure when the film thickness reaches approximately 200 nm. As a result, the overall lifetime of the wetting film formed by a smaller bubble is shorter than that for a large bubble, which provides an explanation for the facts that smaller bubbles have shorter induction times for bubble-particle interaction and are more efficient in flotation.
4.1 Introduction

In froth flotation, solid-solid separation is achieved by selectively attaching hydrophobic particles on the surface of the air bubbles and carrying them to the top of a flotation cell, leaving the hydrophilic particles behind. During the initial stages of the bubble-particle attachment, particles undergo close encounters with air bubbles by colliding and sliding on the surface. As a particle approaches sufficiently close to the surface of an air bubble, a thin liquid film (TLF) is formed, which is referred to wetting film. The water in a TLF is confined between two surfaces, i.e., solid and air (or vapor). Unlike the thin water film confined between two solid surfaces, one of the two surfaces, i.e., air bubble, deforms, and hence create a surface tension (or Laplace) pressure in the film. The excess pressure due to the Laplace pressure causes the film to thin. As the TLF becomes thinner, the two surfaces interact with each other via surface forces, creating a disjoining pressure ($\Pi$). The disjoining pressure due to surface forces plays a dominant role at separations below 300 nm.

Of all the physical and chemical parameters that control the flotation rate and the mineral recovery, the collectors (or hydrophobizing agents) are considered to be one of the most important factors that determine the flotation behaviors. Various reagents were used to render the mineral hydrophobic, varying with the types of the minerals. Typically, short-chain alkyl xanthates and thionocarbamates are used to hydrophobize sulfide minerals and precious metals. For the flotation of silica and other oxide minerals, long-chain amines are commonly used. Regardless of the collector type, the role of collectors is to render a desired mineral hydrophobic and destabilize the TLF so that it can rupture for bubble-particle attachment.

Laskowski and Kitchener [1] suggested that the disjoining pressure in the film should be negative for the wetting film to rupture. The authors recognized, however, that according to the DLVO theory the disjoining pressure should be positive, which led to the suggestion that the negative disjoining pressure may arise from the long-range hydrophobic effect. Blake and Kitchener [2] conducted the measurement of thickness of wetting films on methylated silica and found that the TLF ruptures at thickness much larger than predicted by the DLVO theory, which led to a suggestion that ‘hydrophobic force’ may be present in the wetting film formed on the methylated surface. The Blake and Kitchener is credited for the first recognition of hydrophobic
force. However, it was not until 1982, when Israelachvili and Pashley [3] reported the first direct measurement of long-range hydrophobic force with a decay length of 1.1 nm between mica surfaces in CTAB solutions using a surface force apparatus (SFA). Many follow-up experiments [4-13] showed longer-range hydrophobic forces.

It has been shown in Chapter 2 and 3, a modified thin film pressure balance (TFPB) technique was used to show that long-range attractions exist in the wetting films formed on the xanthate-treated gold surfaces. In this technique, the spatiotemporal thickness profiles of the wetting films were monitored by means of a high-speed camera. Based on these results, it was suggested that the role of collector, such as xanthate, is to create a negative hydrophobic force in a wetting film, which facilitated the film drainage and destabilized the wetting film.

However, the disjoining pressure only act when the thickness of the TLFs were reduced to ~300 nm. At film thickness above 300 nm, surface tension pressure (or Laplace pressure) was the dominant factor in the film drainage. Earlier work showed that flotation rate and recovery increased when smaller air bubbles were used [14, 15]. Anfruns and Kitchener [16] studied the capture rate of a single air bubble in a particle suspension of aqueous solution. The result showed that the use of smaller bubbles improved the collection efficiency of fine particles. Ahmed and Jameson [17] examined the role of the bubble size on the flotation rate of fine particles in turbulent condition. They showed that the flotation rate of fine particles was substantially improved when the smaller bubbles were used.

The benefit of using smaller bubbles for flotation has been attributed to the increase in the probability of the collision with decreasing bubble size. Until 1980s-1990s, many investigators relied on measuring induction times to determine the probability of bubble-particle attachment. They found that the bubble size influenced the attachment efficiency substantially [14, 18]. Two empirical models for predicting the attachment efficiency were developed later by Dobby and Finch Dobby and Finch [19] and Yoon and Luttrell Yoon and Luttrell [14]. Both models used the induction time to predict the attachment efficiency. Note also that neither of these models considers the fundamentals of the thin film drainage and the deformation of air bubbles when colliding with the particles. As suggested by Humeres et al. [20], theoretical approaches for estimating the probability of attachment ($P_a$) have not been successful. It is, therefore, important
to study the fundamentals of the wetting film drainage during the process of bubble-particle attachment.

It is well known that wetting films drain initially by the Laplace pressure and subsequently by the disjoining pressure when the film thickness is below 300 nm. In this chapter, the kinetics of wetting film drainage has been measured using different sizes of air bubbles. The experiments were conducted on both the hydrophilic and hydrophobic gold surfaces. The bubble sizes were controlled by changing the radius ($R_o$) of the capillary tube. The kinetics studies were conducted by measuring the temporal and spatial profiles of the wetting films using the modified thin film pressure balance (TFPB) technique. The film profiles were analyzed on the basis of the Reynolds lubrication theory to calculate the curvature pressure (or local Laplace pressure) and the disjoining pressure in TLFs. The results are particularly useful for predicting the wetting film drainage, flotation rate and consequently the attachment efficiency.

4.2 Experimental

4.2.1 Materials

The gold substrates were prepared by depositing a thin layer of gold on flat silicon surfaces in a vacuum chamber. The deposition was operated using the E-beam physical vapor deposition technique (PVD-250, Kurt J. Lesker) in a class-100 cleanroom. Single-side polished silicon wafers (orientation: $<100>$, University wafer, Inc.) were used as the base substrates. They were cleaned in a boiling piranha solution (70:30 by volume $H_2SO_4:H_2O_2$) for 5 minutes, rinsed thoroughly with water, and deoxidized using buffered oxide etch (BOE) solution for seconds. The removal of the silicon oxide layer enhances the bonding between the deposition metal layers and the silicon surface. The deposition process was operated in a $10^{-6}$ torr vacuum chamber at room temperature. The deposition process follows two steps: a 50 Å thick titanium adhesion layer, and followed by a 500 Å thick gold layer.

The gold coated wafers were diced into the square pieces with a dimension of 0.5” × 0.5”. The dicing process was carried out using a micro-auto dicing saw. Shortly after the dicing process, the square substrates were cleaned in a water-based ultrasonic bath to remove the residual silicon particles. It was followed by immersing the gold substrates in a mild piranha
solution for 2 minutes, rinsed thoroughly with water and dried in a nitrogen gas stream. The gold substrates behaved a perfect mirror, and exhibited a root mean square roughness of below 0.5 nm over an area of $1 \times 1 \, \mu m^2$, as shown by the AFM images. The dynamic contact angles are measured using the dynamic sessile drop technique. The gold plate obtained in this manner exhibited the equilibrium ($\theta_o$), advancing ($\theta_a$) and receding ($\theta_r$) water contact angle of 42°, 60° and 17°, respectively. All the experiments were conducted using the ultrapure water with the resistance of above 18.2 MΩ•cm produced by Direct-Q water purification system (Millipore). All the glassware were soaked in the base bath (a saturated potassium hydroxide in isopropanol) overnight, and rinsed thoroughly with pure water.

The hydrophobic gold surfaces were prepared by immersing the substrates in a $10^{-5}$ M potassium amyl xanthate (KAX) solution for 10 minutes. After the desired immersion time, they were temporally stored in pure water. The hydrophobic gold surfaces exhibited the contact angles of $\theta_o = 91^\circ$, $\theta_a = 99^\circ$ and $\theta_r = 81^\circ$. KAX was purified by dissolving a technical grade KAX (>90%, TCI America) in acetone (HPLC grade, Fisher Sci.), and recrystallized in diethyl ether (99.999%, Sigma-Aldrich). The KAX aqueous solution was freshly prepared before use to minimize the oxidation effect.

4.2.2 Thin Film Pressure Balance

The kinetics of film thinning was studied using the modified thin film pressure balance (TFPB) technique [21]. In the modified TFPB technique, the liquid between vapor phase and solid surface was sucked out by a screw-type pump. Once the water film was drained to a thickness below 1 µm thickness, it began to deform and drained spontaneously by the surface tension pressure (or Laplace pressure). The dynamic film drainage was monitored by recording the interference fringes by means of a high speed camera (HiSpec 4, Fastec Imaging). The obtained fringes showed the temporal and spatial profiles of the TLFs, which can be used to obtain the hydrodynamic pressure and the disjoining pressure in the wetting film. The screw-type pump was custom made with the Teflon head and the brass nuts. The screw connection was sealed with the vacuum grease, and the Teflon head was wrapped with the FEP film to ensure the good impermeability.
The experiments were carried out using three different sizes of the capillary cells. The sizes of Figure 4.1. Spatial and temporal profiles of the wetting films formed on the hydrophilic gold surfaces using air bubbles with radius ($R_0$) of (a) 1.5 mm, (b) 2.0 mm and (c) 3.9 mm. The film profiles were shown at various times after film formation.

The experiments were carried out using three different sizes of the capillary cells. The sizes of
the capillaries determined the radius of the air bubbles. In the present work, we used three different sizes of air bubbles with radii \( R_0 \) of 1.5, 2.0 and 3.9 mm, respectively.

### 4.3 Results

#### 4.3.1 Hydrophilic Surfaces

Figure 4.1 compares the spatial and temporal profiles of the wetting films formed on the hydrophilic gold surfaces using three different sizes of air bubbles. The results were compared using air bubbles with \( R_0 = \) (a) 1.5 mm, (b) 2.0 mm and (c) 3.9 mm, respectively. In the present work, the film size, \( i.e. \), the radius of the flat film, was controlled in the range of 10-30 µm. In general, a dimple was developed when the film size was large. With a small film, the dimple formation was prevented. At \( R_0 = 1.5 \) mm, film thinned from the minimum thickness \( (h_{min}) \) of 400 nm to 300 nm in 0.155 s. The film continued thinning, and reached the equilibrium thickness \( (h_e) \) of 95 nm. At \( R_0 = 2.0 \) mm, the film thinned slower than at \( R_0 = 1.5 \) mm. It took 0.284 s for the film to reach 300 nm. At \( t = 6.016 \) s, the film was in equilibrium with \( h_e = 110 \) nm. Figure 4.1c) shows the spatiotemporal thickness profiles of the wetting films at \( R_0 = 3.9 \) mm. The result showed that the film reached equilibrium in 8.975 s at \( h_e = 147 \) nm. In an equilibrated wetting film, the opposing disjoining pressure was balanced by the surface tension pressure created by the curvature changes. Note that the wetting film using the bigger size of the air bubbles exhibited a thicker equilibrium film thickness than the film using the smaller sized bubble. It is suggested that disjoining pressure in a wetting film formed on a hydrophilic gold surface increased repulsively as decreasing the equilibrium film thickness.

Figure 4.2 compares the drainage rate of the wetting films formed on the hydrophilic gold surfaces using the different sizes of air bubbles. The plot shows a set of the minimum film thickness \( (h_{min}) \) vs. time \( (t) \). As shown, film thinned faster at \( R_0 = 1.5 \) mm than at \( R_0 = 2.0 \) mm. As the bubble size increased, the film thinning was retarded. The faster thinning kinetics obtained using the smaller bubbles were due to the larger curvature pressure.

The drainage of the TLFs between two macroscopic surfaces was commonly described by the Reynolds lubrication theory. For a thin film between two flat surfaces, the Reynolds approximation is commonly used to describe the rate of film thinning \( (dh/dt) \),
where $h$ is the film thickness, $\mu$ the liquid viscosity, $R_f$ the radius of the flat film, and $\Delta P$ is the pressure difference between the flat film and the outer film. $\Delta P$ is given as follows,

$$\Delta P = \frac{2\gamma}{R_o} - \Pi$$

where $R_o$ is the radius of the bubble, $\gamma$ the surface tension of the liquid, and $\Pi$ is the disjoining pressure. $2\gamma/R_o$ represents the pressure contributed from the Laplace pressure. By combining eq. (4.1) with eq. (4.2), one could easily conclude that $dh/dt$ depends on $\Delta P$, which inversely on $R_o$.

The limitation of using eq. (4.1) to describe the wetting film drainage was that the film was assumed to be flat. In order for a qualitative study of both the curvature pressure and the disjoining pressure at a curved interface, Reynolds lubrication equation was used to describe the thin film drainage,
\[
\frac{dh}{dt} = \frac{1}{12\mu r} \left( \frac{\partial}{\partial r} \left( rh \frac{\partial p}{\partial r} \right) \right)
\]  
(4.3)

where \( r \) is the radial position of the film. Eq. (4.3) was derived from the linear Stokes equation with the continuity equation. Eq. (4.3) assumed that no slip boundary conditions held at both the air/water and the solid/water interfaces. One of these two assumptions has been experimentally confirmed that no-slip boundary condition holds for the air/water interface in wetting films of pure water [22, 23]. When the water flows over the hydrophobic surface, the slippage might occur. However, it has been shown that the slip velocity (or slip length) correlated with the surface roughness and the shear rate. Since the shear rate of the liquid in the wetting film (a max of 5000 s\(^{-1}\)) is much smaller than the value obtained for the measurement of the slip lengths using the AFM and SFA, one might assume that no slip boundary condition holds regardless of contact angle.

Thus, one could obtain the expressions for \( p \) by integrating the eq. (4.3) twice with eq. (4.4) [24],

\[
p = 12\mu \int_{r_{\infty}}^{r} \left[ \int_{0}^{r} \frac{dr'}{r'} \frac{\partial h}{\partial t} \right] dr
\]

(4.4)

The boundary condition for solving the Reynolds lubrication equation is a normal stress balance at an air/water interface,

\[
p = p_{\text{cur}} - \Pi
\]

(4.5)

where \( p_{\text{cur}} \) is the curvature pressure created by the curvature changes, and \( \Pi \) is the disjoining pressure due to the surface forces between the air/liquid and solid/liquid interfaces confining a thin film.

The curvature pressure \( (p_{\text{cur}}) \) can be obtained from the following relation,

\[
p_{\text{cur}} = \frac{2\gamma}{R_0} - \frac{\gamma}{r} \frac{\partial}{\partial r} \left( \frac{r \frac{\partial h}{\partial r}}{r} \right)
\]

(4.6)
where $R_o$ is the radius of an air bubble in the far field. Eq. (4.6) is an expression for the curvature pressure due to the changes in the curvature of the air/water interface.

Substituting eqs. (4.4) and (4.6) into (4.5), one can obtain an expression for $\Pi$,

$$\Pi = \frac{2\gamma}{R_o} - \frac{\gamma}{r} \frac{\partial}{\partial r} \left( \frac{\partial h}{\partial r} \right) - 12\mu \int_{r=0}^{r} \frac{1}{r h^3} \left[ \int_{t=0}^{t} \frac{\partial h}{\partial t} dr \right] dr$$

(4.7)

Using Eq. (4.7), the disjoining pressure can be numerically determined from the spatial and temporal profiles of the wetting films.

Figure 4.3 shows a comparison of the curvature pressure ($p_{\text{cur}}$) vs. radial distance ($r$) in the wetting films obtained at a) $R_o = 1.5$ mm and b) $R_o = 3.9$ mm. It was shown that $p_{\text{cur}}$ increased from the far field to the center of the film. As shown in Eq. (4.4), the gradient of the excess pressure ($\partial p/\partial r$) controlled the film drainage. Once the curvature pressure gradient was

![Figure 4.3 Changes in curvature pressure ($p_{\text{cur}}$) with radial distance ($r$) in wetting films formed on bare gold surfaces with $R_o = 1.5$ mm and 3.9 mm. $p_{\text{cur}}$ increases with time as the film becomes flat. The smaller bubble has a larger curvature pressure than the larger bubbles. The larger curvature pressure using the smaller sizes of the air bubbles is responsible for faster thinning kinetics.](image-url)
developed along the radial direction, the film was thinning spontaneously. \( p_{\text{cur}} \) was small at \( t = 0 \), and it became larger as film thinned. It was clearly shown that the curvature pressure was much larger at \( R_o = 1.5 \) mm than those obtained at \( R_o = 3.9 \) mm. At equilibrium, \( p_{\text{cur}} \) reached a maximum value of 92 N/m\(^2\) at \( R_o = 1.5 \) mm, while the maximum of \( p_{\text{cur}} \) was equal to 25 N/m\(^2\) at \( R_o = 3.9 \) mm. According to eq. (4.4), the driving pressure \( p \) was mainly contributed from \( p_{\text{cur}} \), when \( \Pi \approx 0 \). Therefore, the use of the smaller bubbles creates a higher curvature pressure, which is favorable for the wetting film drainage.

Figure 4.4 shows the disjoining pressure isotherm, \( \Pi(h) \) vs. \( h \), in the wetting film formed on a hydrophilic gold surface. The disjoining pressure data were obtained at the flat film using eq. (5.7). It was found that a positive disjoining pressure increased with decreasing the film thickness.

![Figure 4.4](image_url)

**Figure 4.4** Disjoining pressure isotherm in wetting films formed on the bare gold surfaces using the air bubbles in radius of 1.5, 2.0 and 3.9 mm, respectively. \( \Pi_d \) and \( \Pi_e \) represent the disjoining pressure due to the van der Waals dispersion force and electrical double layer force. \( \Pi_t \) is the total disjoining pressure. The smaller bubble has a larger Laplace pressure, which gives a thinner equilibrium film thickness.
thickness, and reached the maximum in equilibrium. According to the DLVO theory, the film reached the equilibrium, when the opposing pressure (in this case, the repulsive disjoining pressure) was equivalent to the curvature pressure. Since the smaller bubble had the larger curvature pressure, one could obtain a smaller $h_e$ for a smaller bubble. At $R_o = 3.9$ mm, the film reached equilibrium at $h_e = 147$ nm where $\Pi = 25$ N/m$^2$. At $R_o = 1.5$ mm, $h_e = 90$ nm where $\Pi = 92$ N/m$^2$.

The obtained disjoining pressure could be expressed in accordance to the classical DLVO theory,

$$\Pi = \Pi_d + \Pi_e$$  \hspace{1cm} (4.8)

where $\Pi_d$ is the disjoining pressure contributed from the van der Waals dispersion force, and $\Pi_e$ is the disjoining pressure due to the electric double-layer force. The disjoining pressure due to the van der Waals force, $\Pi_d$, is given by,

$$\Pi_d = -\frac{A_{132}}{6\pi h^3}$$  \hspace{1cm} (4.9)

and the electric double-layer disjoining pressure, $\Pi_d$, could be represented as,

$$\Pi_e = -\frac{\varepsilon \varepsilon_o \kappa^2}{2\sinh(\kappa h)} \left[ (\psi_1^2 + \psi_2^2) \coth(\kappa h) - 2\psi_1 \psi_2 \coth(\kappa h) \right]$$  \hspace{1cm} (4.10)

in which $A_{132}$ is Hamaker constant for the wetting film of water formed on the gold surface. In using eq. (4.9), $A_{132} = -14.8 \times 10^{-20}$ J was used as reported by Tabor et al from the direct force measurement between an air bubble and a gold surface [25]. In Eq. (4.10), $\varepsilon_o$ is the permittivity in vacuum, $\varepsilon$ is dielectric constant of water, $\psi_1$ and $\psi_2$ are the double-layer potentials at the gold/water and air/water interfaces, respectively, and $\kappa$ is the reciprocal Debye length. In this communication, the subscript 1, 2, and 3 represent solid, vapor and liquid phase, respectively.
Figure 4.5  Spatial and temporal profiles of the wetting films formed on the xanthate-treated hydrophobic gold surfaces using air bubbles with radius of (a) 1.5, (b) 2.0 and (c) 3.9 mm. The film thins faster compared to the profiles obtained on the bare gold surface, which is due to the presence of the hydrophobic disjoining pressure.

The asymmetric double-layer force between the air bubble and the solid surface in the wet-
The obtained Π using the different sizes of air bubbles were scattered along the theoretical Πₜ.

Figure 4.6 Minimum film thickness (hₘᵢₙ) vs. time (t) of the wetting films formed on the xanthate-treated gold surfaces using different sizes of air bubbles with radius of 1.5, 2.0 and 3.9 mm, respectively.
predicted by the DLVO theory. It was found that the disjoining pressure was independent on the bubble size, while on the film thickness only. As shown, the disjoining pressure in the wetting film formed on the hydrophilic gold surface increased with decreasing the film thickness.

4.3.2 Hydrophobic Surfaces

Above we have shown the results of the wetting film drainage on the hydrophilic gold surface. It has been found that the film was drained by the curvature pressure initially, and subsequently by the disjoining pressure. The use of the small bubble was favorable for the film thinning. We have also shown that on the hydrophilic gold surface, the disjoining pressure became more repulsive as decreasing the film thickness. As the disjoining pressure became equivalent to the

![Figure 4.7](image)

Figure 4.7 Changes in disjoining pressure ($\Pi$) with radial distance ($r$) in the wetting films formed on the xanthate-treated gold surfaces at $R_0 = 1.5$ mm and 3.9 mm for various times after film formation. $\Pi < 0$ was observed when $\theta_0 = 91^\circ$, and the negative $\Pi$ increases with time as the film thins. The varying profiles of $\Pi$ obtained using different sizes of the air bubbles was corresponding to the spatial thickness profiles only.
curvature pressure, the film reached the equilibrium.

Figure 4.5 compares the spatiotemporal profiles of the wetting films formed on the hydrophobic gold surfaces using three different sizes of air bubbles. The gold surfaces were rendered hydrophobic by potassium amyl xanthate with $\theta_0 = 91^\circ$. At $R_o = 1.5$ mm, the film thinned to the minimum thickness of 300, 200, and 100 nm in 0.095, 0.205 and 0.420 s, respectively. As the bubble size increased to 2.0 mm, the rate of the film thinning was retarded. The time for film reaching the minimum thickness of 300, 200, and 100 nm increased to 0.11, 0.25 and 0.55 s. At $R_o = 3.9$ mm, it took 0.71 s for $h_{\text{min}} = 100$ nm. Comparing the film profiles obtained on the hydrophobic gold surfaces with those obtained on the hydrophilic gold surfaces, the film thinned much faster when the gold surfaces were treated hydrophobic. It was believed that xanthate adsorption on gold surfaces created a hydrophobic force, facilitating the thinning kinetics and destabilizing the wetting film [28].

![Figure 4.8](image)

Figure 4.8  A comparison of curvature pressure ($p_{\text{cur}}$) vs. radial distance ($r$) in the wetting films formed on the xanthate-treated gold surfaces using the air bubbles with $R_o = 1.5$ mm and 3.9 mm.
Figure 4.6 compares the rate of the wetting film drainage on the xanthate-treated gold surfaces at $R_o = 1.5, 2.0$ and $3.9$ mm, respectively. As shown, the film thinning was initially drained by the curvature pressure only. As the minimum film thickness was below $100$ nm, rate of film thinning no longer decayed exponentially with time. Instead, the film thinning was accelerating due to the attractive force. As $h < 100$ nm, the film became unstable and ruptured at a critical rupture thickness ($h_c$). It was found that the use of the small bubbles thinned fast above $100$ nm. As $h < 100$ nm, the slopes for the film thinning curves using the different sizes of bubbles were similar.

We compared both $p_{cur}$ and $\Pi$ in the wetting film formed on a hydrophobic gold surface. Figure 4.7 shows the evolution of the spatial profiles of $p_{cur}$ in the wetting film formed on the hydrophobic gold surface at $R_o = a) 1.5$ mm and b) $3.9$ mm. As shown, the value of $p_{cur}$ was much bigger using a small air bubble ($R_o = 1.5$ mm) than a larger bubble ($R_o = 3.9$ mm). The larger $p_{cur}$ drove the film thinning faster, and ruptured the film in a shorter time. At $R_o = 1.5$ mm, $p_{cur}$ increased with time, and reached a plateau value of $92$ N/m$^2$ at the center of the film. In the same manner, $p_{cur}$ increased with time at $R_o = 3.9$ mm, while the maximum value of $p_{cur}$ at the center was only $25$ N/m$^2$. The higher $p_{cur}$ obtained using the smaller bubble was responsible for the faster thinning kinetics, as shown in Figure 4.5.

Figure 4.8 compares the disjoining pressure ($\Pi$) developed in the wetting film formed on the xanthate-treated gold surfaces. It showed that $\Pi <0$ in the wetting film formed on the gold surface treated by xanthate. $\Pi$ became more negative as the film thinned, and reached a value of $-700$ N/m$^2$ at the center at $t = 0.42$ s for $R_o = 1.5$ mm. The $\Pi$ vs. $r$ obtained at $R_o = 3.9$ mm showed the similar results with that obtained at $R_o = 1.5$ mm. Note that, $\Pi$ became much larger than the $p_{cur}$ at $t > 0.205$ s for $R_o = 1.5$ mm, or at $t > 0.4$ s for $R_o = 3.9$ mm, indicating that the film thinning was initially controlled by $p_{cur}$, and subsequently by $\Pi$.

Figure 4.9 shows the disjoining pressure isotherm in the wetting film formed on a hydrophobic gold surface treated by xanthate. The plot shows $\Pi$ obtained from the spatiotemporal thickness profiles of the wetting films at $R_o = 1.5, 2.0$ and $3.9$ mm, respectively. As shown, the disjoining pressure is negative and become more negative as the film thickness decreased. In a wetting film, the disjoining pressure due to the van der Waals dispersion force was always positive. The zeta potential of gold sphere was not changed after the xanthate
treatment; therefore, the electric double-layer force was repulsive. Only the hydrophobic force can destabilize the wetting film. Thus, one might consider an inclusion of the hydrophobic force in the extended DLVO theory [29, 30],

$$\Pi_t = \Pi_d + \Pi_e + \Pi_h$$

(4.11)

in which $\Pi_h$ represents the hydrophobic disjoining pressure. Since the value of $\Pi_t$, $\Pi_d$ and $\Pi_e$ are known, one might back-calculate the values of $\Pi_h$ using Eq. (4.11). The hydrophobic force was represented as a power law [31, 32],

Figure 4.9 Disjoining pressure isotherm in the wetting film formed on xanthate-treated gold surfaces using different sizes of the air bubbles with radius of 1.5, 2.0 and 3.9 mm, respectively. $\Pi < 0$ was found on the hydrophobic gold surface, regardless of the size of the air bubbles. The hydrophobic disjoining pressure was represented as a power law. The best fit was obtained with an inclusion of the hydrophobic force with force constant $K_{132} = 1.1 \times 10^{-17}$ J.
\[ \Pi_h = -\frac{K_{132}}{6\pi h^3} \]  

(4.12)

Eq. (4.12) is of the same form as the van der Waals-dispersion force, and \( K_{132} \) is the hydrophobic force constant. \( K_{132} = 1.1 \times 10^{-17} \) J was obtained from a best fit of the theoretical disjoining pressure curve with the experimental data. We have shown that the hydrophobic force dominated over the electrical double-layer force and the van der Waals force in wetting films. The net attraction brought the film to be sequenced, and ruptured afterwards. The results showed that the possibility of bubble-particle attachment was enhanced using the smaller sizes of the air bubbles and the collectors.

4.4 Conclusions

The effect of bubble size on the wetting film drainage was studied using the modified thin film pressure balance (TFPB) technique. Effect of bubble size was studied using different sizes of capillary tubes. The spatiotemporal film profiles were extracted from the interference fringes and used to determine both the hydrodynamic pressure and the disjoining pressure in wetting films.

It has been found that the film thinning was initially controlled by the curvature pressure (\( p_{\text{cur}} \)) due to the deformation of the air bubble, and subsequently by the disjoining pressure (\( \Pi \)) created by surface force in wetting films. The results showed that the use of small bubbles increased the thinning kinetics of the wetting films formed on both the hydrophilic and the xanthate-treated hydrophobic gold surfaces. On a hydrophilic surface, \( p_{\text{cur}} \) was balanced by \( \Pi \) arising from the van der Waals dispersion force and the electrostatic double-layer force. On a xanthate-treated gold surface, the film thinned expeditiously, leading to a rupture where the film became unstable. The short lifetime of the wetting films using the smaller air bubbles were attributed to a higher curvature pressure. The present results suggested that the use of the small bubble was favorable for the wetting film drainage, resulting in an increase of the attachment efficiency. It was also found that a negative disjoining pressure was present in wetting films due to the presence of the hydrophobic force.
4.5 References


Chapter 5. Predicting the Asymmetric Hydrophobic Interactions in Wetting Films from the Symmetric Hydrophobic Interactions in Colloid and Foam films

ABSTRACT

A modified thin film pressure balance (TFPB) technique has been used to determine the disjoining pressures ($\Pi$) in the wetting films of water formed on the surfaces of different hydrophobicities. After subtracting the contributions from the double-layer and van der Waals forces, the hydrophobic disjoining pressures were determined and converted to asymmetric hydrophobic interaction forces using the Derjaguin approximation. It has been found that the asymmetric force constants ($K_{132}$) can be predicted from the symmetric hydrophobic force constants ($K_{131}$) between hydrophobic surfaces of identical hydrophobicity and the symmetric hydrophobic force constant ($K_{232}$) between two air bubbles ($K_{232} = 5.3 \times 10^{-17}$ J) in pure water using the geometric mean combining rule. This finding suggests that hydrophobic forces may be of molecular origin, which is in agreement with the results of the recent thermodynamic studies that hydrophobic forces are the consequence of the water molecules forming H-bonded structures in the thin liquid films confined between hydrophobic surfaces (Wang et al., J. of Colloid and Interface Sci. 379 (2012) 114-120).


5.1 Introduction

The DLVO theory is named after Derjaguin and Laudau, Verwey and Overbeek, and has been used as the guiding principle in colloid chemistry for more than 70 years [1, 2]. The early application of the theory was found for wetting films by Derjaguin and his colleagues [3, 4], who showed that a wetting film, i.e., a thin liquid film between a solid surface and an air bubble, was distinct from the bulk liquid. In a wetting film, both the van der Waals-dispersion force and the electrical double-layer force are repulsive for many systems. Therefore, both of the DLVO forces are stabilizing wetting films when the surface is hydrophilic [5, 6]. When the surface becomes hydrophobic, however, the film becomes unstable and ruptures to form a contact angle. Laskowski and Kitchener [7] suggested that for a contact angle to form on a solid surface, the disjoining pressure (Π) of the wetting film must be negative. It is now known that the negative disjoining pressure arises from the hydrophobic force, which has been a topic of contentious discussion for a long time.

Rabinovich and Derjaguin [8] suggested that the hydrophobic force is a structural force created due to overlapping boundary layers of two approaching surfaces. The concept of structural force was first conceived to explain in the experimental data obtained from wetting film studies conducted on hydrophilic surfaces. It was found that the equilibrium film thicknesses formed on hydrophilic surfaces were much thicker than predicted by the DLVO theory [9, 10]. As the solid surfaces became more hydrophobic, however, wetting films became less stable and ruptured. Israelachvili and Pashley [11] were the first to measure an attractive hydrophobic force with a decay length of 1.1 nm between two hydrophobized mica surfaces with $\theta = 64^\circ$. Many follow-up experiments were conducted, showing that both short- and long-range hydrophobic forces were present in the TLFs formed between two hydrophobic surfaces [12-15]. The origin of the hydrophobic force, however, has been controversial after more than two decades of contentious debates. Some investigators suggested that the hydrophobic force originates from the changes in water structure [16], while others showed that it is caused by the correlation of charged patches [17, 18]. Some researchers believe that the long-range hydrophobic force was an artifact caused by the pre-existing nanobubbles on hydrophobic surfaces [19, 20]. Wang and Yoon [21] showed that hydrophobic interaction entails a enthalpy
decrease, which has been attributed to the formation of the low density liquids (LDLs) species in the TLFs confined between hydrophobic surfaces.

Most discussions regarding the hydrophobic interaction were based on the force data obtained between two symmetric surfaces. The surface force data obtained with asymmetric hydrophobic surfaces exhibited unexpected results. Claesson et al. [22] conducted surface force measurement between a bare mica surface and a hydrophobic mica surface. The latter was prepared by depositing the dimethyldicylammonium (DDOA+) ions by means of the Langmuir-Blodgett technique. It was found that a stronger attraction was present in TLFs between a bare mica surface and a hydrophobic mica surface than those conducted between two hydrophobic mica surfaces. They suggested that the attraction was an electrostatic mechanism, in which the overlaps of the oppositely charged double layers created a net attractive force. Tsao et al. [23] reported results between a bare mica and a dieicosyldimethylammonium treated hydrophobic mica surface across a thin liquid of water. These authors suggested, however, that the long-range attraction is due to the local “amphiphilic structure” rather than the double-layer interaction. Meyer et al. [17] obtained results that were similar to those reported by Tsao et al. with mica surfaces coated with a long-chain ammonium salt, and attributed the results to changes in amphiphilic structure. Rabinovich and Yoon [24] conducted asymmetric force measurements between a hydrophilic glass sphere on one side and a robust hydrophobic glass surface on the other. The silica surface and glass sphere were treated with octadecyltrichlorosilane and trimethylchlorosilane. The results showed that the forces measured at $h < 5$ nm deviated from the DLVO theory, which was contributed to a short-range hydrophobic force. In a follow-up paper by Yoon et al. [25], force measurement was conducted between a hydrophobic glass sphere with $\theta = 109^\circ$ and a silica plate with the varying hydrophobicities. It was found that the hydrophobic force became stronger as the solid hydrophobicity increased.

We recently measured the disjoining pressure in the TLFs of water between an air bubble and a hydrophobic gold surface [26]. The gold surface was hydrophobized using potassium amyl xanthate (KAX), which is commonly used as collector for the flotation of sulfide minerals and precious metals. It was found that the disjoining pressure in a wetting film was repulsive on a bare gold surface. It became attractive when the gold surfaces were rendered hydrophobic by KAX. It was found that the hydrophobic forces calculated from the negative disjoining pressures were somewhat stronger than the asymmetric hydrophobic forces measured between two gold
surfaces with identical hydrophobicity. This finding qualitatively explained by the fact that air bubble is more hydrophobic than hydrophobic gold in view of the interfacial tensions involved.

In the present work, a series of AFM surface force measurements using symmetric hydrophobic surfaces, and a series of disjoining pressure measurements in wetting films using the modified TFPB technique were conducted. The disjoining pressure were converted to the corresponding hydrophobic forces using the Derjaguin approximation [27]. A set of symmetric and asymmetric hydrophobic forces are then compared to see if the geometric mean combining rule is applicable. As is well known, this rule is applicable for predicting molecular forces such as van der Waals force. If it is found that the geometric combining rule is applicable for hydrophobic interactions, the hydrophobic interaction may be considered a molecular force. It has been already been shown that the combining rule can be applicable for predicting the asymmetric hydrophobic interactions between two solid surfaces from the symmetric hydrophobic interactions between two like surfaces [25].

5.2 Materials and Methods

5.2.1 Materials

Potassium ethyl xanthate (KEX, > 90%, TCI America) was used to hydrophobize the gold surfaces. KEX was purified by dissolving in acetone, and recrystallized in diethyl ether twice before use. All experiments were conducted using the ultrapure water obtained from a Direct-Q3 water purification system (EMD Millipore). The ultrapure water has a resistivity of 18.2 MΩ•cm and < 10 ppb of total organic carbon.

5.2.2 Substrate preparation

The gold substrates were prepared by depositing a thin layer of gold on a flat silicon surface using the physical vapor deposition technique. The deposition was performed using the PVD-250 system (Kurt J. Lesker) in a class-100 cleanroom. Single-side polished silicon wafers (orientation: < 100 >, University wafer, Inc.) were used as the base substrates. They were cleaned in a boiling piranha solution (70:30 by volume H₂SO₄:H₂O₂) for 10 minutes, rinsed thoroughly with water, and deoxidized using buffered oxide etch (BOE) solution for 10 seconds. The deposition process
was operated in a 10^{-6} torr vacuum chamber at room temperature. It was composed of two steps: 50 Å thick titanium layer was deposited as a bond layer, followed by a 500 Å thick gold layer. The gold substrates were prepared by dicing the wafers into 0.5” × 0.5” size square pieces using a Micro-Auto dicing saw. During the dicing process, the gold substrates were contaminated with tiny silicon particles and water impurities. Prior to the force measurement, the gold substrates were cleaned in pure water ultrasonically to remove the residual silicon particles on surface. The cleaning procedure was followed by immersing the gold substrates in a mild piranha solution for 2 minutes, rinsed thoroughly with water, and dried in a nitrogen gas stream. The substrates behaved as a perfect mirror, and exhibited a root mean square roughness of below 0.5 nm over an area of 1 × 1 µm^2, as determined from the AFM images.

The gold spheres were obtained by employing a short circuit on a thin gold wire (0.005 inch dia, Alfa Aesar) using a 120V AC power. The gold particles produced in this manner were perfectly spherical, but came in a variety of sizes. In the present work, the sphere with radii of 3.5 - 7.5 µm was picked and glued onto the tip of an AFM cantilever using EPON 1004F resin (Shell Chemical Co.) by means of a home-built 3-axis translation stage. The cantilevers were further cleaned by gently washing with ethanol and exposing under UV light for 2 hours before use.

5.2.3 Atomic Force Microscopy

The surface force measurements between two hydrophobic gold surfaces in the aqueous solution were conducted using a NanoScope V multimode AFM (Digital Instruments, Inc) [28]. The spring constant of the cantilever was determined using the thermal tuning technique. The gold surfaces were rendered hydrophobic by injecting the xanthate solution in the fluid cell after both the sphere attached cantilever and the gold substrate were assembled on the AFM, and sealed with an O-ring. In this manner, the gold sphere and the gold plate exhibited identical hydrophobicities. The hydrophobicity of the gold surfaces was controlled by varying the KEX concentration and the immersion time. The force measurement was conducted in water by flushing the fluid cell thoroughly with water after the desired immersion time in the KEX solution. The obtained force curves were normalized by the radius (R) of the gold sphere.
5.2.4 Thin Liquid Pressure Balance

The asymmetric surface force measurement between a hydrophobic gold plate and an air bubble in water was conducted by monitoring the kinetics of film thinning using the modified thin film pressure balance (TFPB) technique [26]. In this technique, the information of the surface force in the wetting film was extracted from the spatial and temporal thickness profiles of the wetting films using the Reynolds lubrication theory [29].

The gold substrates were rendered hydrophobic by immersing them in a desired concentration of KEX solution. The KEX-treated gold substrates were gently rinsed with water to remove the residual xanthate solution, and temporarily stored in water. A meniscus-shaped film was formed by sucking the liquid out of the glass cell using a custom-made Teflon piston. When the intervening film drained within a few microns, a visible interference fringe (or Newton rings) was observed. The fringes were recorded by a high speed camera (Hi-spec 4, Fastec) at 150-300 fps, and used to construct the spatiotemporal thickness profiles of the wetting films, i.e., $h(r,t)$.

The disjoining pressure ($\Pi$) can be thus obtained using the eq. (5.1)

$$\Pi = \frac{2\gamma}{R} - \frac{\gamma}{r} \left( \frac{\partial^2}{\partial r \partial r} \right) - 12\mu \int_{r=0}^{r} \frac{1}{r} \left( \frac{\partial h}{\partial t} \right) dr$$

in which $\gamma$ is the surface tension, $\mu$ the viscosity of the fluid, $h$ the film thickness, $R$ the radius of the bubble, and $t$ is the time. Eq. (5.1) was derived under the no-slip boundary conditions at both the air/water and the solid/water interfaces [29]. It has been shown previously that in the wetting films of water, no-slip boundary conditions hold at both the solid/water interface [30, 31] and the air/water interfaces [32, 33].

5.3 Results

5.3.1 Symmetric Hydrophobic Interactions

Figure 5.1 shows the normalized forces ($F/R$) measured in pure water between two identical gold surfaces with the same hydrophobicities using the atomic force microscopy (AFM). The surfaces were hydrophobized in $10^{-5}$ and $10^{-4}$ M KEX solutions for varying immersion time. The measured force ($F$) was normalized by the radius ($R$) of the sphere, and plotted vs. the closest
separation distance \((h)\). In DLVO theory, the total surface force is represented as a sum of van der Waals dispersion force \((F_d)\) and electrical double-layer force \((F_e)\),

\[
F/R = F_d/R + F_e/R
\tag{5.2}
\]

The van der Waals dispersion force between a spherical solid and a flat solid surface is given by,

\[
F_d/R = -\frac{A_{131}}{6h^2}
\tag{5.3}
\]

where \(A_{131}\) is the Hamaker constant for the solid-solid interaction in water, and \(h\) is the closest separation distance. The subscripts 1 and 3 represent the solid and liquid phase, respectively. The electrical double-layer force between two identical surfaces was given by,

\[
F_e/R = 2\pi \frac{64nkT}{\kappa} \tanh^2 \left(\frac{ze\psi_1}{4kT}\right) e^{-\chi h}
\tag{5.4}
\]

where \(\psi_1\) is the surface potential on the gold interface, \(\kappa\) the reciprocal Debye length, \(k\) the Boltzmann constant, \(T\) the temperature, \(z\) the valence of the ions, and \(n\) is the number of ions. Figure 5.1a shows the results obtained when the gold substrates were immersed in \(10^{-5}\) M KEX solution for different immersion time. The force curve for “0 min” immersion time represents the surface force between two bare gold surfaces in water. As shown, the force curve matches with the prediction from the DLVO theory using eq. (5.2). The Hamaker constant, \(A_{131} = 2.0 \times 10^{-19}\) J, were obtained by fitting the short-range part of the surface force data with eq. (5.2), where the van der Waals dispersion force dominated. The parameters for the electrical double-layer force, \(\psi_1 = -40\) mV and \(\kappa = 90\) nm, were obtained by fitting the long-range part of the force data. The obtained Hamaker constant for gold-gold interaction in water was in the range of values predicted by the full Lifshitz theory \((10-40 \times 10^{-19} \text{ J})\) [27]. The value of \(\psi_1\) \((= -40 \text{ mV})\) was close to the zeta potential of the micron sized gold particles in water \((-40 \pm 2 \text{ mV})\), as shown previously [26].
When the gold substrates were immersed in the KEX aqueous solution, the hydrophobicity of the gold surfaces increased with the immersion time. As shown, the measured forces became

Figure 5.1 Normalized AFM force curves obtained in water between gold surfaces hydrophobized in a) $10^{-5}$ M and b) $10^{-4}$ M KEX solution at different contact times. The solid line represents the force curves predicted using the extended DLVO theory in which the hydrophobic force was represented as a power law.

When the gold substrates were immersed in the KEX aqueous solution, the hydrophobicity of the gold surfaces increased with the immersion time. As shown, the measured forces became
attractive and reached a maximum at $t = 40$ min. When the gold surfaces were left in the KEX aqueous solution for more than 40 min, the surface force became less attractive, which might be attributed to a formation of xanthate multilayer. It has been well documented that the xanthate adsorption on gold surfaces is followed by two steps: the chemisorbed metal xanthate is initially covered on the gold surface, then followed by the dixanthogen formation. The results obtained from Infrared spectrometry showed that the multilayer xanthate formation took place on the gold surface exposing the hydrophilic group (-OCSSAu) towards the aqueous phase. As a consequence, the hydrophobic force diminished with decreasing the hydrophobicities of the gold surfaces. Fig. 5.1b shows the force data obtained when the gold substrates were immersed in $10^{-4}$ M KEX aqueous solution. It was found that the hydrophobic force increased with increasing the immersion time. However, both the dispersion force and the double-layer force remained the same after xanthate treatment. It was anticipated that the attractive force induced by the hydrophobization in KEX solution might be attributed to the presence of the hydrophobic force.

One might consider the inclusion of the hydrophobic force in the extended DLVO theory,

$$F/R = F_d/R + F_e/R + F_h/R$$

in which $F_h$ represents the hydrophobic force. In the present work, the hydrophobic forces measured from AFM were represented as a power law,

$$F_h/R = K_{131}/6h^2$$

where $K_{131}$ represents the hydrophobic force constant. The power law had the same form as the expression for the dispersion force. The hydrophobic force has been shown using both the exponential law and the power law interchangeably. Mathematically, both the exponential law and the power law follow the similar curves at long-range distance, while the power law decays much faster than the exponential law at short range. This is because the power law function decays with the cubic thickness, unless the decay length used in the exponential law was significantly small ($< 1$ nm). Meanwhile, the power law function holds the advantage over the exponential law function, since it could be used to directly compare the magnitude of the hydrophobic interaction between the asymmetric hydrophobic surfaces and the symmetric hydrophobic surfaces, which turned out to be a major objective in this work.
As shown in Figure 5.1b, the hydrophobic force constant $K_{131}$, \textit{i.e.}, between two identical hydrophobic gold surfaces in water was $1.5 \times 10^{-18}$ J when the gold plates were rendered hydrophobic in a $10^{-5}$ M KEX for 5 min. The $K_{131}$ increased to $6.5 \times 10^{-18}$ J after a 40 min immersion time. As the gold surfaces were hydrophobized in the $10^{-5}$ M KAX solution for 60 minutes, the $K_{131}$ decreased to $4.3 \times 10^{-18}$ J. Likewise, in a $10^{-4}$ M KEX solution, $K_{131}$ increased with increasing the immersion time. $K_{131} = 6.6 \times 10^{-18}$, $1.2 \times 10^{-17}$, and $1.3 \times 10^{-17}$ J for the immersion time of 2 min, 10 min, and 40 min, respectively.

Note that the theoretical curve did not fit the experimental data perfectly at $h < 50$ nm. As shown, the obtained force curve was slightly overestimated than the predicted using eqs. (5.5) and (5.6) at short-range distance, which left a supposition that the double-exponential law might give a better fit for the experimental data. At this time, I do not have any good explanations for such discrepancies. However, in the present work, the use of the power law representing the hydrophobic interaction was considered to be valid, if one accepts that the curve fitting by the power law works well at the long-range distance with $h > 50$ nm.

5.3.2 Asymmetric Hydrophobic Interactions

Figure 5.2 shows the disjoining pressure ($\Pi$) in the wetting films of water formed on the gold surfaces hydrophobized by KEX. The disjoining pressure was determined by analyzing the spatial and temporal profiles of the wetting films using the eq. (5.1). As shown, the disjoining pressure in the wetting film obtained at “0 min” immersion time, \textit{i.e.}, on the bare gold surface, was repulsive. As the gold surfaces became hydrophobic by immersing the gold plates in a $10^{-5}$ M xanthate solution, the disjoining pressure became negative (or attractive). At $t = 40$ min, the negative disjoining pressure reached a plateau and became less attractive as the immersion time increased. Recalling the diminished effect of the hydrophobic interaction occurring between two identical hydrophobic gold surfaces at $t > 40$ min, the decrease of the asymmetric hydrophobic interaction in the wetting film might be also attributed to the reverse adsorption of the excess ethyl xanthate on the hydrophobic gold surface. The exposure of the hydrophilic head groups toward the liquid phase diminished the hydrophobicities of the gold surfaces. Figure 5.2(b) shows the disjoining pressure in the wetting films formed on the gold surfaces hydrophobized in
10^{-4} \text{ M KEX solution. The results showed that } \Pi \text{ became more attractive when the gold plates were left in } 10^{-4} \text{ M KEX solutions for 40 minutes.}

The disjoining pressure due to the hydrophobic force was determined by fitting the disjoining pressure data with the extended DLVO theory,

\[
\Pi = \Pi_d + \Pi_e + \Pi_h
\]

\[
= -\frac{A_{132}}{6\pi h^3} - \frac{\varepsilon \varepsilon_0 K^2}{2 \sinh(kh)} \left[ \left( \psi_1^2 + \psi_2^2 \right) \sinh(kh) - 2 \psi_1 \psi_2 \coth(kh) \right] - \frac{K_{132}}{6\pi h^3}
\]

in which \( \Pi_d, \Pi_e, \Pi_h \) represent the disjoining pressures contributed from the van der Waals dispersion force, electrical double-layer force and hydrophobic force, respectively. In using eq. (5.7), the value of \( A_{132} = 8.6 \times 10^{-20} \text{ J} \) was obtained by multiplying the square root of the Hamaker constants for gold-water-gold (\( A_{131} = 2.0 \times 10^{-19} \text{ J} \)) with the Hamaker constant for air-water-air (\( A_{232} = 3.7 \times 10^{-20} \text{ J} \)) using the geometric mean combining rule. In the present work, the van der Waals dispersion force in the wetting film is always repulsive, which could not bring the wetting film to be ruptured.

The disjoining pressure due to an electrical double-layer force could be obtained using the Hogg-Healey-Fuerstenau (HHF) equation, in which \( \varepsilon_0 \) is the permittivity in vacuum, \( \varepsilon \) dielectric constant of water, \( \psi_1 \) and \( \psi_2 \) the double-layer potentials at the solid/water and air/water interfaces, respectively. The HHF equation assumes that both interfaces maintain constant potentials when two dissimilar double layers overlap. The HHF theory has shown a great success in calculating the electrical double-layer force between air bubbles and solid surfaces in water. In general, the double-layer force was repulsive in the wetting film between two dissimilar interfaces with like surface potentials.

Since both the van der Waals dispersion force and the double-layer force are repulsive, one must recognize the presence of the hydrophobic force in the wetting film formed on the hydrophobic surface. In the present work, the disjoining pressure contributed from the hydrophobic force (\( \Pi_h \)) is represented as a power law, which shares the same form with the dispersion force. The \( K_{132} \) is the hydrophobic force constant in the wetting film between solid and air bubble interacting in water.

As shown, \( \Pi \) obtained in a wetting film formed on a bare gold surface was in a good agreement with the classical DLVO theory. \( \psi_1 \) was taken to be the same as the surface potential.
of the gold obtained above by AFM. The values of $\psi_2 = -29$ mV and $\kappa^{-1} = 42$ nm were taken from a fit of the disjoining pressure using the eq. (5.7). Note that the values of Debye length in pure water obtained from AFM measurement and the wetting film experiments were different. It is noteworthy to mention that the hydrophobic force was determined by subtracting the
disjoining pressure obtained on the xanthate-treated gold surface by those obtained on the bare gold surface. Therefore, the calculated hydrophobic force was separated from the electrical double-layer force and van der Waals dispersion force.

As shown in Figure 5.2, the \( K_{132} \) obtained at \( 10^{-5} \) M KEX increased from \( 1.45 \times 10^{-17} \) J at \( t = 10 \) min to \( 1.90 \times 10^{-17} \) J at \( t = 40 \) min. As the immersion time increased to 90 min, the \( K_{132} \) decreased to \( 1.24 \times 10^{-17} \) J. At \( 10^{-4} \) M KEX, the hydrophobic force become more attractive at \( t = 2 \) min with \( K_{132} = 1.9 \times 10^{-17} \) J. \( K_{132} = 2.3 \times 10^{-17} \) J and \( 2.6 \times 10^{-17} \) J when the gold plates were hydrophobized in \( 10^{-4} \) M KEX solution for 10 and 40 minutes.

5.4 Discussion

Above we have shown the results of both the symmetric hydrophobic interaction measured between two hydrophobic gold surfaces and the asymmetric hydrophobic interaction between an air bubble and a hydrophobic gold surface in water. The results showed that the asymmetric hydrophobic interaction behaved in the same manner as the symmetric hydrophobic interaction. Yoon et al. [25] compared the hydrophobic interaction measured between two hydrophobic surfaces having the different hydrophobicities with those between two identical ones. The results showed that the hydrophobic force constant between two dissimilar surfaces were close to the geometric mean of the hydrophobic force constants between two similar surfaces. We recently measured the disjoining pressure in the wetting films of water formed on the KAX-treated gold surfaces [26]. It was found that the geometric mean combining rule was valid for predicting the asymmetric hydrophobic interaction between a hydrophobic gold surfaces and an air bubbles from those between two identical hydrophobic gold surfaces.

The geometric mean combining rule has been used to determine the Hamaker constants for the van der Waals dispersion force between two dissimilar surfaces from those between two similar surfaces. It is based on the Berthelot relation, derived originally for molecular interaction [34]. The geometric mean combining rule for the hydrophobic interaction between two dissimilar hydrophobic surfaces shared a similar form with the one for the dispersion force,

\[
K_{132} = \sqrt{K_{131}K_{232}}
\]  
(5.8)
in which $K_{131}$, $K_{232}$, and $K_{132}$ represent the hydrophobic force constant for solid-solid, air-air, and air-solid interaction, respectively.

Figure 5.3 shows a plot of $K_{132}$ vs. square root of $K_{131}$ in logarithmic scale. The data points marked by red squares were cited from the previous work, in which potassium amyl xanthate (KAX) was used for hydrophobization of the gold surfaces [26]. The green triangles were the data points obtained in the present work using KEX as the hydrophobizing agent. The present results showed a linear relationship between $K_{132}$ and square root of $K_{131}$. The blue line shows a fit curve with $K_{232} = 5.3 \times 10^{-17}$ J using the eq. (5.8). As shown, the experimental points were evenly scattered around the fit line, confirming the previous supposition of the use of the combining rule for the asymmetric hydrophobic interaction between air bubbles and hydrophobic particles. The value of $K_{232}$ in pure water was close to that estimated by extrapolating the
hydrophobic force constant in foam film \((K_{232})\) at zero concentration of the surfactant [35]. Note that the hydrophobic force constant between air bubbles \((K_{232} = 5.3 \times 10^{-17} \text{ J})\) was stronger than those between two common hydrophobic solid surfaces \((K_{131} = 1.2 \times 10^{-17} \text{ J})\), showing that air bubbles are the more hydrophobic.

The presence of the hydrophobic force in the wetting films between air bubbles and hydrophobic surfaces is more readily recognized if one can accept that the air bubbles in pure water are hydrophobic. Van Oss et al. [36] suggested that the air bubbles were the most hydrophobic substances known in that the interfacial tension at vapor-water interface (=72.4 mN•m\(^{-1}\)) was much higher than the interfacial tension at the hydrophobic surface-water interface (=50 mN•m\(^{-1}\)). It has been found from the vibrational sum frequency (VSF) spectra of the water molecules at vapor-water interface was similar to those at the hydrophobic liquid-water interface. Note that the free OH peaks at CCl\(_4\)-water and hexane-water interfaces were observed at 3669 ± 1 cm\(^{-1}\), where it represented the characteristic non-hydrogen-bonded (free) OH stretch vibration [37, 38]. Interestingly, the free OH peaks at vapor-water interface were also observed at ~3700 cm\(^{-1}\), which was close to those at the hydrophobic liquid-water interface. The shift of the characteristic peak indicates an attraction between the free-OH molecules and the organic molecules at interface; those attractions lowered the interfacial tension and hydrophobicity. It has been shown that the bond energy for CCl\(_4\)-water was estimated to be -1.4 kcal•mol\(^{-1}\) [39]. Such results were in good agreement with the dispersion component of \(W_a\) at hydrophobic liquid-water of 20 mN•m\(^{-1}\), while \(W_a = 0\) at vapor-water interface. Therefore, it is reasonable to believe that the air bubble was more hydrophobic than the commonly used hydrophobic liquid. Wang and Yoon studied the film drainage confined between two air bubbles in water, and they found that the film thinning was faster than those predicted by the Reynolds lubrication theory when considering the van der Waals force and the electrical double-layer force only. They suggested the presence of the hydrophobic force in the TLFs confined between two vapor phases in water. It has also been shown that the presence of surfactant and electrolyte could damped the hydrophobic force in TLFs, leading to a supposition that the hydrophobic force might be related to structure changes at interface. Similar conclusions were also achieved independently from other investigators, who showed the hydrophobic force was more significant in the surfactant-free water [40] and it became dominant in the degassed and deionized water [41].
The rise of the hydrophobic force might be attributed to the reconstructed water structure when two hydrophobic surfaces in water overlap. A recent publication by Wang and Yoon [21], who conducted the force measurements between two hydrophobized gold surfaces at varying temperatures. They showed that both enthalpy and entropy were negative and became more negative as the film thickness decreased. A more significant finding was that the absolute value of the enthalpy change was larger than the entropy change, indicating that the macroscopic hydrophobic interaction between two hydrophobic surfaces was enthalpy driven rather than entropically driven. Such conclusion was contrary to the conventional illusion of the microscopic hydrophobic interaction, such as micelle formation. The results showed that the hydrophobic force might originate from a formation of an enhanced H-bond network (or water structure) in the vicinity of the hydrophobic surfaces. Such reconfiguration released the energy i.e., a decrease of enthalpy for building the enhanced H-bond network.

In the present work, we obtained the stronger hydrophobic interaction between an air bubble and a hydrophobic solid surface than between two hydrophobic solid surfaces. When the vapor-water interfaces overlapped, the energy consumed to build the H-bond network on the vapor-water interface was stronger than those on the hydrocarbon-water interface. This present finding suggests that hydrophobic force may be a molecular force representing the properties of the thin liquid films between two hydrophobic surfaces, regardless of whether the interacting surfaces were solid, liquid, or gas.

5.5 Conclusions

We have conducted force measurements between symmetric hydrophobic surfaces between two gold surfaces of identical hydrophobicity and between asymmetric hydrophobic surfaces, i.e., air bubble and hydrophobic gold. The former was conducted using an AFM, while the latter was determined using the modified TFPB technique. The results showed that both the symmetric and asymmetric hydrophobic forces became more attractive when the solid hydrophobicities increased. It has been found that the asymmetric and symmetric hydrophobic interaction constant can be related to each other by means of the geometric mean combining rule. In this regard, the hydrophobic force is considered to originate from molecular interactions, regardless of whether the confining surfaces are solid, liquid, or vapor. The obtained hydrophobic force constant for
the air-water-air interactions was found to be $5.3 \times 10^{-17}$ J, which is larger than those obtained between two macroscopic hydrophobic surfaces with the water contact angle above $90^\circ$. Such a finding coincides with the previous result showing that air bubbles are more hydrophobic than any other hydrophobic solid or liquid. That the asymmetric hydrophobic interaction constants in wetting films can be predicted from the symmetric hydrophobic interaction constants will be useful for many industrial applications such as flotation, wetting, lubrication, etc.

5.6 References


Chapter 6. Dewetting of Hydrophilic Surfaces in the Presence of Al$^{3+}$ Ions

ABSTRACT

The effect of Al$^{3+}$ ions on the stability of the thin liquid films (TLF) of water formed on hydrophilic silica surfaces has been studied by monitoring the dynamics of the wetting film drainage and rupture using the microinterferometry technique. A high-speed video camera was used to monitor the fast-evolving interference patterns of the TLFs formed on the surface. By analyzing the recorded fringes offline, it was possible to reconstruct the spatial and temporal profiles of the wetting films with a nano-scale resolution. The film profiles were then used to derive the kinetic information necessary to calculate the disjoining pressures ($\Pi$) in the wetting films.

In the presence of $10^{-6}$ M AlCl$_3$, both the air/water and silica/water interfaces were negatively charged; therefore, $\Pi > 0$ and the wetting film was stable. As the Al$^{3+}$ ion concentration was increased to $3\times10^{-5}$ M, silica surface became positively charged, while the surface charge of the bubble remained negative. Therefore, $\Pi < 0$ and the wetting film became unstable, drained fast, and ruptured, forming a small contact angle. The contact angle measured at the three-phase contact line was in a close agreement with the value predicted from the Frumkin-Derjaguin isotherm. As the Al$^{3+}$ ion concentration was further increased to $10^{-3}$ M, the bubble charge became positive, causing the disjoining pressure to become repulsive and hence causing the wetting film to be stable.
6.1 Introduction

Wetting occurs when vapor (or liquid) substitutes the immiscible phase on a solid surface. The wetting property is of critical importance in controlling the complex geometry of colloidal bodies [1, 2] and the stability of colloidal systems [3, 4]. In froth flotation, for example, separation of minerals are commonly carried out on the basis of surface wettability [5, 6]. When air bubbles come in close contact with solid surfaces, they selectively pick up hydrophobic particles, leaving hydrophilic ones behind. A variety of techniques have been used for characterizing the wetting properties of the solid surfaces [7]. Contact angle measurement is one of the most widely used methods. One of the key characteristics for a hydrophobic surface is the high water contact angle. Thermodynamic analysis on the three-phase contact point showed that the surface wettability is controlled by the disjoining pressure in a thin liquid film (TLF) [8]. When a TLF is subjected to an attraction, wetting transition occurs [9, 10].

Wetting transitions are commonly observed on hydrophobic surfaces. When a small water droplet sits on a hydrophobic surface, a finite contact angle is developed at the three-phase contact line. Laskowski and Kitchener suggested that the formation of the water contact angle on a hydrophobic surface can be attributed to a negative disjoining pressure in accordance to the Frumkin-Derjaguin theory [11]. The authors also commented that the contact angle developed on a hydrophobic surface might be attributed to the enhanced hydrogen bonding in the vicinity of a hydrophobic surface. It was well documented that the coagulation occurs in water between hydrophobic bodies, such as coal and oil droplets [12, 13]. A significant feature for the hydrophobic coagulation is that it requires a high energy input to break the coagulated system and it is non-reversible.

In droplet-based microfluidic applications, a reversible wetting property is favorable for manipulating the desirable properties of the colloidal systems. The tuning of the intermolecular interaction, such as electrostatic double-layer force and van der Waals dispersion force, showed a potential impact on the reversal wetting property. According to the Frumkin-Derjaguin theory, the wetting transition occurred when two confining surfaces were attracted to each other. By manipulating the charges at interfaces, the wetting transition can be achieved by the electrical double-layer attraction alone. The electrolytic coagulation has been shown in many colloidal
systems, for example, between air bubbles and particles [14-16], between air bubbles and oil droplets [17], or between particles and particles [18, 19].

The early work was done by Derjaguin et al. [20] showed that bubbles and particles can be attracted to each other when they are oppositely charged. During the bubble-particle interaction, double-layer force prevails over the van der Waals dispersion force which is repulsive, so that the particles can be fixed on the surfaces of the bubble. Schulze et al. [21] found that the bubble can be pinned on a silica surface in the presence of Al$^{3+}$ ions. The authors showed that the silica surface was positive charged with a potential of 35 mV, while the air bubble remained was negatively charged with the surface potential of -35 mV. It was found by Tabor et al. [17] that an air bubble coagulated with an oil droplet in a surfactant-free aqueous solution at pH = 3.2. The results showed that the disjoining pressure changed from a repulsion at pH = 5 to an attraction at pH = 3.2. Jiang et al. [14] showed that air bubbles can float the naturally hydrophilic α-Al$_2$O$_3$ particles at the pH range of 4.0 - 5.8, where bubbles and particles were oppositely charged.

The electrolytic coagulation phenomenon described above were interpreted by measuring the zeta potentials of the particles and the air bubbles, based on which disjoining pressures can be calculated. However, it is difficult to determine measure the disjoining pressures of unstable wetting films. First, when a bubble or droplet approaches a rigid surface, the air/water interface deforms in response to the external force, which make it difficult to determine the actual separation distance during the course of the interaction [22]. Additionally, the wetting film on a hydrophobic surface is metastable and, thus, the disjoining pressure cannot be determined using the thin film pressure balance (TFPB) technique by balancing the capillary pressure and the disjoining pressure, because the latter is negative.

We have recently developed a methodology to determine both the negative and positive disjoining pressures in wetting films. The transient changes in the interference fringes of the wetting films were captured by means of a high-speed camera. By analyzing the interference fringes, we were able to reconstruct the spatiotemporal profiles of the wetting films formed between a continually deforming air bubble and a solid surface [23]. The thickness profiles can be used to determine the disjoining pressure from the numerical analysis on the basis of the Reynolds lubrication theory.
In the present work, we undertook a detailed study of the wetting film drainage on a hydrophilic silicon surface in the presence of Al\textsuperscript{3+} ions. The wetting property on a hydrophilic surfaces varied by changing the Al\textsuperscript{3+} concentration. We have shown that an ultrathin wetting film in a 3x10\textsuperscript{-5} M Al\textsuperscript{3+} solution was formed on a silicon wafer surface until a small contact angle was formed. The results are discussed in view of the Frumkin-Derjaguin isotherm [24]. It is hope that the present study will shed a light on the mechanisms involved in wetting transition.

6.2 Experimental and Methods

6.2.1 Materials

Polished silicon wafers (<100> orientation, University Wafer, Inc.) were used as the substrates for the study of wetting films. The use of silicon wafers exhibits two benefits over the fused quartz plates. First, they are ultra-flat with r.m.s roughness of 0.5 Å, as determined from the AFM contact images. Secondly, the refractive index (n) of silicon is 4.1 at light wavelength (λ) of 546 nm, which gives a better contrast than the fused quartz (n = 1.46) with respect to water (n = 1.33). As a consequence, the interference fringes reflected from the silicon surfaces are much clearer than that reflected from the quartz plates, which allows to obtain a higher resolution in film thickness.

The silicon wafer was cleaned in a boiling Piranha solution (7:3 by volume of H\textsubscript{2}SO\textsubscript{4} :H\textsubscript{2}O\textsubscript{2}) at 125 °C for 5 min, followed by rinsing with amounts of ultrapure water and dried in a pure nitrogen gas stream. The wafer was hydrophilic after Piranha treatment, with 0° water contact angle. The hydrophilic nature of the silicon surface was attributed to a formation of the silicon oxide layer during the process of Piranha cleaning. The ultrapure water (>18.2 MΩ/cm) was supplied from the Direct-Q water purification system(Millipore). Aluminum chloride (99.999%, Alfa Aesar) was used as received.

6.2.2 Thin Film Pressure Balance
The wetting properties on the silicon surfaces were studied by monitoring the drainage of the wetting film between an air bubble and a hydrophilic surface. A high-speed camera (Fastcam 512 PCI, Photron) was used to capture the interference fringes of wetting films using a 5x long-working distance objective. By analyzing the changes in the gray value across the interference fringes, one was able to draw the temporal and spatial thickness profiles. The high-speed camera was operated at 200-1000 frames per second (fps). The bubble was artificially formed in a small capillary cell, when the liquid inside the small capillary was sucked out by means of a manual piston pump. A monochromatic green light ($\lambda = 546$ nm) was produced by passing the light produced from a mercury-vapor lamp (USH-103OL, Ushio Inc) through a bandpass filter (10 nm bandwidth, Edmund Optics).

The interference patterns obtained in the present work are shown in Figure 6.1a. The fringe behaves perfectly in an axial symmetric manner, and thus the film profiles are shown in the cylindrical coordinate. The spatial and temporal profiles of the wetting films were obtained by

![Figure 6.1](image_url)

Figure 6.1 (a) Interference fringes of the wetting films recorded by a high-speed video camera. The spatial and temporal profiles of the wetting films are obtained by monitoring the changes in the pixel values of interference images as function of time. (b) Local film thickness ($h$) vs. time ($t$) at the radial position of the wetting film. (c) Spatial thickness profiles of a wetting film corresponding to the red line in (a). The profiles were obtained by analyzing the temporal thickness profiles of the wetting film at each pixel point along the red line.
analyzing the changes in gray value ($I$) of interference patterns using the following Eqs. (6.1)-(6.3),

$$h = \frac{\lambda}{2\pi n_2} \left[ \frac{2m + 1}{2} \pi \pm \arcsin \left( \frac{\Delta}{\sqrt{1 + (1 - \Delta)^2}} \frac{\sqrt{R_{12}R_{23}}}{(1 - \sqrt{R_{12}R_{23}})^2} \right) \right]$$  

(6.1)

$$\Delta = \frac{I - I_{\text{min}}}{I_{\text{max}} - I_{\text{min}}}$$  

(6.2)

$$R_{12} = \frac{(n_1 - n_2)^2}{(n_1 + n_2)^2} \quad \text{and} \quad R_{23} = \frac{(n_2 - n_3)^2}{(n_2 + n_3)^2}$$  

(6.3)

where $n_1 = 1$, $n_2 = 1.33$ and $n_3 = 4.1$ are used to represent the refractive index of air (1), water (2) and silicon surface (3), respectively; $m$ is determined by the order of fringes; and $I_{\text{min}}$ and $I_{\text{max}}$ are the minimum and maximum gray values in each order of the interference. The temporal profiles of the wetting film at the center (labeled as a yellow triangle) and at the outer region (labeled as a green triangle) are shown in Fig. 6.1(b). Figure 6.1(c) shows the spatial profiles of the wetting films, obtained from the temporal profiles at each pixel along the red line shown in Fig. 6.1(a). By analyzing the spatiotemporal profiles of the wetting films on the basis of the Reynolds lubrication theory, one can obtain the information on rate of the film drainage and determine the disjoining pressure in wetting films.

The experiments were conducted using small films. The size of the film was controlled by means of a manual piston pump. It was shown that a large film can form a convex shaped wetting film, known as a dimple, trapping the liquid at the center. The formation of the dimple was attributed to the uneven thinning rate along the radial direction by a high pressure gradient at the rim than at the center. The higher pressure gradient drove the liquid preferentially from the rim to the outer region. In the present work, small film is used so that the film at the center could be considered flat.

6.2.3 $\zeta$ -potential Measurement
The ζ-potential measurements were conducted using the Zetasizer (Nano-ZS, Malvern Instrument Ltd, UK) at temperature of 25 °C. The surface potential of the oxidized silicon wafer

![Graphs showing spatial and temporal thickness profiles](image)

Figure 6.2 Spatial and temporal thickness profiles of the non-dimpled wetting film formed on the freshly oxidized silicon surface in (a) $10^{-6}$ M, (b) $3 \times 10^{-5}$ M and (c) $10^{-3}$ M AlCl₃ solution. $h_0$ in (a) and (c) represents the film thickness at equilibrium. The dark red line shown in (b) at $t = 2.00$ s represents the film profile after the bubble touches the solid surface.
was obtained by measuring the $\zeta$-potential of the glass beads (3-10 µm, polycliences) in water. Prior to the measurement, the glass microspheres were suspended in the AlCl$_3$ aqueous solution using a magnetic stirrer. It was assumed that the surface property of the oxidized silicon wafers and the glass beads were the same. Each experiment was conducted at least 5 times, and the average value was used.

### 6.3 Results

Figure 6.2 shows the temporal and spatial thickness profiles of the wetting films formed on the freshly cleaned silicon surfaces in (a) $10^{-6}$ M, (b) $3 \times 10^{-5}$ M and (c) $10^{-3}$ M AlCl$_3$ solution. In order to show the comparison, the initial time ($t = 0$) was set when the film thickness at the center is 300 nm. As shown, the spatiotemporal film profiles behaved differently at varying Al$^{3+}$ concentrations. In a $10^{-6}$ M Al$^{3+}$ solution, the shape of the film was initially spherical with the minimal deformation. As the film continued to thin, it reached a state of equilibrium at film thickness ($h_e$) of 147 nm.

The thinning kinetics of the wetting film in a $3 \times 10^{-5}$ M AlCl$_3$ solution was much faster, as shown in Fig. 6.2(b). Initially, the film thinned gradually, behaving similarly with that in the $10^{-6}$ M AlCl$_3$ solution. When the film thickness was below 100 nm, the film thinned accelerated at the center than the outer region, pulling the film at the center until it ruptured. It was found that the film was drained to a thickness of 50 nm at the center when $t = 1.6$ s, while the thickness at the outer region was not significantly changed. As the film thinned, a new equilibrium was reached by forming an ultrathin $\alpha$-film, where $\Pi = 0$. The $\alpha$-film spread on the solid surface to a state of equilibrium. As shown, at $t = 2.0$ s, a three-phase contact line was developed at the radial position ($r$) of 8 µm. Note that film thickness below 5 nm could not be accurately obtained in the present work using monochromatic interferometry technique. The film thickness of $\alpha$-film can be obtained using the ellipsometry technique, as reported by Derjaguin et al. [25]. In general, $h < 1$ nm for the $\alpha$-film formed on the hydrophobic surface. The thickness of the $\alpha$-film can also be theoretical estimated by the Frumkin-Derjaguin isotherm, when the disjoining pressure was known. In the present work, for a simplification, we assumed that the film thickness after the bubble touched the solid surface was zero.
Figure 6.2c shows the film profiles of wetting films in a 10\(^{-3}\) M AlCl\(_3\) solution. It was found that the film profiles exhibited similarly to that in a 10\(^{-6}\) M AlCl\(_3\) solution. The film was thinning gradually, and became stabilized at \(h_e = 30\) nm. The Debye length of the aqueous solution can be calculated based on the Grahame equation for the interaction between two surfaces with low potentials. In the 10\(^{-3}\) M Al\(^{3+}\) solution, \(\kappa^{-1} = 3.5\) nm. In a solution with a small Debye length, the double-layer force was negligible at \(h > 15\) nm. Therefore, the film was stabilized by the van der Waals dispersion force in a 10\(^{-3}\) M AlCl\(_3\) solution.

Figure 6.3 compares the thinning kinetics of the wetting films in the presence of 10\(^{-6}\) M, 3\(\times\)10\(^{-5}\) M and 10\(^{-3}\) M AlCl\(_3\). The plot shows the minimum film thickness \((h_{\text{min}})\) vs. time (t). It was shown that the thinning kinetics of the wetting film in the 10\(^{-6}\) M AlCl\(_3\) solution was much slower than the film in the 3\(\times\)10\(^{-5}\) or 10\(^{-3}\) M AlCl\(_3\) solution. It has been shown above that the film profiles obtained at varying Al\(^{3+}\) concentrations were close to the same at \(h > 100\) nm, indicating that the curvature pressure was not be responsible for the retarded thinning kinetics at
10^{-6} \text{ M AlCl}_3. It is the long-range repulsive double-layer force preventing the film drainage and stabilizing the film.

In the presence of higher concentrations of Al^{3+} ions, the thinning kinetics were much faster at \( h > 120 \) nm. In a 3×10^{-5} M or more Al^{3+} aqueous solution, the Debye length (\( \kappa^{-1} \)) was 24 nm or less. The disjoining pressure contributed from the electrical double-layer force was almost negligible at \( h > 120 \) nm, and thus, the wetting film drainage was dominated by the curvature pressure at thick film only. As \( h < 120 \) nm, the wetting film in the presence of 3×10^{-5} M AlCl_3 thinned much faster due to the strong double-layer attraction. In a 10^{-3} M AlCl_3 solution, the film was thinning gradually at \( h < 120 \) nm, and reached equilibrium at \( h_e \approx 30 \) nm.

It has been shown that the process of the wetting film drainage is controlled by both the capillary pressure and disjoining pressure in the film [25, 28]. The capillary pressure (\( p_{\text{cur}} \)) created by the surface tension pressure drove the film thinning at \( h > 200 \) nm, while the disjoining pressure (\( \Pi \)) created by the surface force dominated the film thinning at \( h < 200 \) nm. In a thin film, \( p, p_{\text{cur}} \) and \( \Pi \) satisfy the pressure balance across the air/water interface at normal direction,

\[
p = p_{\text{cur}} - \Pi \tag{6.4}
\]

The \( p \) was derived on the basis of the Reynolds lubrication theory, \( p_{\text{cur}} \) was obtained by calculating the curvature at interface, and \( \Pi \) was obtained using the Eq. (6.4),

\[
p = 12 \mu \int_{r=0}^{r=h} \frac{1}{r} \left[ \int_{\gamma = 0}^{r} \frac{\partial h}{\partial t} dr \right] dr \tag{6.5}
\]

\[
p_{\text{cur}} = \frac{2 \gamma}{R} - \frac{\gamma}{r} \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) \tag{6.6}
\]

\[
\Pi = \frac{2 \gamma}{R} - \frac{\gamma}{r} \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) - 12 \mu \int_{r=0}^{r=h} \frac{1}{r} \left[ \int_{\gamma = 0}^{r} \frac{\partial h}{\partial t} dr \right] dr \tag{6.7}
\]

in which \( h \) is the film thickness, \( r \) the radial position, \( \mu \) the fluid viscosity, \( R \) is the radius of the bubble and \( \gamma \) is the air/water interfacial tension. Equations (6.5)-(6.7) were derived on the basis of the non-slip boundary conditions at both the air/water and the solid/water interfaces. The hydrodynamic boundary conditions at the solid/water and vapor/water interfaces in confined
geometries have been studied recently. The results showed that the non-slip boundary conditions were valid at the surfactant-free air/water interface of a wetting film. This might be attributed to the trace of air pollutants or particles on the vapor/water interface holding the stress in a low-shear-rate flow [26, 28]. The same statement might also apply to the solid/water interface regardless of the solid hydrophobicities. The experiments conducted by the surface force apparatus (SFA) and the atomic force microscopy (AFM) showed that the slip length varied with the hydrophobicities and the shear rate of the liquid. When the liquid was confined in a thin film with a low shear rate, the liquid on the solid surface might be stationary regardless of the hydrophobicity [29].

By analyzing the temporal and spatial profiles of the wetting films using the equations (6.5)-(6.7), one can compare the profiles of $p$, $p_{\text{cur}}$ and $\Pi$ in a wetting film. Figure 6.5(a) shows the changes in $p$, $p_{\text{cur}}$ and $\Pi$ in a wetting film in the presence of $10^{-6}$ M AlCl$_3$. As shown, $p_{\text{cur}}$ increased from the far field to the center of the film. The higher $p_{\text{cur}}$ at the center than the outer region drained the liquid in a film. As the film thinning continued, $p_{\text{cur}}$ increased gradually with time along the radial direction, and reached a plateau value of 72 N/m$^2$ at the center of the film at $t = 12$ s. The increase of $p_{\text{cur}}$ with time was due to the increase of the deformation area. On the other hand, $p$ decreased with time, and became zero when the film was in equilibrium. The disjoining pressure ($\Pi$) was obtained by subtracting $p$ by $p_{\text{cur}}$ using Eq. (6.4). It was shown that $\Pi$ gradually increased with time, and reached the maximum value of 72 N/m$^2$, where $\Pi = p_{\text{cur}}$. A detailed analysis showed that the arising repulsive disjoining pressure prevented the film drainage by killing the curvature pressure.

The profiles of $p$, $p_{\text{cur}}$ and $\Pi$ in $3 \times 10^{-5}$ M AlCl$_3$ behaved in the different manners, as shown in Fig. 6.4(b). It was found that $p_{\text{cur}}$ was small in a $3 \times 10^{-5}$ M AlCl$_3$ solution in that the bubble was not significantly deformed in a small film. The excess pressure ($p$) increased slightly at $t < 1.34$ s when $h_{\text{min}}$ dropped from 300 to 100 nm, while the $p$ increased dramatically when $h_{\text{min}} < 100$ nm. The $p = 500$ N/m$^2$ at the center of film at $t = 1.6$ s. By subtracting $p$ from $p_{\text{cur}}$, one can obtain $\Pi$. The results showed that $\Pi$ became strongly negative (or attractive) when $t > 1.34$ s. Therefore, it is readily concluded that the faster drainage rate of the wetting film was driven by a negative $\Pi$. Note that $p_{\text{cur}}$ decreased with time after the film thickness was below 200 nm. The reversal of the curvature pressure indicated that the curvature of the vapor/water interface became small or negative. This was partially due to the deformation of the air/liquid interface at the center by a
strongly attractive disjoining pressure, which created a lower curvature pressure at the center compared to that at the outer region.

In a $10^{-3}$ M AlCl$_3$ solution, $p_{\text{cur}}$ behaved similarly with that in a $10^{-6}$ M AlCl$_3$ solution, as shown in Fig. 6.5(c). It was found that $p_{\text{cur}}$ increased with time, and $p_{\text{cur}} = 70$ N/m$^2$ at equilibrium. The hydrodynamic pressure behaved similarly with $p_{\text{cur}}$ at $t < 1.5$ s, while it diminished at $t = 17.60$ s. As shown in $\Pi$-plot, the disjoining pressure was negligible when $h_{\text{min}}$ decreased from 300 nm to 100 nm. As the film thinning continued, the repulsive $\Pi$ dominated in the thin liquid film. The film became stabilized when the curvature pressure was balanced by a repulsive $\Pi$ contributed from the van der Waals dispersion force.
An analysis of the pressure distribution in wetting films showed that the film was initially drained by the curvature pressure created by the changes in curvature at the air/liquid interface, and afterwards by the disjoining pressure created by surface force. In a thin film, the thinning kinetics were either accelerated by the attractive disjoining pressure or retarded by the repulsive disjoining pressure. The results above showed that disjoining pressure in the wetting film had a transition from repulsion to attraction at AlCl$_3$ concentration of $3\times10^{-5}$ M. A plot of $\Pi$ vs. $h$ in presence of AlCl$_3$ was shown in Fig. 6.5. The disjoining pressure was obtained from the center of the film where the film was considered flat. As shown, the long- and short-range repulsive disjoining pressures were found in wetting films in the presence of $10^{-6}$ M and $10^{-3}$ M AlCl$_3$, respectively. At $3\times10^{-5}$ M AlCl$_3$, however, a strongly attractive disjoining pressure was found.

Figure 6.5  Disjoining pressure isotherm of a wetting film in the presence of AlCl$_3$ electrolyte. Repulsive disjoining pressures with Debye length ($\kappa^{-1}$) of 90 and 3 nm were found for $10^{-6}$ M and $10^{-3}$ M AlCl$_3$ solution, respectively. A strong attractive disjoining pressure with $\kappa^{-1}=24$ nm was detected in $3\times10^{-5}$ M AlCl$_3$ solution, due to the electrostatic attraction created by the oppositely charged interfaces of the wetting film.
The disjoining pressure was explained by the classic DLVO theory,

$$\Pi = -\frac{A_{132}}{6\pi h^3} - \frac{EE_0 K^2}{2 \sinh(\kappa h)} \left[ (\psi_1^2 + \psi_2^2) \cos \sinh(\kappa h) - 2\psi_1 \psi_2 \coth(\kappa h) \right]$$  \hspace{1cm} (6.8)

in which the van der Waals dispersion and the double-layer force were included. In Eq. (6.8), $A_{132}$ is the Hamaker constant for the wetting film of water formed on the silicon surface, and $A_{132} = -4.0 \times 10^{-19}$ J [30]. The disjoining pressure contributed from the electrostatic double-layer force was calculated using the Hogg–Healey–Fuerstenau (HHF) approximation [31]. The HHF model assumes that both interfaces maintain a constant potential when the double layers overlap. The best fit was obtained when the Debye lengths were 90, 24 and 3 for $10^{-6}$ M, $3 \times 10^{-5}$ M and $10^{-3}$ M AlCl$_3$, respectively. These values were close to those predicted from the Lifshitz theory. The surface potentials of solid surfaces can be determined by measuring the zeta potentials of the silica particles in the AlCl$_3$. With the values of both the Debye length and the surface potential of the solid surface, one could obtain the surface potential of the air bubble by fitting the disjoining pressure data with Eq. (6.5). The fitting parameters are listed in Table 6.1. As shown, the surface potentials of the air bubbles and the solid surfaces had transitions from a negative value to a positive value as the ion concentration increased, while the aluminum ions preferentially reversed the charge at the silicon surface than the bubble surface. The uneven charge distribution in both interfaces created a net attraction.

When the attractive force dominated in a thin wetting film, the wetting transition occurred by moving a three-phase contact line on the surface. It was initialized by the formation of the $\alpha$-
film where $\Pi = 0$, and followed by an expansion of the three-phase contact line. In equilibrium, a finite contact angle was formed where the interfacial tensions at the three-phase contact point were balanced with each other. Fig. 6.5 shows the microscopic photos of the moving contact line in a $3 \times 10^{-5}$ M AlCl$_3$ aqueous solution. The $h$ vs. $r$ plot shows the thickness profiles of the wetting films corresponding to the interference fringes. It was found that an $\alpha$-film was formed at $t = 1.88$ s, followed by a spreading of the contact line on an oxidized silicon surface until a finite contact angle was formed. At $t = 2.28$ s, the radii of the contact area where the bubble touched the solid surface was 20 µm. This value increased to 50 µm at $t = 3.00$ s. At $t = 5.08$s, the film stabilized with a spreading area of 70 µm in radius. The contact angle developed on the silicon surface could be calculated using the simple geometry equation, $\sin \theta = r/R$. Given $r = 70$ µm, the contact angle developed in a $3 \times 10^{-5}$ M AlCl$_3$ solution is approximately 2.0°. We have shown above that a strong attractive disjoining pressure contributed from the double-layer attraction was present in a wetting film of the $3 \times 10^{-5}$ M AlCl$_3$ solution. According to the Frumkin-Derjaguin theory of wetting, a strongly attractive disjoining pressure can create a negative surface free energy. Such negative free energy can destabilize the wetting film, resulting in a contact angle on the solid surface.

### 6.4 Discussion

In flotation, the dewetting transition is a process when the vapor phase is replacing the liquid on a solid surface. Thermodynamically, the changes in the free energy can be described by the Dupre’s equations,

<table>
<thead>
<tr>
<th>AlCl$_3$ (M)</th>
<th>$\psi_1$ (mV)</th>
<th>$\psi_2$ (mV)</th>
<th>$\kappa^{-1}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-6}$</td>
<td>-48</td>
<td>-50</td>
<td>90</td>
</tr>
<tr>
<td>$3 \times 10^{-5}$</td>
<td>54</td>
<td>-23</td>
<td>24</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>97</td>
<td>60</td>
<td>3.5</td>
</tr>
</tbody>
</table>
\[ \Delta G = \gamma_{12} - \gamma_{13} - \gamma_{23} \]  

(6.9)

where \( \gamma \) is the interfacial tension, and the subscript 1, 2 and 3 represent the solid, air and liquid, respectively. When the dewetting transition occurs, a contact angle (\( \theta \)) is developed on the solid surface along the three-phase contact line. In equilibrium, the contact angle is defined using Young’s equation,

\[ \gamma_{12} = \gamma_{13} + \gamma_{23} \cos \theta \]  

(6.10)

Combining Dupre’s equation with Young’s equation, one can obtain the following expression for the free energy changes of the wetting transition,

\[ \Delta G = \gamma_{23}(\cos \theta - 1) \]  

(6.11)

In Eq. (6.3), for the wetting transition to occur (\( \Delta G < 0 \)), the contact angle of the liquid on a solid surface should be greater than zero.

Churaev [24] interpreted the wetting transition as a spontaneous process. Thermo-dynamically, the changes in Gibbs free energy during the wetting transition can be related to an integral of the disjoining pressure with the changes in the film thickness,

\[ \Delta G = \int_{h_o}^{\infty} \Pi(h)dh \]  

(6.12)

where \( h_o \) is the thickness of the thin liquid film after the wetting transition occurs. Mathematically, \( h = h_o \) at \( \Pi = 0 \). Combining Eq. (6.11) with Eq. (6.12), one can obtain the Frumkin-Derjaguin isotherm as,

\[ \cos \theta_o = 1 - (1/\gamma_{23}) \int_{h_o}^{\infty} \Pi(h)dh \]  

(6.13)

It is shown that the contact angle is directly related to the disjoining pressure. If the integral of the disjoining pressure with respect to the thickness is larger than zero, the contact angle will be developed and consequently the wetting transition can occur.

The disjoining pressure in the thin liquid film between an air bubble and a hydrophilic solid surface can be described by Eq. (6.5). By substituting Eq. (6.5) with Eq. (6.13) and integrating
the thickness from $h_0$ to infinity, one can obtain an expression for the Frumkin-Derjaguin isotherm in view of the disjoining pressure in a wetting film,

$$
\cos \theta = 1 + \frac{1}{\gamma_{23}} \left[ - \frac{A_{132}}{12\pi h_0^2} + \varepsilon e_o \kappa \frac{2\psi_1 \psi_2 \exp(\kappa h_0) - \psi_1^2 - \psi_2^2}{\exp(2\kappa h_0) - 1} \right]
$$

(6.14)

Eq. (6.14) shows the modified Frumkin-Derjaguin isotherm relating with the free energy changes per unit area accompanied with the wetting transition on a hydrophilic solid surface. In a wetting film formed on a solid surface, the free energy changes due to the van der Waals force are positive. The positive disjoining pressure prevents developing a contact angle on a solid surface. However, the free energy change due to the electrical double-layer force varies with the values of $\psi_1$ and $\psi_2$. It is positive if $\psi_1$ and $\psi_2$ have the close values, and negative if $\psi_1$ and $\psi_2$ have the opposite signs or have the same sign but the large difference in magnitude. Therefore, it is suggested that the wetting transition might be possible on a hydrophilic surface by manipulating the surface potentials of two interfaces.

We have shown that the aluminum ions preferentially reversed the charge of the solid surface from negative to positive, while maintaining the negative charge at the air/water interface. The opposite charge brought the vapor phase to “contact” with the solid surface, and formed an equilibrium $\alpha$-film. As shown by Churaev, the formation of the three-phase contact line was attributed to the presence of a negative disjoining pressure [8]. During the course of three-phase contact formation, the attractive disjoining pressure contributed by the double layer force overwhelms the repulsive van der Waals pressure. Note that the van der Waals force decays much faster than the double layer force, and thus, an equilibrated film exists where the repulsive van der Waals force is balanced by the attractive double layer force. In an ultra-thin film, the film reached a new equilibrium by forming an $\alpha$-film where $\Pi = 0$. In general, the thickness of the $\alpha$-film is only a few Å on a hydrophobic surface, which is approximately equivalent to the thickness of a few layers of water molecules. The thickness of the $\alpha$-film might be thicker on a less hydrophobic surface. Once the $\alpha$-film is formed, it begins to spread on a solid surface until a finite contact angle is formed. The wetting dynamics have been studied widely and the results showed that the spreading of the $\alpha$-film depended on the activation energy of the solid surface. When the free energy changes of the wetting transition become more negative, the spreading becomes more significant.
As shown above, the interaction force between an air bubble and a solid surface was attractive in a wetting film of \( h > 10 \) nm. Such attraction resulted in the wetting film being optically ruptured. An estimated contact angle was calculated using Eq. (6.14) by inputting the values of \( \psi_1, \psi_2 \) and \( \kappa \). In Eq. (6.14), \( A_{132} = -4.0 \times 10^{-20} \) J, and \( h_o \) is determined from the disjoining pressure curve where \( \Pi = 0 \). The calculated contact angle from Eq. (6.14) is equal to 9.1\(^o\). The calculated value is larger than the value optically obtained from the interference fringes (\( \theta = 2^o \)). The most reasonable explanation is the dewetting process might be hindered at the three-phase contact line due to the adsorption of tiny particulates on the solid surface, or contact hysteresis. It was well known as the pinning effect on the three-phase contact line. It might be due to the presence of the structure force in the wetting film formed on a hydrophilic surface with contact angle less than 20\(^o\).

The adsorption of inorganic ions on a solid surface has been widely investigated since the 1940s. It was shown that the electrophoretic mobility of the particles could be dramatically changed in the presence of the multivalent cation ions, such as Co(II), Al(III) and Th(IV) [25-27]. It was found that the multivalent ion adsorption on the solid surface could substantially improve flotation behavior [28, 29]. Fuerstenau et al. [30] found that the pH range in the sulfonate flotation of quartz could vary depending on the type of ions. The result showed that the effective pH value for a floating quartz particle is 2.4 \( \sim \) 3.2 in the presence of \( \text{Fe}^{3+} \) ions and 4.4 \( \sim \) 7 in the presence of \( \text{Al}^{3+} \) ions, respectively. The authors suggested that the varying flotation behaviors in the presence of different metal ions were attributed to the precipitation of the metal hydrolysis products on the solid surface, which changed the surface potential of the quartz surface [31]. It has been shown from the distribution diagram of the 0.1 mM \( \text{Al}^{3+} \) hydrolysis products that \( \text{Al}_{13}\text{O}_{4}(\text{OH})_{24}^{7+} \) was the dominating species at pH of 5.7 \( \sim \) 7.8 [32]. The coverage of aluminum hydrolysis species on a quartz surface reversed the surface charge of the quartz. In the current work, we observed the attractive surface force in the presence of a 0.03 mM \( \text{Al}^{3+} \) ion. The result was consistent with the data obtained by Fuerstenau et al. [30] that the flotation recovery was close to 90\%, indicating that the surface charge was reversed.

However, the adsorption of the \( \text{Al}^{3+} \) hydrolysis products at the air/water interface behaves differently from those at the solid/water interfaces. Yang et al. [33] measured the zeta potential of the air bubbles in the electrolyte solution. They found that the bubble potential was not significantly changed at \( 10^{-5} \) M \( \text{AlCl}_3 \). As the \( \text{AlCl}_3 \) concentration increased to \( 10^{-3} \) M, the zeta
potential of the air bubble was dramatically changed, indicating that the aluminum hydrolysis species were adsorbed on the surfaces of the air bubbles. It was found that the surface charge had a charge reversal at an AlCl$_3$ concentration of $10^{-4}$ M at pH = 6. Similar results were also reached by Li and Somasundaran [34], who showed that the presence of a positively charged Al(OH)$_3$ species in 1mM AlCl$_3$ solution reversed the charge at air-water interface.

Due to the different charge behaviors in respect to the adsorption of Al$^{3+}$ hydrolysis products at interfaces, hetero-coagulation is possible if the interfaces are oppositely charged. We found that the aluminum ion was preferred to adsorb on the silicon surface to reverse the charge over the air/water interface. The transition of the charge reversal creates an attractive disjoining pressure between two asymmetric surfaces, which has been described previously as heterocoagulation between two oppositely charged surfaces. The result and methodology suggested in the present work might be useful in the microfluidic applications for desired wetting properties of air bubbles and oil droplets. The theoretical analysis based on the Frumkin-Derjaguin isotherm might shine a light on the microscopic study of the dewetting phenomena.

6.5 Conclusions

The interaction forces in the wetting films formed on a hydrophilic silicon surface was analyzed by studying the kinetics of wetting films on the basis of the Reynolds lubrication theory. The results showed that the double-layer force becomes either attractive or repulsive depending on the Al$^{3+}$ ion concentration in solution. In a $10^{-6}$ M AlCl$_3$ solution, the wetting film is stabilized by the long-range double-layer repulsion. As the concentration of Al$^{3+}$ ions increased to $3 \times 10^{-5}$ M, the wetting film ruptured, followed by an expansion of the three-phase contact line on the hydrophilic silicon surface. The thin liquid film was subjected to an electrostatic attraction between oppositely charged surfaces. As the Al$^{3+}$ ion concentration was increased to $10^{-3}$ M, the wetting film regained its stability, denying bubble-solid contact, due to a repulsive dispersion force. The analysis of the disjoining pressure by the DLVO theory combined with the zeta potential measurement showed that the Al$^{3+}$ ions preferentially reversed the charge at the silicon/water surface rather than at the air/water interface, possibly due to the preferential adsorption of the hydroxylated aluminum ions on the solid/water interface.
Moreover, a microscopic study of the contact-line showed that the wetting film of water formed on a hydrophobic silicon surface ruptured and formed a small contact angle of 2°. Development of the contact angle by a double-layer attraction can be predicted by the Frumkin-Derjaguin isotherm. This is the first microscopic proof showing that the air bubble can dewet a hydrophilic surface by preferentially reversing the surface charge of one surface.

6.6 References


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Chapter 7. Development of the Force Apparatus for Deformable Surfaces (FADS)

ABSTRACT

Many investigators reported the measurement of the forces acting between bubbles and particles during flotation. However, most of the results were inconsistent with the flotation practice, which can be attributed to the fact that air bubbles deform during the approach and detachment cycles of the measurement. For one thing, deformation of bubbles makes it difficult to determine the separation distances between two macroscopic surfaces. For another, the deformation may absorb part of the interaction energies, making it difficult to accurately determine the forces involved. To overcome these problems, a new device named tentatively, “Force Apparatus for Deformable Surfaces (FADS),” has been developed. It included two optical systems, one for direct measurement of forces, and the other for monitoring deformation of the bubble. The force measurement involves monitoring of the deflection of a cantilever of known spring constant, while the bubble deformation is monitored by recording the interference patterns of the wetting films in motion by means of a CCD camera and subsequently reconstructing the spatiotemporal film profiles with a nano-scale resolution. The results obtained with both the hydrophilic and hydrophobic surfaces are consistent with what is known from flotation practices.
7.1 Introduction

Surface force arises when two macroscopic bodies are confining a third phase. As the deformable bodies, such as air bubbles or droplets, encounter with other bodies in a close proximity, they undergo deformation in response to the hydrodynamic forces arising from the fluid motion and the surface forces. Such scenario has been widely shown in a variety of industrial, biological and medical applications, ranging from froth flotation for mineral separation [1, 2], oil emulsification in food processing [3] and membrane fusion in biological engineering [4, 5]. Surface forces originate from the intermolecular interactions between the neighboring molecules during an overlap of the boundary layers. It plays a critical role in shaping the confining surfaces and controlling the stability of the colloidal systems. The ability to study the intermolecular forces has been evolved since the 1950s owing to the advancement of various scientific instruments, permitting the measurements of the interaction force between the macroscopic surfaces.

The first measurement of the surface forces between two macroscopic surfaces was conducted in 1951 by Overbeek and Sparnaay [6-8]. They designed a scientific instrument capable of measuring the interaction force between two solid surfaces in air. Later in 1969, Tabor and his co-workers [9, 10] developed the surface force apparatus (SFA) for the measurement of the forces acting between two mica surfaces in a 0.1 μN resolution. An alternative method of measuring surface force was to use the atomic force microscope (AFM) [11, 12]. By monitoring the deflection of a cantilever, it was possible to measure the forces acting between a spherical colloidal particle and a flat solid surface. When the SFA and AFM methods were used to measure the forces between deformable bodies, such as air bubbles and oil droplets, interpretation of the experimental results become complicated as it is difficult to determine the separation distances.

Many investigators attempted to measure the interaction forces between a spherical particle and an air bubble in an aqueous solution. The attempts were initialized by Ducker et al. [13], which was followed by Fielden et al. [14] and Preuss and Butt [15]. The measurements were conducted by approaching an air bubble to a sphere attached at the end of the cantilever spring of an AFM while monitoring the deflection of the spring. Recently, Dagastine and Chan developed
a methodology to attach an air bubble or an oil droplet to a cantilever surface [16, 17]. Using a droplet-attached cantilever, Dagastine and his co-workers have studied a variety of the colloidal systems, including oil-oil [18], bubble-bubble [19], and bubble-solid [20] interactions. Horn et al. showed the results of the interaction force between a mercury droplet and a solid surface [21] and between an air bubble and a solid surface [22]. The multi-wavelength beam interferometry technique was used to visualize the thickness of the thin liquid film (TLF) between two cylindrical curved surfaces.

Alternatively, some investigators indirectly studied the interaction forces between air bubbles and solid surfaces by monitoring the thickness of the thin liquid film using the interferometry technique. Earlier studies were done by Derjaguin et al. in the 1930s [23]. They studied the TLF between an air bubble and a quartz surface by monitoring the interference patterns of the TLFs using an optical technique. Similar approaches were taken by releasing a small sized air bubble towards a flat solid surface in an aqueous solution [24, 25]. The profiles of the TLFs were monitored using the interferometry technique. More recently, we have developed a methodology to determine an attractive force between an air bubble and a hydrophobic solid surface by monitoring the 3D thickness profiles of the TLFs using the high-speed micro-interferometry technique, as described in Chapters 2 and 3. The interaction forces were determined by analyzing the results on the basis of the Reynolds lubrication theory [26, 27].

All previous approaches on the measurements of the bubble-plate interaction were focused on either the dynamic behaviors of the film profiles or the interaction force between an air bubble and a solid surface. As commented by Chan et al. [28], “challenge still remains to develop experimental methods to improve understanding of the interaction forces with soft bodies.” To address this limitation of the force measurement between soft bodies, the development of a novel force apparatus is needed to determine the interaction forces with a real-time view of the interfacial deformation.

In this work, we have developed and built a novel scientific instrument to measure the interaction forces directly between an air bubble and a solid surface with a real-time view of the spatial and temporal film thickness profiles, \( h(r, t) \). This instrument is referred to as force apparatus for deformable surfaces (FADS). This instrument can be operated a
t varying approach speeds up to 12 µm/s under the maximum allowance of S/N (signal to noise ratio) using the current experimental set-up. The maximum approach distance was 15 µm, as determined by the length of the piezo stack. The instrumental designs were given in the following sections along with the results obtained on a hydrophilic silica surface and a hydrophobic silica surface. The hydrophobic silica surface was prepared by in-situ hydrophobization in a 2.2×10⁻⁵ M cetyltrimethylammonium bromide (CTAB) solution. FADS has several advantages over the AFM and SFA: i) capable of conducting force measurements between a millimeter sized air bubble and a flat solid surface with a force resolution of 1 nN, ii) high-speed imaging of the spatiotemporal profiles of the thin wetting film, iii) live view of both the microscopic and macroscopic spreading of the three-phase contact line.

7.2 Instrumental Design

7.2.1 Force Sensor

A force sensor is essential in developing a force apparatus. In the AFM, optical beam deflection is commonly used for the force measurement using a small cantilever with 20-100 µm long and 1-5 µm thick. When a longer beam is used as a cantilever, beam deflection method is limited to amplify the sub-nanometer deflection changes. An alternative technique for the force measurement is the piezoelectric method, which uses the PZT material as the cantilever to measure the charge generated from the external force. However, the electronic drift in PZT material is very sensitive to the environment and naturally inevitable. As a result, the use of the piezoelectric materials in force measurement is limited for the applications operated at high frequency. Optical interferometry offers the best solution for measuring the deflection of a longer beam. The interferometry technique determines the interference patterns of the returned light beams reflected from two adjacent interfaces. A sub-nanometer resolution is theoretically achievable with a low-drift laser and a stable mechanical design.
Figure 7.1 shows a schematic drawing of a home-built fiber optic interferometer used as the force sensor. The principle of the interferometry-type force sensor is to determine the deflection of the cantilever by monitoring the length of a cavity between the fiber end face and the upper surface of a cantilever. The cleaved single-mode fiber is aligned on top of a cantilever at a distance of ~100 µm. A butterfly packaged laser diode (2mW, Applied Optoelectronics, Inc.) is used to inject 1310 nm laser light into a fiber optic circulator (PIOC313P2111, AC Photonics). The optical circulator allows the laser light traveling in one direction with a minimal loss. As the injected laser light enters into a cavity, the returned light beams interfere with each other. The intensity of the returned light is a sinusoidal function of the traveling distance.

A balanced photoreceiver (2117-FC, Newport) is used to collect the intensity of the returned light in real time with a gain of 10 V/mW. The voltage data are collected through a data acquisition card (Model: USB-6218, National Instrument) and analyzed using a custom-written Matlab program. A bandpass filter was pre-built in photoreceiver to filtrate the background signal noise. The cutoff frequency can significantly reduce the noise from the thermal and aerobic vibrations. Signal conditioning can also be carried out digitally using the Matlab signal
processing toolbox or a smoothing function. In the present work, the lower and upper cutoff frequencies are set to be DC and 10 kHz, respectively.

The fiber interferometer requires a low noise and low drift laser output for the sensor. To ensure a constant laser output, an ultra-low noise constant current LD driver (LDC201CU, Thorlab) was used to drive the laser diode. A second prerequisite for the low-noise output is maintaining a constant temperature. The butterfly packaged laser diode has an integrated thermoelectric cooler and a thermistor, allowing a precise control of the temperature in the laser diode. A constant temperature within 0.002 °C changes over 24 hours was achieved using a LD temperature controller (TED200C, Thorlabs). A third feature to ensure the low noise output was to reduce the optical feedback by decreasing the coherence of the light. The noise was reduced by injecting a 201 Mhz radio frequency (rf) low current into a laser driver circuit using an ultra-low noise coaxial voltage controlled oscillator (ZX-209+, Mini-Circuits) [29].

The signal output is a sinusoidal function of the light traveling distance in a cavity. Note that the sensitivity of interferometer varies with the position of the sinusoidal function. The sensitivity is good at the midpoint, but poor at the peak or the valley of the signal. Therefore, it requires the calibration to ensure the maximum sensitivity prior to each measurement. A piezo stack (AE0203D04F, Thorlabs) was used as a fine control for the fiber position vertically. The cleaved fiber was fixed inside a metal tubing using the UV glue (NOA 61, Norland). As shown in Fig. 7.1, the length of the free fiber is 0.2 - 0.5 mm to ensure the minimum vibration of the free fiber. The fiber was aligned above the end of a cantilever by a home-built fiber positioner. The performance of the fiber optic interferometer is determined by the visibility of the signal. The visibility ($f_{vis}$) is given by the following relation,

$$f_{vis} = \frac{V_{max} - V_{min}}{V_{max} + V_{min}}$$

where $V_{max}$ and $V_{min}$ represent the peak and the valley values of a sinusoidal signal. To ensure the maximum performance of the fiber interferometer, we manually adjusted the length of a cavity to 50-150 µm, where a good signal visibility was achieved. Once the fiber was placed in a good performance position, the SS tubing was secured using a locking screw. The values of $V_{max}$ and $V_{min}$ were determined by changing the length of a cavity.
The deflection of the cantilever can be obtained using a following relation,

$$V = \frac{V_{\text{max}} + V_{\text{min}}}{2} \left[ 1 - \frac{V_{\text{max}} - V_{\text{min}}}{V_{\text{max}} + V_{\text{min}}} \cos \left( \frac{4 \pi \Delta n}{\lambda} + \phi \right) \right]$$

(7.2)
where $V$ is the signal readout, $\varphi$ is a constant representing the phase difference and $n$ represents the reflective index of the light traveling medium. For water, $n = 1.33$. By multiplying the deflection ($\Delta d$) with the spring constant ($k$), one can determine the force using the following relation,

$$F = k \times \Delta d$$  \hspace{1cm} (7.3)

### 7.2.2 Microscopic View of Interfacial Deformation

This new force apparatus was developed to measure the interaction force directly between an air bubble and a solid surface in water. When a deformable air bubble approached a solid surface, the bubble underwent a deformation when the hydrodynamic and surface forces acted on the surface. Although the deformation of the air bubble under the external force has been widely recognized, the challenge remains for the commercial force apparatuses, such as AFM, to determine the exact separation distance when the interacting surfaces are deformable.

Here, the monochromatic microinterferometry technique was applied to monitor the spatial and temporal profiles of the TLF between an air bubble and a solid surface. When a light beam enters into a space with the separation distance below 10 µm, an interference pattern with dark and bright crossed rings are formed. In principle, when the return light reflected from two adjacent interfaces exhibit 180° phase differences from each other, the dark fringe is formed. On the other hand, when the light reflected from two interfaces are in the same phase with each other, a bright fringe is formed. The interference patterns can be used to reconstruct to obtain the spatial and temporal thickness profiles.

In the FADS, the light interferometry system was built on a commercial inverted microscope (IX51, OLYMPUS). An ULWD (ultra-long working distance, WD=65.4 mm) 5x objective lens (MM6-OB5X, OLYMPUS) was used to observe the interference patterns. A monochromatic light with a center wavelength of 546 nm was obtained from a 100W mercury arc lamp through a bandpass interference filter (FWHM =10 nm). A clear interference pattern (or Newton ring) was formed when the film thickness of the confined liquid film was below 14 µm. The interference patterns are captured by a high-speed camera (Hi-spec 4, Fastec Imaging) at a frame rate of 100-500 frames per second (fps).
Figure 7.2(a) shows a schematic drawing of the light interferometry technique used to obtain the spatial and temporal profiles of the TLF between an air bubble and a lower surface of the cantilever. The interference pattern is shown in Fig. 7.2(b). Figure 7.2(c) shows the gray values of each pixel along the radial direction. The changes in the gray values are corresponding to the changes in film thickness. However, due to the poor spatial resolution, the accurate measurements of the film thickness are not possible by analyzing each interference fringe along the radial direction. Additionally, the light spot that each interference pattern covers is not uniform over the entire image. An alternative method to determine the film thickness accurately is by analyzing the temporal changes in the gray value at each pixel. The temporal methodology takes the advantage of the use of a high-speed camera to monitor the transient changes in the film thickness over time. Meanwhile, it overcomes the problem of the non-uniform light intensity across the entire thin liquid film by looking at the changes in the gray values at each pixel. The resolution using the temporal method is significantly improved compared to the spatial method. By obtaining the temporal thickness profiles at each pixel along the radial direction, one is able to reconstruct the spatial and temporal profiles of the TLFs. The information on the thickness profiles can be used to obtain both the hydrodynamic and surface force in a thin liquid film.

7.2.3 Contact Angle Measurement

Unlike the force measurement between two solid surfaces, force measurements with the soft materials are often accompanied with the spreading of a three-phase contact line. For example, an air bubble dewets on a hydrophobic surface by forming a three-phase contact line. In the present work, a side-view camera was used to monitor the dewetting phenomena when an air bubble dewet on a hydrophobic solid surface. Additionally, the side-view camera was used to align the position of both the air bubble and the cantilever. In our experimental set-up, a side-view camera was mounted on the side of the force apparatus with a 2-axis translation stage. A red LED with a center wavelength of 630 nm was used as the illuminator. A prism was positioned on the bottom of the quartz plate immersed in liquid. It was coated with a gold layer as the reflecting mirror. A second prism was placed on the upper quartz plate. The live images of the bubble and the cantilever were reflected from the third prism beneath the camera. Figure 7.3 shows a schematic drawing of the camera-based side view monitoring system for positioning the
cantilever and viewing the dewetting process. As shown, a small contact angle ($\theta$) is formed at a three-phase contact line on a less hydrophobic surface.

7.3 Experimental

7.3.1 Cantilever Fabrication

The force measurement between an air bubble and a flat solid surface was conducted at near DC frequency, requiring the cantilevers with the high resonant frequencies and high spring constants. On the other hand, the spring constants of the cantilevers need to be small, allowing the cantilevers to sensor the force accurately. To compromise the high resonant frequency with the great sensitivity, the cantilevers need to be thin and small. In the present work, we used 50 $\mu$m thick silicon wafers and glass sheets interchangeably to fabricate the cantilevers.

The resonant frequency of the cantilever is determined by the load applied on the cantilever. In order to reduce the vibrational noise of the cantilever in liquid, the lower surface of the cantilever was used as a target surface to maximize the stability of the signal. In the present work, we used a silicon wafer to fabricate the cantilevers for measuring the interaction between an air bubble and a hydrophilic silicon surface. An ultra-thin silicon wafer was obtained from
University Wafer Inc., and it was double-side polished with a thickness of 50 µm. A gold layer was deposited on the back side of the silicon wafer, and used to reflect the light from the fiber. The other side of the wafer was used as the target surface. The wafer was carefully handled in the class-100 cleanroom. The wafers were coated by a 50 nm thick gold layer with 5 nm thick titanium adhesion layer using E-beam physical vapor deposition system (PVD-250, Kurt J. Lesker). The ultra-thin silicon wafer was fragile, requiring a special care during the cantilever fabrication process. The ultrathin wafer was bonded on the carrying wafer using a low melting adhesive (crystalbond 555) with the gold layer facing downwardly to the carrying wafer. The bonded wafers were then cut into the rectangular pieces with dimension of 4 x 20 mm using the Automation dicing saw.

The cantilevers were picked in hot water, washed with acetone and dried on the clean tissues. The dried cantilever was glued with thick glass pieces using the Crystalbond 509 adhesive, while leaves the unglued with a length of 13 -15 mm. By considering the weight of the cantilever itself,
the resonant frequency of the cantilever was about 1 KHz. Figure 7.4 shows a photo of a cantilever fabricated for the force sensor in FADS.

 Prior to the force measurement, the cantilever is cleaned in a boiling Piranha solution (a mixture of H$_2$SO$_4$ and H$_2$O$_2$, 7:3 by volume) for 2 min. The mixture solution is a strong oxidizing agent and it removes the most organic matter. Additionally, it hydroxylates the silicon surface, rendering the silicon wafer hydrophilic.

### 7.3.2 Cantilever Calibration

The spring constant ($k$) can be geometrically determined from the dimensions of cantilevers and the Young modulus,

$$ k = \frac{Ewt^3}{4L^3} \quad (7.4) $$

where $E$ is Young’s modulus of the cantilever material, $L$ is the beam length, $w$ is the beam width and $t$ is the thickness cantilever.

In the present work, the spring constant of the cantilever is *in-situ* calibrated by applying a weight on a cantilever surface. A procedure for calibration of the cantilever spring is shown in appendix A. The weight was applied by an air bubble across a thin layer of water. As a repulsive disjoining pressure became equivalent to the curvature pressure due to the bubble deformation, a flat film was formed. The film spread at equilibrium film thickness when the bubble approached a cantilever surface. The curvature pressure ($p_{cur}$) at flat film is equivalent to the Laplace pressure ($2\gamma/R$). Therefore, the weight can be estimated from an integral of the curvature pressure across the entire thin liquid film. Here, the total force can be determined from the geometry of the TLF using the eq. (7.5),

$$ F = 2\pi \int_{r=0}^{R} p_{cur} r dr = 2\pi \int_{r=0}^{R} \left( \frac{2\gamma}{R} - \frac{\gamma}{r} \left( \frac{\partial h}{\partial r} \right) \frac{r}{R} \right) r dr \quad (7.5) $$

where $\gamma$ is the surface tension and $R$ is the radius of the air bubble. With knowing the interaction force and the deflection, one was able to determine the spring constant.
7.3.3 Instrumental Operation

An air bubble was generated by injecting the air through a tube using an air-tight syringe. It was fixed on the bottom of the quartz plate. In order for the air bubble to be fixed on the bottom of a quartz plate, the plate was hydrophobized in a $10^{-3}$ M OTS-in-toluene solution for 1 hour, soaked ultrasonically in chloroform and followed by rinsing with isopropanol. The equilibrium contact angle of water on the quartz plate was above 95°. The cantilever was glued on the upper quartz plate and fixed on with a 5-axis ($x$, $y$, $z$, $\theta_x$, $\theta_y$) translation stage.

Prior to the force measurement, the upper quartz plate was lowered to a position where the cantilever was approximately 3 mm above the lower quartz surface. It was followed by injecting the fluid in the liquid cell through the bottom quartz surface. An O-ring was used to fix the liquid between two quartz surfaces. The use of the O-ring can reduce the airflow perturbations by decreasing the area of the free air/liquid interface. The air bubble was generated afterwards, and its size was controlled using the air-tight syringe. In the present work, the size of the air bubble is about 2 mm.

The cantilever was aligned above the air bubble before the force measurement. The position of the cantilever was observed by both the side-view and the bottom-view cameras. The position of the air bubble can be adjusted coarsely by a screw actuator and finely by a piezo actuator. The piezo stack was driven using an open-loop piezo controller (MDT693A, thorlab).

The force measurement between an air bubble and a lower layer of the cantilever surface was conducted by elevating the bottom quartz plate upwards at a constant velocity. The initial distance was adjusted to a distance of 6-10 µm, where the interference fringes became slightly visible. As the distance became smaller, the interference fringes became clearer with a higher contrast. The data from the balanced photoreceiver and the high-speed camera were recorded in real time with the approach of the bubble. The trigger signal was sent by the data acquisition card for all acquisition systems.

7.4 Results and Discussion
7.4.1 Interaction between Bubbles and Hydrophilic Surfaces

Figure 7.5 shows the results of the force measurement between an air bubble of 2 mm in radius and a hydrophilic silicon surface in water. The experiment was conducted at an approaching velocity of 0.75 µm/s. At $t = 16$ s, the piezo stopped. Figure 7.5(b) shows the signal data obtained from a photoreceiver. Using eqs. (7.2)-(7.3), one can obtain the force $(F)$ vs. time $(t)$, as shown in (c). The force calculation requires an input of the peak $(V_{\text{max}})$ and valley $(V_{\text{min}})$ values of the signal, which was obtained from the cantilever calibration process. The spring constant $(k)$ was obtained through the calibration process. Figure 7.5(d) shows the spatial and

![Graphs and images showing experimental results](image-url)

Figure 7.5 Results of the dynamic force measurement between an air bubble and a hydrophilic silicon surface in water. (a) driving distance, i.e., the elevating distance of the hemispherical bubble at the outer region; (b) raw signal obtained from the photoreceiver for the force measurement; (c) overall interaction force obtained by converting the signals from the photoreceiver; (d) spatiotemporal profiles of the wetting film obtained from the interference fringes, as shown in (e).
temporal thickness profiles of the thin liquid film (TLF) between an air bubble and a solid surface. It was obtained by analyzing the interference fringes, as shown in (e), using the temporal method.

It was shown that the force increased slowly when the minimum film thickness was above 300 nm at \( t = 7 \) s. At \( h > 300 \) nm, the film drainage was dominated by the hydrodynamics, which the viscosity of liquid, boundary conditions at interfaces and driving velocities controlled the film drainage and the interaction force. As \( h < 300 \) nm, an arising repulsive disjoining pressure prevented the film drainage. Instead, the film became flat and the area of the flat film became larger as the air bubble approached the cantilever surface. Here, the arising repulsive disjoining pressure was mainly contributed from the electrostatic double-layer force. Since the interacting area between the air bubble and the solid surface increased, the interaction force increased sharply during the approach of the bubble. Both the disjoining pressure and hydrodynamic pressure contributed to a sharp increase of the interaction force. When the bubble approaching stopped at \( t = 16 \) s, the interaction force became constant and the film reached equilibrium at an equilibrium film thickness \( (h_e) \) of 115 nm.

### 7.4.2 Interaction between Bubbles and Hydrophobic Surfaces

Figure 7.6 shows the results of the force measurement between an air bubble and a hydrophobic silicon surface. The silicon surface was in-situ hydrophobized in a \( 2.2 \times 10^{-3} \) M CTAB aqueous solution. The driving velocity of the air bubble is 1.5 \( \mu \)m/s. At \( t = 8 \) s, the bubble approaching stopped, and the film was allowed to drain spontaneously by the higher curvature pressure at the center of the film than at the edge. Figure 7.6 (b) and (c) show the signal readout and the force obtained as a function of time, respectively. As shown, the signal increased slightly when a bubble was pressed against a silicon surface at \( V = 1.5 \) \( \mu \)m/s. When the wetting film became metastable and ruptured at \( t = 9.8 \) s, the signal changed as a sinusoidal function of time. The results showed that the force was close to zero at \( t < 7 \) s. As \( t > 7 \) s, the force slightly increased over the time, and became strongly attractive after the film reached a critical rupture thickness. Figure 7.6 (d) shows spatiotemporal thickness profiles, \( h(r, t) \), of the TLFs, which were obtained from the interference fringes as shown in (e). The film thinned gradually and remained spherically. At \( t = 9.8 \) s, the film became unstable and pinned at the center of the film.
The pinning phenomena can be observed from the interference fringe. It was shown that a bright spot was observed at center of the fringes, indicating that the film thickness was small at the center of the film.

Both the interaction force and the spatiotemporal profiles of the wetting films obtained on a hydrophobic silicon surface behaved differently from those obtained on a hydrophilic silicon surface. For a wetting film on a hydrophilic surface in water, the force increased sharply to 500 nN when the radius of a flat film was about 50 µm. The flat film became larger with time. On the other hand, the bubble remained spherical for a wetting film formed on a hydrophobic silicon surface. When the film reached a critical rupture thickness, it pinned onto the silicon surface. The difference might be attributed to the different peculiarities of the disjoining pressure. When a negatively charged air bubble was against a similarly charged silicon surface separated by a thin
liquid film, a repulsive disjoining pressure was arisen when the electrostatic double layers overlapped. When the disjoining pressure became equivalent to the Laplace pressure, \( i.e., \) 72 N/m\(^2\) for a 2 mm radius air bubble, the film became stable. However, an attractive disjoining pressure between an air bubble and a hydrophobic silicon surface destabilized the wetting film by pulling the film to be thinned acceleredly and ruptured afterwards.

Figure 7.7 shows the interaction force between an air bubble and a hydrophobic silicon surface after a three-phase contact is formed. As shown, the interaction force became increasingly attractive when the bubble was dewetting on the hydrophobic silicon surface. The
dewetting radius \( (r_d) \) was the radius for the bright area in interference fringes. As shown in (d), \( r_d \) increased sharply after the film was ruptured at \( t = 9.8 \) s. When \( r_d = 500 \) µm, the kinetics of dewetting on the hydrophobic surface became retarded. The force reached \(-30\) µN when \( r_d = 600 \) µm.

The result presented in this work showed the interaction force was related to the transient changes in the film profiles between an air bubble and a solid surface. Both film profiles and interaction force behaved differently when an air bubble encountered with a hydrophilic silicon surface or a hydrophobic surface. We have shown that the film profiles varied with the nature of the disjoining pressure. A brief indication for the repulsive disjoining pressure in TLF was the formation of a flat film. When the TLF was subjected to an attractive disjoining pressure, the film thinned faster and ruptured. The instrument we have developed in this work might also be applied to study the other soft bodies, such as oil droplets, and supercritical CO\(_2\).

7.5 Summary

In the present work, we have developed and constructed a novel surface force apparatus (FADS) for direct measurement of the interaction forces between air bubble and solid surface. It is possible to study both stable and unstable TLFs in aqueous solutions using the new instrument. A significance of the FADS is its ability to monitor the deformation of thin liquid films (TLFs) in real-time during the dynamic force measurement. It is also capable of monitoring the changes in the adhesion forces associated with the dewetting processes occurring on solid surfaces immersed in aqueous solutions.

The results showed both the time evolution of TLFs and the interaction forces between air bubble and silicon surface. It was found that a wetting film undergoes a minor deformation in thick film at a low approach velocity, where the interaction force was dominated by the hydrodynamic force. As the film thinning continued to a thickness below 200 nm, the interaction force between air bubble and hydrophilic surface increased sharply when a flat film was formed and spread. When an attraction force was present in the TLF formed between an air bubble and a hydrophobic solid surface, the attraction force pulled the film to be ruptured through the formation of a pimple. The interaction force increased slightly and jumped to a negative value
when the TLF was ruptured, forming an $\alpha$-film. The interaction force became increasingly attractive when the bubble spread on a hydrophobic surface.

7.6 References


Chapter 8. Dynamic Force Measurement between an Air Bubble and a Solid Surface I: A Case for Repulsive Disjoining Pressure

ABSTRACT

The force apparatus for deformable surfaces (FADS) developed in the present work was used to directly measure the interaction forces between an air bubble and a hydrophilic (bare) gold surface in water. The measured forces were analyzed using the Reynolds lubrication theory and the extended DLVO theory to determine the contributions from the hydrodynamic and surface forces, respectively. The results showed that the interaction forces were dominated initially by the hydrodynamic force and subsequently by the repulsive surface force. The film drainage process stopped when the capillary force became equal to the disjoining pressure, and the film reached an equilibrium film thickness. It was found also that as the interaction force was increased, e.g., by increasing the approach speed of the bubble toward the surface, the flat area of the wetting film increased. We have also shown that the Debye length in a wetting film decreased with increasing approach speed, which was attributed to the accumulation of counter ions in the vicinity of the solid surfaces during the film thinning process. The film thinning process can be fitted to the Reynolds lubrication theory using the non-slip boundary condition at the air/water interface.
8.1 Introduction

The ability to manipulate the surface force between two macroscopic surfaces is essential in controlling the behaviors of the colloidal bodies in suspension. Non-deformable bodies, such as solids, interact with neighboring rigid bodies by the intermolecular interaction only. However, soft materials, such as bubbles, can be deformed during the course of the interaction with the neighboring bodies. The colloidal systems with soft materials are ubiquitous in a variety of industrial, medical, and biological applications, e.g., froth flotation, oil emulsions, microfluidic devices, biological interactions, etc. Among all the applications using the soft bodies, a desired colloidal configuration is significantly affected by the surface properties of the soft bodies, which is also controlled by intermolecular forces. In recent years, the interest of understanding the intermolecular interactions between soft matters has been increasing significantly in both the scientific community and industry [1-10]. However, little is known on the intermolecular interactions between two macroscopic bodies when at least one of the surfaces is deformable.

Historically, the early measurements of the surface force were carried out between two solid surfaces in the early 1950s. In Holland, Overbeek and his co-workers measured the interaction forces directly by monitoring the deflection of the spring using the electric capacity method [11-13]. The alignment and separation between two quartz plates were carefully controlled by monitoring the Newton’s fringes. In the USSR, Derjaguin and his co-workers employed a negative feedback balance to measure the force between a sphere and a plate [14, 15]. The negative feedback method was able to estimate the deflection of the spring by monitoring the current by means of a galvanometer.

In the 1970’s, Tabor and his co-workers at Cambridge University developed the surface force apparatus (SFA) for direct measurement of surface force between two cylindrically curved surfaces [16, 17]. An improved version of SFA, developed by Israelachivilli [18, 19], is capable of measuring both normal and tangential (or friction) forces either in air and a liquid. The principle of force detection in the SFA is to monitor the deflection of the cantilever using the multi-wavelength interferometry technique. However, it can be used to measure the forces between two transparent surfaces only [20]. It was not until the early 1990’s that the AFM technique was first introduced by Ducker et al. [21, 22] for the measurement of repulsive forces between hydrophilic solid surfaces. Rabinovich and Yoon [23, 24] were the first to measure
attractive hydrophobic forces using AFM. The AFM technique was to measure the interaction force between a microsphere and a flat solid surface.

The surface force measurements were initially conducted between two solid surfaces, such as silica, mica, or metal surfaces [11, 15, 25]. A number of studies reported in the literature during the last three decades showed different origins of the surface forces, such as hydrophobic force, hydration force, and steric force. The surface forces research has recently been extended to deformable soft materials, such as air bubbles [1-5], oil droplets [6, 7], mercury [8, 9], membranes and biological cells [10]. In flotation, air bubbles are used to collect hydrophobic particles, while leaving the hydrophilic ones behind. Direct surface force measurement involving bubbles is difficult, however, due to bubble deformation.

Many attempts have been made to measure the bubble-particle interaction forces [1-4, 26] using the atomic force microscopy (AFM). Ducker et al. [1] might be the first to measure the DLVO forces between an air bubble and a spherical particle using AFM. A follow-up experiment was conducted by Preuss and Butt [2], showing a repulsion due to the electrostatic double-layer force between an air bubble and a particle. When a bubble approached a hydrophobic sphere, the force jumped to a negative value at a large separation distance. Nguyen et al. [3] measured the interaction force between an air bubble and a particle using the AFM. The interaction force increased with the approaching velocity.

The surface force measurement between bubble and particle has been shown successfully in obtaining the overall interaction force with a sub-nano newton resolution using the AFM. However, a challenge remains to determine the real-time separation distance between an air bubble and a solid surface during the force measurement. It has been well documented that an air bubble undergoes a significant viscous deformation in response to both the drag force due to the motion of the bubble and the surface force created by intermolecular interaction [27]. It is, therefore, important to monitor the bubble deformation when both the viscous drag and surface forces are exerting forces on the bubble-particle interaction.

Chan and his co-workers derived a mathematical model on the basis of the Reynolds lubrication theory to simulate both the force exerting on the surfaces and the thickness profiles of the thin wetting film [28]. The force measurements were conducted by Manor et al. [29, 30] between an air bubble and a flat mica surface in an aqueous solution. The lubrication model
quantitatively predicted the film profiles of the wetting film. However, the film profiles varied when the interfacial boundary condition was slightly changed. As commented by Chan et al. [31], “the challenge remains to develop experimental methods underpinned by a quantitative theory to improve our understanding in fundamental problems in the interaction involving soft deformable systems.”

To address this challenge, we have developed a novel scientific instrument capable of monitoring both the interaction force and film profiles between a millimeter-sized air bubble and a flat surface, as described in Chapter 7. The force was obtained by monitoring the deflection of the cantilever using the fiber optical interferometry technique. The temporal and spatial thickness profiles of the thin liquid films were obtained from the interference fringes recorded by a high-speed camera. The film thickness profiles were used to predict the hydrodynamic force on the basis of the Reynolds lubrication theory. The information on the surface force can be obtained by fitting the measured force to the forces due to the sum of the surface and hydrodynamic forces. Here, we report the results obtained between an air bubble and a bare gold surface in pure water. It will be shown that the TLF of water formed between an air bubble and a bare gold surface is stable due to the presence of the repulsive disjoining pressure in the film. The measurements were also conducted by varying the approach speeds.

8.2 Mathematical Model

In a thin liquid film with the negligible characteristic thickness scale \( h \) relative to the characteristic length scale \( r \), i.e., \( h \ll r \), the liquid flow is described by the lubrication theory. Here, we use the Reynolds lubrication theory to describe the drainage of the thin liquid film (TLF) between an air bubble and a solid surface. For a radially symmetric flow, the governing equation for the film drainage is given in cylindrical coordinate,

\[
\frac{\partial h}{\partial t} = \frac{1}{12 \mu r} \left( rh^3 \frac{\partial p}{\partial r} \right)
\]

(8.1)

where \( \mu \) is the viscosity of liquid and \( p \) is the hydrodynamic pressure in the liquid film relative to in the bulk. Equation (8.1) is derived under the non-slip boundary condition. In a thin liquid film, the non-slip boundary condition for water flowing over the hydrophilic solid surface has been confirmed by both the experiments [32, 33] and computer simulations [34]. At one side of two
interfaces in the wetting film, i.e., surfactant-free air/water interface, the classical fluid theory predicts a stress-free boundary condition. In other words, the boundary condition at air/water interface is considered full-slip to guarantee the stress-free condition. The recent evidence of the spatiotemporal thickness profiles of the thin liquid film showed that the air/water interface remained stationary in a thin liquid film for a low shear rate flow, when a tiny bubble was freely arising towards a solid surface. The apparent non-slip hydrodynamic boundary condition was observed independently at both a normal laboratory condition [35] and a dust free environment [36]. A similar conclusion was also reached at the surfactant-free mercury/water interface [9]. Noting the evidence of the non-slip boundary conditions at surfactant-free air/water interface in a confined geometry, we assumed that eq. (8.1) might work in describing the wetting film drainage.

In a thin liquid film, the hydrodynamic pressure, \( p(r, t) \), is the driving pressure for the film drainage. It is obtained by integrating eq. (8.1) twice,

\[
p = 12\mu \int_{r=\infty}^{r} \frac{1}{r^3} \left[ \int_{0}^{r} r \frac{\partial h}{\partial t} dr \right] dr
\]

Eq. (8.2) is derived under the boundary conditions of \( p(r = \infty) = 0 \) and \( \partial p/\partial r|_{r=0} = 0 \). Thus, \( p \) can be determined when \( h(r, t) \) is available.

When the film thins to a thickness below 200 nm, the disjoining pressure plays a significant role in controlling the film drainage. It has been well documented that the wetting films formed on the hydrophilic surfaces were stable, while the films formed on the hydrophobic surfaces thinned expeditiously and ruptured spontaneously. According to the DLVO theory, the former occurred when the Laplace pressure was balanced by the repulsive disjoining pressure contributed from the double-layer force (\( \Pi_e \)) [37]. In the latter case, the hydrophobic disjoining pressure (\( \Pi_h \)) accelerated the film drainage and ruptured the film expeditiously [38, 39].

In a wetting film formed on a bare gold surface, \( \Pi \) may consist of two components in accordance to the classical DLVO theory,

\[
\Pi = \Pi_d + \Pi_e = -\frac{A_{32} \kappa^2}{6\pi h^3} - \frac{\varepsilon \varepsilon_0 K^2}{2 \sinh(\kappa h)} \left[ (\psi_1^2 + \psi_2^2 \psi_3 \coth(\kappa h) - 2\psi_1 \psi_2 \cosh(\kappa h)) \right]
\]

(8.3)
in which $\Pi_d$ and $\Pi_e$ represent the disjoining pressure contributed from the van der Waals dispersion force and the electrostatic double-layer force, respectively. In eq. (8.3), $A_{132}$ is the Hamaker constant for a wetting film of water formed on a solid surface. In general, $A_{132}$ is negative in wetting films and therefore the van der Waals dispersion force in wetting films is always repulsive. The $\Pi_e$ is obtained using the Hogg–Healey–Fuerstenau (HHF) approximation. The HHF approximation works well in predicting the interaction force between two dissimilar surfaces with low surface potentials. In eq. (8.3), $\varepsilon_0$ is the permittivity in vacuum, $\varepsilon$ is dielectric constant of water, $\psi_1$ and $\psi_2$ are the double-layer potentials at the solid/water and air/water interfaces, respectively, and $\kappa$ is the reciprocal Debye length. The subscripts 1, 2, and 3 represent solid, gas, and liquid, respectively.

By integrating the hydrodynamic pressure and disjoining pressure over the film area from $r = 0$ to $r = R$, one is able to determine the interaction force exerting on the cantilever surface using the following relation,

\[
F(t) = 2\pi \int_{r=0}^{r_e} \left[ p(r,t) + \Pi(r,t) \right] dr \\
= 2\pi \int_{r=0}^{r_e} \left[ p(r,t) + \Pi(r,t) \right] dr + 2\pi \int_{r=r_e}^{R} p(r,t) r dr \tag{8.4}
\]

in which $r_e$ represents the maximum radial position where the film thickness can be obtained from the fringes. The $r_e = 120 \, \mu m$ in our current experimental set-up. At $r > r_e$, the interference fringes overlap due to the low spatial resolution. The local film thicknesses at the outer region were obtained by evaluating the curvature at $r = r_e$. Note that the local film thickness is far beyond the thickness where disjoining pressure plays a role, and therefore, the total interaction force is evaluated by considering the hydrodynamic force only. The film thickness at $r > r_e$ is evaluated using the eq. (8.5),

\[
h = h_e + \frac{r}{2R_0} \tag{8.5}
\]

in which $R_0$ is the radius of the bubble and $h_e$ is the film thickness at $r = r_e$. The interaction force is evaluated at $r = 0 - 300 \, \mu m$. At $r > 300 \, \mu m$, the contribution from the $p$ to the overall interaction force was considered negligible compared to the pressure developed in the thin liquid.
The interaction force can be obtained when both $p(r, t)$ and $\Pi(r, t)$ are known. In the present work, $p(r, t)$ was obtained using eq. (8.2) from $h(r, t)$ at $r = 0 – 300 \mu$m. The $\Pi(r, t)$ was obtained from eq. (8.3). The simulated total force was fitted with the total force experimentally measured to obtain the information of the surface force.

### 8.3 Materials and Methods

#### 8.3.1 Materials

The cantilevers were in-house fabricated in class-100 cleanroom. They were made from a 50 $\mu$m thick ultra-thin glass sheets with a dimension of approximately $15 \times 4 \times 0.05$ mm. The glass cantilevers were cleaned in a boiling Piranha solution at 120 °C for 5 minutes, followed by rinsing thoroughly with ultrapure water and dried with the stream of nitrogen gas. The freshly-cleaned glass cantilevers were double-side coated by a 60 nm thick gold layer with a 5 nm thick titanium adhesion layer. The metal deposition was carried out in a $2 \times 10^{-6}$ torr vacuum chamber using the E-beam physical vapor deposition technique (PVD-250, Kurt J. Lesker).

The fluid cell was customized from two quartz plates (dimensions: 50 x 50 x 6 mm, TCP Inc). The fluid was injected from the bottom plate and fixed using an O-ring. In order for an air bubble to be fixed on the bottom quartz plate, the quartz plate was ex-situ hydrophobized in a $10^{-3}$ M octadecyltrichlorosilane-in-toluene solution for 1 hour. The equilibrium contact angle of water on the hydrophobic quartz plate was above 95°. The O-ring, tubing and connectors were washed ultrasonically in ethanol and followed by water for 20 minutes. They were dried with a stream of nitrogen gas. The liquid was injected into the cell using a glass syringe. All glassware was soaked in a base bath (saturated KOH solution in isopropanol) overnight to remove the organic residue and rinsed thoroughly with the ultrapure water before use.

The experiments were conducted using the ultrapure water produced from Direct-Q3 water purification system (Millipore). The produced water has a resistivity of 18.2 M$\Omega$•cm and < 10 ppb of total organic carbon. The water was used as obtained without degassing and further purification. The pH of the fresh ultrapure water was approximately 7.1 and decreased to a value of 6.4 when leaving in air for a half hour. The decreasing pH of the pure water when exposed in air was attributed to the adsorption of CO$_2$ from atmosphere in water.
8.3.2 Methods

The force measurement was conducted using a home-built force apparatus for deformable surfaces (FADS). The detailed construction of this instrument was described in Chapter 7. Figure 8.1 shows a schematic drawing of the force apparatus for a study of the bubble-solid interaction across a thin liquid film. Briefly, it is composed of three major systems: I) fiber interferometry system for the direct measurement of the force, II) high-speed microinterferometry system for
monitoring the bubble deformation, III) side-view camera for monitoring the dewetting of the thin liquid film.

The first major feature of the FADS was to directly measure the interaction force between the air bubble and the solid surface in water. The force was obtained by monitoring the deflection of the cantilever using the fiber optical interferometry technique. A single mode fiber was positioned at 100 µm above the upper cantilever surface, and used to sensor the changes in separation distance between the end face of the fiber and the upper surface of the cantilever. A piezoelectric stack (AE0203D04F, NEC-Tokin) was used to adjust the position of the fiber in nanometer resolution for calibration and fine position purpose.

The high-speed imaging microinterferometry technique was used to determine the spatiotemporal thickness profiles of the wetting films. The interference fringes were formed when the light reflected from the upper and lower interfaces of the wetting films interfere with each other. A high-speed camera was used to capture the temporal changes in the interference fringes. The spatial and temporal thickness profiles, $h(r, t)$, were reconstructed from the fringes. The resolution of the radial position and thickness are 1.6 µm and 0.5 nm, respectively. The microinterferometry technique was built on an inverted light microscope with a 5x long-working distance objective.

The side-view camera was used to monitor the dynamics of the three-phase contact and also used to align the position of the cantilever properly. The video camera was positioned on a multi-axis translation stage, which was used to monitor the position and size of the air bubble. During the force measurement, the video camera was triggered in real-time with the high-speed camera to capture the motion of three-phase contact line.

All experiments were conducted using the ultrapure water. The gold cantilever surface was fixed on the upper quartz surface using the Crystalbond 509 adhesive. An air bubble was created using an air-tight syringe, and it was fixed on the lower quartz surface. The radius of the air bubble was about 2 mm. The cantilever was manually positioned at approximately 10 µm above the surface of air bubble. At a separation distance of 10 µm, an interference fringe with less contrast was observed on the camera. The velocity and driving distance of the air bubble were controlled by means of the piezoelectric actuator (AE1414D16F, NEC-Tokin), which was driven by an open-loop piezo controller (MDT693A, Thorlabs). The maximum drive distance is
approximately 18 µm at 150 Vdc. The maximum velocity is 12 µm/s at a maximum allowance of signal to noise ratio. The experiments were controlled and recorded using a national instrument data acquisition (DAQ) card using the Labview software. The force data were recorded in real-time with interference fringes, and analyzed off-line using the home-programmed codes in Matlab.
8.4 Results

The experiments were conducted at different approaching velocities ($V$) ranging from 0.75 to 12 µm/s. Both interaction force and interference fringes were recorded simultaneously. In order for a comparison, we reported the results at $t = 0$ when the film thinned to a minimum thickness of 2 µm. The initial separation distance between the air bubble and the lower cantilever surface was controlled at 6-9 µm, where the interference fringes were lightly visible. Figure 8.2(a) shows the temporal changes in the interference fringes of the thin liquid film between an air bubble and a bare gold surface at $V = 0.75$ µm/s. The fringes were captured by the high-speed camera at 150 fps. The spatiotemporal thickness profiles, $h(r, t)$, were reconstructed from the interference fringes by analyzing the temporal thickness profiles at each pixel of the interference fringes along the radial direction. Figure 8.2(b) shows the thickness profiles of the wetting films corresponding to the interference fringes shown in (a). As shown, film thinned with a rise of the air bubble by the piezoelectric actuator. As the minimum film thickness was below 300 nm, the film became flattened with a continuous approach of the bubble. As a result, the film size, i.e., the size of the flat film, became larger. Figure 8.2(c) and (d) show the driving distance ($D$), and the temporal profiles ($h$ vs. $t$) at $r = 0$ and at $r = 0.1$ mm. Bubble rising stopped at $t = 11.5$ s. It was shown that the film thickness at $r = 0$ remained constant at $t > 5$ s, indicating that an equilibrium film thickness was reached at $t = 5$ s.

The interaction force was obtained by monitoring the deflection of the cantilever using the fiber optic interferometry technique. The deflection of the cantilever was obtained by monitoring the changes in the separation distance between the end fiber surface and upper cantilever surface. When light traveled in a cavity, the intensity of the returned light changed as a sine-wave function and became equivalent to the intensity at a relative distance of $\lambda/n$. In the present work, the wavelength ($\lambda$) of the injected laser light was 1330 nm. When the measurement was conducted in water with $n = 1.33$, the length of cavity, i.e., half of the light traveling distance between two neighbor peak values was equivalent to 500 nm. By knowing the peak and valley values of the signal, one can obtain the relative deflection of the cantilever when subjected to external force. Figure 8.2(e) shows the measured force between an air bubble and a bare gold surface in water at $V = 0.75$ µm/s. The interaction force increased slowly when the film thinned from 2000 nm to 300 nm. As the bubble continued pressing against the cantilever surface, the
interaction force increased sharply. A comparison of the spatiotemporal profiles with the measured force revealed that an increase of the interaction force was mainly attributed to the increasing areas of the flat film. As the approach stopped at \( t = 12 \) s, the interaction force became constant.

The measured force was compared with the force predicted from the Reynolds lubrication theory, in which both the hydrodynamic and surface force were considered. The red, blue and black lines show the hydrodynamic force, surface force and a sum of both, respectively. The
The hydrodynamic force was obtained by integrating the hydrodynamic pressure over the film area from \( r = 0 \) to \( r = R \). The hydrodynamic pressure was evaluated independently using eq. (8.2) at \( r < r_c \) and \( r > r_c \). At \( r < r_c \), the spatiotemporal profiles can be experimentally determined from the interference fringes, and used to obtain the hydrodynamic pressure in the liquid film. At \( r > r_c \), the film profiles were estimated using eq. (8.5), and the temporal velocity \( (\partial h/\partial t)_{r > r_c} \) was assumed to be the same as the temporal velocity at \( r = r_c \). It gives a close approximation for the hydrodynamic force in a thin film of water.

The disjoining pressure was predicted using eq. (8.3). In the present work, the electrostatic double-layer force was only considered for calculating the surface force between an air bubble and a hydrophilic surface in water. Van der Waals dispersion force was negligible at a separation distance above 100 nm. The fitting parameters for the double-layer force, e.g., Debye length and surface potentials, were obtained from a fit of the simulated force curve using eq. (8.4) with the measured force.

We showed that the total force was initially contributed from the hydrodynamic force only at \( h > 300 \) nm, where the disjoining pressure was negligible. When the film continued thinning, the repulsive disjoining pressure played a role in stabilizing the film. Note that the curvature pressure was developed to balance the hydrodynamic pressure due to the fluid drag according to the stress balance at air/water interface,

\[
p = p_{\text{cur}} - \Pi \quad \text{(8.6)}
\]

When a flat film was formed, a higher curvature pressure developed in the thin film drained the liquid to the outer region by the pressure gradient. It was found that as the bubble approaching continued, a flat film became larger resulting an increase of the total force with the area of the flat film. At \( t > 12 \) s, the approaching drive stopped and the force remained constantly.

At a lower approaching velocity \( (V = 0.75 \, \mu m/s) \), the hydrodynamic force developed was not significant in altering the interfacial geometry of the air bubble. It was shown that the maximum hydrodynamic pressure developed in the wetting film was 80 nN at \( V = 0.75 \, \mu m/s \). Only when the repulsive disjoining pressure played a role, the bubble became significantly deformed and flattened at the center. Figure 8.3 shows the results of both the interaction force and spatiotemporal profiles of the thin liquid films between an air bubble and a bare gold surface at \( V \).
At $V = 6 \mu$m/s, the hydrodynamic force contributed to a sharp increase of the overall interaction force.

As shown from the interference fringes and film profiles, a significant bubble deformation was not observed at an approaching velocity which was twice faster ($V = 1.5 \mu$m/s). Only when $h < 300$ nm, did the repulsive disjoining pressure began to prevent the film drainage.

Figure 8.3(c), (d) and (e) show the drive, a plot of $h$ vs. $t$ at $r = 0$ and $r = 0.1$ mm and both the measured and simulated forces, respectively. At $t = 4.3$ s, the bubble approaching stopped. It was shown that the film thickness decreased with time. As the bubble approaching stopped, the film thickness remained constant. The interaction force measured at $V = 1.5 \mu$m/s behaved similarly.
with the force measured at $V = 0.75 \, \mu m/s$. The red, blue and black line represents the hydrodynamic force, surface force, and a sum of both predicted using eqs. (8.1)-(8.5). A close fit was found between the predicted and measured force. It was shown that the interaction force between the air bubble and the solid surface was attributed to the hydrodynamic force due to the flow drag at $t < 2.2 \, s$, when $h > 300 \, nm$. As the film thinned, the repulsive disjoining pressure due to the electrostatic double-layer force became significant in preventing the film drainage. At $t = 8 \, s$, the surface force became significant in determining the overall interaction force between an air bubble and a cantilever surface.

At a higher approach speed, e.g., $V = 6 \, \mu m/s$, the film profiles behaved differently from those obtained at $V < 1.5 \, \mu m/s$. Figure 8.4 shows the results of the dynamic force measurement at $V = 6 \, \mu m/s$. It was shown that the film was flattened at the radial position of 0 - 0.025 mm when the film thickness became approximately 300 nm. As the bubble rising continued, a subtle dimple with inverted curvature at the center of the film was developed at $t = 1.95 \, s$. The repulsive disjoining pressure played a role at $t > 2 \, s$, the film became stabilized and flat when the curvature pressure was balanced by the double-layer disjoining pressure.

The interaction force both measured and simulated at $V = 6 \, \mu m/s$ were shown in Fig. 8.4(e). It was found that the force operated at $V = 6 \, \mu m/s$ was substantially larger than those obtained at a lower approach speed. However, the interaction force behaved similarly as those obtained at the lower approach speed. It was shown that the total force was initially dominated by the hydrodynamic force. As $h < 300 \, nm$, the arising disjoining pressure contributed from the double-layer force contributed to an increase of the total force. When the bubble rising stopped, the force became constant.

Figure 8.5 shows the results between an air bubble and a solid surface at $V = 12 \, \mu m/s$. $V = 12 \, \mu m/s$ is the maximum velocity that can be achieved in current experimental condition for an acceptable signal-to-noise ratio. We have found that bigger interference fringes were developed at a higher approach speed. As shown in Fig. 8.5(b), a visible dimple was developed at $t = 1.8 \, s$. As the film thinning continued, a dimpled film became flat. Figure 8.5(e) shows the interaction force exerted on the cantilever surface. The interaction force increased sharply with time. As the piezo drive stopped, the force reached a plateau. The maximum force of 850 nN was obtained at $V = 12 \, \mu m/s$ for an air bubble interacting with the cantilever surface across a thin liquid of water.
It was shown that a peak of the total force was observed at a high approach speed, while the simulated force failed to predict. The existence of a peak was mainly attributed to the sudden decrease of the hydrodynamic force when the piezo stopped. A failure of detecting the sudden decrease of the hydrodynamic force might be attributed to the digital noise cancellation, which covers up the transient changes in the film thickness right after the piezo stopped.

The results showed that a dimple was formed when a large hydrodynamic force was developed in the film at a faster approach speed. When a large repulsive force was developed in...
the film, it created a higher hydrodynamic pressure in the film. The balance of the hydrodynamic pressure was achieved by reversing the curvature of the thin film at the center while increasing the curvature at the outer region. When the hydrodynamic pressure was higher than the curvature pressure due to bubble deformation, the film apparently became larger to distribute the energy over the larger film area. We have observed that the film became larger when the bubble kept approaching toward the cantilever surface.

8.5 Discussion

8.5.1 Curvature Pressure

Above we have shown the results of the force measurement between an air bubble and a bare gold surface operated at different approaching velocities. The interaction force behaved similarly at varying speeds. It was found that the interaction force was initially controlled by
hydrodynamic force only, and subsequently by both the hydrodynamic and surface forces when 
the thickness of the TLF was below 300 nm. In a TLF where the repulsive disjoining pressure 
dominated, the interaction force increased with increasing the size of the flat film.

The spatiotemporal thickness profiles of the wetting films behaved differently at varying 
velocities in response to the hydrodynamic force and surface force in TLF. At a lower 
approaching velocity, e.g., \( V = 0.75 \) \( \mu \text{m/s} \), the film profiles was not significantly deformed due 
to a small hydrodynamic force exerting on the surface of the air bubble. Only when film 
thickness was below 300 nm, did the repulsive disjoining pressure become significant in 
preventing the film drainage. As a result of the bubble rising, the film underwent an apparent 
spreading process at an equilibrium film thickness of 115 nm.

At a higher approach speed \( (V = 12 \) \( \mu \text{m/s}) \), the wetting film was deformed before the surface 
force began to impact the drainage behavior. As shown in Fig. 8.5, the center of film was getting

![Graphs showing variances of the thickness (h), hydrodynamic pressure (p), disjoining pressure (Π) and total pressure (p_{cur}) vs. the radial position (r) of the film.]

Figure 8.7  Variances of the thickness \( (h) \), hydrodynamic pressure \( (p) \), disjoining pressure \( (Π) \) and total pressure \( (p_{cur}) \) vs. the radial position \( (r) \) of the film. The 
measurement was conducted between an air bubble and a bare gold surface in 
water at \( V = 12 \) \( \mu \text{m/s} \).
flat when the bubble was subjected to a 850 nN hydrodynamic force. As the bubble approaching continued, a dimple was developed with the minimum film thickness occurring at an edge of $r = 0.05$ mm. The dimple was allowed to drain spontaneously by the higher curvature pressure in the center, and eventually a flat film was formed when the arising disjoining pressure balanced the disjoining pressure.

Figure 8.6 shows the temporal variance of the thickness profiles ($h$), hydrodynamic pressure ($p$), disjoining pressure ($\Pi$) and curvature pressure ($p_{\text{cur}}$) along the radial position of the film at $V = 1.5$ µm/s. It was shown that the hydrodynamic pressure increased as the film thinned. At $t = 2.67 - 4.33$ s, the $p$ reached a peak value of 33 N/m$^2$ at the center of the film. As the bubble rising stopped, the $p$ decreased with time. $p = 5$ N/m$^2$ at $t = 7.33$ s. The disjoining pressure was only dependent on the film thickness. At $t = 1.5$ s, the disjoining pressure was nearly negligible at $h > 500$ nm. When the film continued thinning to a thickness below 300 nm, the disjoining pressure played a role and increased with decreasing the film thickness. The total pressures are a sum of the hydrodynamic pressure and disjoining pressure. As shown, the total pressure increased with time, and it reached the maximum after the bubble rising stopped. Figure 8.7 shows the temporal variance of the spatial profiles of $h$, $p$, $\Pi$ and $p_{\text{cur}}$ at $V = 12$ µm/s. The profiles of $p$ behaved similarly with those obtained at $V = 1.5$ µm/s. As shown, the hydrodynamic pressure increased when the bubble was rising by the piezoelectric actuator. When the bubble rising stopped, the hydrodynamic pressure decreased with time. A subtle dimple was developed when a large hydrodynamic pressure was exerted on the surface of the air bubble. The fitting parameters for calculating the disjoining pressure from the double-layer force were shown in Table 8.1. At $t = 3.0$ s, we have shown that $\Pi$ was large at the edge of the film, where the minimum film thickness occurred at the edge. As the film was allowed to drain spontaneously by the curvature pressure, the film was getting flat and stabilized. As a result, $\Pi$ became larger, while $p$ became smaller. The $p_{\text{cur}}$ representing the surface tension pressure due to the curvature changes at interface remained closely constant.

A close comparison of the spatial profiles of $h$, $p$, $\Pi$ and $p_{\text{cur}}$ obtained at $V = 1.5$ µm/s and $V = 12$ µm/s showed that the film profiles of the wetting films were strongly correlated with the pressures developed in the TLF. When the TLF was subjected to a higher hydrodynamic pressure created by the fluid drag, the film underwent a deformation in order to create a larger curvature pressure to balance the hydrodynamic pressure. When the repulsive disjoining pressure began to
play a role, the hydrodynamic pressure decreased with time in order to satisfy the condition that the curvature pressure along the interface must be balanced by the sum of the disjoining pressure and hydrodynamic pressure. We have shown that the film became stabilized by forming a flat film when subjected to a repulsive disjoining pressure.

8.5.2 Double-layer Force

The disjoining pressures between air bubbles and cantilever surfaces were determined by simulating the interaction force to the experimental data. In the present work, the disjoining pressure in the wetting films was estimated using the Hogg-Healey-Fuerstenau (HHF) approximation. HHF approximation was derived under the assumption that both interfaces maintained the constant potentials during the overlaps of the electrostatic double layers. Note that all the approximations for estimating the electrostatic double-layer force assumed the low

Figure 8.8 Disjoining pressure isotherm in a thin film of water between an air bubble and a bare gold surface at varying approach velocities. At a higher approach speed, the disjoining pressure contributed from the electrostatic double layer force decays faster.
surface potentials at interfaces. The HHF equation has been commonly used in predicting the electrostatic interaction between the air bubbles and the solid surfaces.

Figure 8.8 shows the curves of the disjoining pressure between an air bubble and a bare gold surface at varying velocities. Table 8.1 lists the values of surface potentials of gold surfaces and air bubbles, and decay lengths. The surface potentials of gold surfaces were fixed at -0.04 V, which were obtained from the zeta potentials of the gold colloidal particles in water. It was shown that the zeta potentials of air bubbles were about the same. \( \psi_2 = -0.034 \) V at varying velocities from 0.75 \( \mu m/s \) to 12 \( \mu m/s \). However, the decay length (\( \kappa^{-1} \)) decreased from 84 nm at \( V = 0.75 \mu m/s \) to 38 nm at \( V = 12 \mu m/s \). It was shown that the disjoining pressure between the air bubbles and the gold surfaces in a thin liquid film of \( h > 130 \) nm was relatively smaller at a higher approaching velocity.

In a thin liquid film, the distribution of the ions near the charged surface follows the Boltzmann distribution. When two charged surfaces are close in aqueous solutions, the counter ions are preferentially distributed near the surface. The population of the ions decay exponentially as a function of the position away from the surfaces. As the film was squeezed by the approach of the bubble, the fluid in the film behaved as the pipe flow with zero velocity at solid surface and maximum velocity at the center of the pipe. Recognizing the ion distributions and flow patterns in a thin liquid film, the relatively low concentration of counter ions were squeezed out, leaving more concentrated ions in the film. An accumulation of the ions in the

<table>
<thead>
<tr>
<th>( V ) (( \mu m/s ))</th>
<th>( \psi_1 ) (mV)</th>
<th>( \psi_2 ) (mV)</th>
<th>( \kappa^{-1} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>-40</td>
<td>-36</td>
<td>84</td>
</tr>
<tr>
<td>1.5</td>
<td>-40</td>
<td>-37</td>
<td>81</td>
</tr>
<tr>
<td>6</td>
<td>-40</td>
<td>-32</td>
<td>78</td>
</tr>
<tr>
<td>12</td>
<td>-40</td>
<td>-34</td>
<td>38</td>
</tr>
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</table>
vicinity of the charged surface increases the overall concentration of ions in a thin liquid film, and thus decreases the Debye length.

The values of the Debye length for the pure water have been investigated widely. Different research groups have reported the varying values of Debye length for the pure water. A more accepted value is 90 nm when considering the dissolution of the atmosphere CO$_2$ in water. However, some investigators showed a 40 nm Debye length for the pure water using the AFM. The unique feature in determining the interaction force using the AFM was that the force measurement was often conducted at 1-10 Hz, which was equivalent to the approaching velocity of 2-20 µm/s. At a high shear rate, the pure water might behave differently. A further investigation on effect of the approaching velocities on the Debye length of the pure water will be further conducted.

Figure 8.9 Interaction force vs. minimum separation distance between an air bubble and a bare gold surface. The solid and dashed lines represent the numerical predictions using the non-slip and full-slip boundary condition at air/water interface.
Non-slip Boundary Condition at Surfactant-free Air/water Interface

Here we have shown that the simulated interaction force exhibits a close fit with the measured force between the air bubble and gold surface. It should be noted that the numerical analysis was based on the Reynolds lubrication theory assuming the no-slip boundary conditions at both the air/water and solid/water interfaces. It appears that the common concept of the full-slip boundary condition at surfactant-free air/water interface might not be valid in a confined geometry.

Figure 8.9 shows the interaction force vs. minimum film thickness in a water film between an air bubble and a bare gold surface at $V = 1.5 \mu m/s$. The solid and dashed lines represent the simulated result on the basis of the non-slip boundary condition and the full-slip boundary condition at the surfactant-free air/water interface, respectively. It is clearly shown that the solid line fits the experimental data, confirming the non-slip boundary condition at the air/water interface. Figure 8.10 shows the effect of the approach speed on the interaction force between an air bubble and a bare gold surface. The results were shown from $V = 0.75 \mu m/s$ to $V = 12 \mu m/s$. It was found that at approach velocities up to $12 \mu m/s$, no-slip boundary condition for air/water interface is valid in a wetting film.

This finding was initialized in our previous work [40], showing that the Reynolds approximation works well in predicting the thinning kinetics of the wetting film in the surfactant free aqueous solution containing electrolyte. Note that the Reynolds approximation was derived for film drainage between two flat solid surfaces. The non-slip boundary condition at air/water interface was also recently found by many other investigators. Parkinson and Ralson [36] showed that the air bubble behaved more like a solid surface in retaining the fluid at interface. They found that the boundary conditions at the surface of a surfactant-free bubble in water was no-slip in a confined geometry. Hendrix et al. [35] tracked the spatial and temporal profiles of TLF when millimeter-sized air bubbles were freely arising towards a solid surface. A similar conclusion was drawn that the bubble surface was considered as tangentially immobile. A surprising phenomenon might be related with the low shear rate of liquid [29]. Note that, the experiments in this work were conducted at a normal laboratory condition. Thus, the trace of the air pollutant and particles might be present at the air/water interface, rendering the air/water interface non-slip.
We have conducted the real-time force measurements between an air bubble and a bare gold surface separated by a thin liquid film. Both the interaction forces and the interfacial profiles of the thin liquid films were tracked simultaneously. It was found that the interaction force was initially followed by the hydrodynamic force only, and subsequently by the surface force. When the air bubble was driven towards the cantilever surface at a low velocity, the film profiles were not deformed until the surface forces emanating from both the air/water and solid/water interfaces began to interact with each other. On a hydrophilic surface, the surface forces and the disjoining pressure were repulsive; therefore, the film drainage began to retard at $h < 300$ nm. Due to the repulsive disjoining pressure, the film was flattened. At a higher approach velocity, a subtle dimple was formed before the film was thinned to a thickness to less than 300 nm by the large hydrodynamic force. As the film continued to drain spontaneously by the curvature

Figure 8.10 Effect of approach speed on the interaction force between an air bubble and a bare gold surface in water. The lines show the numerical results using the non-slip boundary condition at air/water interface.

8.6 Summary

We have conducted the real-time force measurements between an air bubble and a bare gold surface separated by a thin liquid film. Both the interaction forces and the interfacial profiles of the thin liquid films were tracked simultaneously. It was found that the interaction force was initially followed by the hydrodynamic force only, and subsequently by the surface force. When the air bubble was driven towards the cantilever surface at a low velocity, the film profiles were not deformed until the surface forces emanating from both the air/water and solid/water interfaces began to interact with each other. On a hydrophilic surface, the surface forces and the disjoining pressure were repulsive; therefore, the film drainage began to retard at $h < 300$ nm. Due to the repulsive disjoining pressure, the film was flattened. At a higher approach velocity, a subtle dimple was formed before the film was thinned to a thickness to less than 300 nm by the large hydrodynamic force. As the film continued to drain spontaneously by the curvature
pressure, the thin liquid film was stabilized. At this point, the curvature pressure became equal to the surface pressure acting in opposite direction.

A numerical analysis based on the Reynolds lubrication theory was carried out to determine the disjoining pressure in the wetting film. A close fit was found between the simulated and measured forces. The simulation was made under the no-slip boundary condition at the surfactant-free air/water interface. The repulsive disjoining pressure in the wetting film formed on a gold surface was created by the electrostatic double-layer repulsion. It was found that the Debye length of the ultrapure water decreased with increasing approach speed.

8.7 References


Chapter 9. Dynamic Force Measurement between an Air Bubble and a Solid Surface II: A Case for Attractive Disjoining Pressure

ABSTRACT

Measurement of the attractive surface forces between the air bubbles and the solids was a challenge due to the limited information on bubble deformation during the force measurement. In the present work, the force apparatus for deformable surfaces (FADS) was used to study the dynamic interaction between a positively charged air bubble and a negatively charged silicon surface at different approach speeds. The interaction force was measured by monitoring the deflection of the cantilever spring, while simultaneously monitoring the deformation of the wetting films. The results showed that the interaction force increased when the air bubble was pushed towards the cantilever surface. The interaction force remained constant when the bubble approach stopped, and the film was allowed to drain spontaneously by the curvature pressure. The measured interaction force jumped to a negative value when the film ruptured.

Two types of the film profiles were observed: a concave (or pimpled) film with a sharpness at the center of the film, and a convex (or dimpled) film with an inverted curvature at the center. A pimpled film was observed when the film was subjected to a strong long-range surface force and a weak hydrodynamic force. A dimpled film was observed when surface forces were weak and hydrodynamic forces were strong.


9.1 Introduction

Coagulation is a process when two bodies are attracted together to a lower the free energy. Such phenomenon is ubiquitous in many industrial and medical processes, ranging from froth flotation, food processing, and from self-assembly materials to the droplet-based microfluidic devices. Coagulation of soft materials such as bubbles and drops involve changes in interfacial tensions and shapes. According to the Frumkin-Derjaguin theory, the changes in the interfacial tension (or free energy) can be related to the disjoining pressure \[1, 2]\,

\[
\Delta \gamma = -\int_{h_0}^{h} \Pi(h)dh
\]  \hspace{1cm} (9.1)

where \(\Delta \gamma\) is the changes in interfacial tension, \(\Pi\) the disjoining pressure, \(h\) the film thickness and \(h_0\) is the thickness of the liquid film in equilibrium with the meniscus. When the free energy changes become negative, the disjoining pressure must be attractive at a film thickness of \(h_0\). As suggested by Laskowski and Kitchener [3], the criteria for the coagulation was that two bodies must be attracted to each other across in a thin liquid film (TLF).

According to the DLVO theory, the attractions between two colloidal particles or between two macroscopic surfaces can be van der Waals dispersion force [4, 5], electrostatic double-layer force [6, 7], hydrophobic force [8, 9], or a mix of multiple origins [10, 11]. The Van der Waals dispersion force originated from the instantaneously induced dipoles of the molecules at interfaces. Because of the anisotropic nature of dipoles, the dispersion force is always attractive when two like molecules are close to each other. Depending on the dielectric properties of the molecules, the dispersion force can become more attractive when the metal particles are interacting with each other [4, 5]. The electrostatic double-layer attraction occurs when two oppositely charged surfaces interact with each other in a dielectric medium. Jiang et al. [6] studied the coagulations between bubbles and Al\(_2\)O\(_3\) particles in aqueous solutions at varying pH. The coagulation was significantly improved when both interfaces were oppositely charged. Tabor et al. [7] showed that the heterocoagulation occurred between an air bubble and a oil droplet in water at a pH where two interfaces were oppositely charged. Hydrophobic coagulation is a third mechanism for the coagulations occurred between particles and droplets in water [8, 9]. In froth flotation, air bubbles are more likely to coagulate with the hydrophobic particles in water [12, 13].
An ability to manipulate the surface forces is central in the coagulation process. Atomic force microscopy (AFM) and surface force apparatus (SFA) are the most widely used techniques in the surface force measurement between two solid surfaces in liquid. It has been reported by many investigators that the attractive hydrophobic forces can be experimentally measured between two hydrophobic surfaces in water [14-18]. However, when the studies were extended to the soft bodies, such as air bubbles and oil droplets, the interpretation of the experimental results was complex [19, 20]. The interaction forces involving soft bodies often include hydrodynamic forces, which causes the soft bodies to deform during interaction. Additionally, the TLFs between two soft bodies or between a soft body and a rigid surface are unstable and, therefore, rupture catastrophically. Connor and Horn [21] showed that the lifetime of an unstable thin liquid film is 0.64 s when the attractive force is present due to the double-layer interaction. A set of the interference fringes obtained after the film rupture showed that the lifetime of a metastable wetting film is 1 ms on a hydrophobic surface [22]. Therefore, a challenge remains in measuring and analyzing the complex interplay between the hydrodynamic and surface forces during the bubble-particle interaction.

Many attempts have been made to measure the surface forces between soft bodies. Connor and Horn monitored the profiles of the thin liquid film between a mercury droplet and a mica surface by monitoring the fringes of equal chromic order (FECO) [21]. It was shown that the TLF between a mercury droplet and a mica surface was metastable when the charges at two interfaces were opposite. The disjoining pressure in the liquid film was estimated by simulating the film profiles on the basis of the Reynolds lubrication theory [23]. Tabor et al. [7] directly measured the interaction forces between two droplets using an AFM. By analyzing the force curve numerically, they were able to determine the attractive surface forces between two oppositely charged surfaces. Pan et al. [24, 25] monitored the dynamics of the thin liquid film between an air bubble and a hydrophobic gold surface using a high-speed camera. It was found that an attractive disjoining pressure was present in the wetting film formed on a hydrophobic gold surface. The disjoining pressure was obtained by subtracting the Laplace pressure due to the curvature changes from the hydrodynamic pressure in the film that causes film thinning.

As discussed above, the surface forces between air bubbles and solid surfaces were measured either directly or calculated from the real-time spatiotemporal profiles of the TLFs. During the course of the bubble-particle interaction, the deformation of the TLFs and the changes in
intermolecular forces are intertwined with each other. Thus, the overall interaction force becomes a combination of the hydrodynamic force and the surface forces, or the surface tension force from the normal stress balance. Chan et al. [26, 27] derived a detailed mathematical model to predict both the interaction force and the profiles of the thin liquid film between an air bubble and a solid surface. Yet, the model needs to be corrected experimentally with an appropriate estimation of the boundary conditions at interfaces. Recently, we have developed the novel force apparatus called FADS for direct measurement of dynamic force while monitoring the deformation of FLFs simultaneously, as described in Chapter 7. FADS is capable of measuring the force directly with a real-time view of the spatiotemporal thickness profiles of the thin liquid films.

In this work, we studied the interaction between a positively charged air bubble and a negatively charged silicon surface across a TLF of water and simultaneously monitored the spatiotemporal deformation of the film. A millimeter-sized cantilever was used to monitor the forces acting between the lower surface of the cantilever and the air bubble across a thin film of water. The deflection of the cantilever was monitored using the fiber optical interferometry technique. We compared both the overall interaction forces and the film profiles. Two cases are compared, one is in the presence of a long-range attractive force and other is in the presence of a short-range attractive force.

9.2 Materials and Methods

9.2.1 Materials

The interaction forces were measured by monitoring the deflection of the cantilever using the fiber optical interferometry technique. A 50 µm thick silicon wafer (University Wafer, Inc) was used to fabricate the cantilevers. The wafer was double-side polished with a diameter of 100 mm as received. The cantilevers were fabricated in a class-100 cleanroom to minimize the surface contamination. A 600 Å thick gold with a 50 Å thick titanium adhesion layer was deposited on one side of the wafer by the E-beam physical vapor deposition technique (PVD-250, Kurt J. Lesker). The gold coated wafer was diced into rectangular pieces with dimensions of 20 x 4 x 0.05 mm. The rectangular piece of silicon was glued onto a 5 x 4 x 1 mm square glass piece, and
used as the cantilever. The upper gold layer served as a mirror to reflect the laser light from the fiber.

Before the cantilever was assembled into the fluid cell, it was cleaned in a freshly prepared Piranha solution (a mixture of H₂SO₄:H₂O₂, 7:3 by volume) for 3 minutes at 90 °C, rinsed with a sufficient amount of ultrapure water for 30 seconds and dried carefully with a stream of nitrogen gas. During the Piranha treatment, the bare surface of the silicon wafer was oxidized, rendering the surface hydrophilic. Cetyltrimethylammonium bromide (CTAB) was obtained from TCI America with a >98% purity. It was recrystallized in ethanol twice before use. All the aqueous solutions were prepared using the ultrapure water produced from the Direct-Q water purification system (Millipore, Inc.). The ultrapure water has a resistivity of 18.2 MΩ·cm and < 10 ppb of total organic carbon. The water was used as obtained without degassing and any further purification. The pH of the pure water is 6.9 - 7.1. The pH value of the pure water decreases to 6.4 when exposed in air for 20 minutes or longer.

9.2.2 Methods

Force measurements were conducted between an air bubble and a silicon cantilever surface in the aqueous solutions using a home-built force apparatus for deformable surfaces (FADS). An air bubble with 2 mm in radius was fixed on a hydrophobic quartz surface. The force measurement was carried out by approaching an air bubble towards the lower surface of the cantilever at varying approaching speeds. Both the interaction force and the deformation of the air bubble were monitored simultaneously. The interaction force was obtained directly by monitoring the deflection of the cantilever spring using the fiber optic interferometry technique. Simultaneously, the spatiotemporal profiles of the TLF were obtained by recording the interference fringes of the TLF using a high-speed camera. By analyzing the interference fringes, we were able to reconstruct the temporal and spatial profiles of the TLF.

The measured force was compared with the simulation results by considering both the hydrodynamic and surface forces. The force can be obtained using the following relation,

\[
F(t) = 2\pi \int_{r=0}^{\infty} \left[ p(r,t) + \Pi(r,t) \right] rdr \\
= 2\pi \int_{r=r_p}^{\infty} \left[ p(r,t) + \Pi(r,t) \right] rdr + 2\pi \int_{r=r_p}^{R} p(r,t) rdr
\] (9.2)
in which $r_e$ represents the maximum radial position where the film thickness can be obtained from the fringes. In our current experimental set-up, $r_e = 120 \, \mu m$. At $r > r_e$, the black-white fringes overlapped due to the low spatial resolution. The film profiles at the outer region were obtained by evaluating the curvature at $r = r_e$.

In a thin liquid film, the hydrodynamic pressure ($p$) is the driving pressure for the film drainage. The hydrodynamic pressure is obtained from the Reynolds lubrication theory,

$$p = 12\mu \int_{r_e}^{r} \frac{1}{r h^3} \left[ \int_{r=0}^{r} \frac{\partial h}{\partial t} \, dr \right] dr$$

where $\mu$ is the viscosity of liquid, $r$ is the radial position of the film and $h$ is the film thickness. Eq. (9.3) was derived under the conditions of zero slip velocity at interfaces, which might work in a thin film of a low shear-rate liquid.

The disjoining pressure may consist of two components in accordance to the classical DLVO theory,

$$\Pi = \Pi_d + \Pi_e$$

$$= - \frac{A_{32}}{6\pi h^3} - \frac{\varepsilon \kappa^2}{2 \sinh(kh)} \left[ \psi_1^2 + \psi_2^2 \right] \left( \cos \epsilon h(kh) - 2 \psi_1 \psi_2 \coth(kh) \right)$$

in which $\Pi_d$ and $\Pi_e$ represent the disjoining pressures due to the van der Waals dispersion force and electrostatic double-layer force, respectively. By substituting eq. (9.3) and (9.4) to eq. (9.2), one can obtain an expression for the overall interaction force exerting on the cantilever surface. Therefore, the disjoining pressure in the film can be obtained when the result obtained using eq. (9.2)-(9.4) fits the experimental data.

Here, we compared the results of the force measurements between an air bubble and a silicon surface separated by a thin liquid film at varying approaching speeds. In the present work, we studied the deformation of the TLF when subjected to the electrostatic double-layer attractions between two oppositely charged surfaces. A long-range attractive force was created between an air bubble and a hydrophilic silicon surface in a $10^{-6}$ M CTAB solution. In the $10^{-6}$ M CTAB aqueous solution, the charge at air/water interface was preferentially reversed, while the silica/water interface remained negatively charged. When electrolyte was present in the $10^{-6}$ M CTAB aqueous solution, the screening effect diminished the double-layer attraction, so that a
short-range attractive force was present between an air/water interface and a solid/water interface. Figure 9.1 shows a schematic drawing of the force apparatus for deformable surfaces (FADS). Attraction was created by the electrostatic double layer force between a negatively charged solid/water interface and a positively charged air/water interface across a thin liquid film of cetyltrimethylammonium bromide (CTAB) solution.

Figure 9.1  Schematic drawing of the bubble-solid interaction using the force apparatus for deformable surfaces (FADS). Attraction was created by the electrostatic double layer force between a negatively charged solid/water interface and a positively charged air/water interface across a thin liquid film of cetyltrimethylammonium bromide (CTAB) solution.

9.3 Results

9.3.1 Long-range Attractive Disjoining Pressure

Figure 9.2 shows the results of the force measurements conducted between an air bubble and a silicon surface in a $10^{-6}$ M CTAB solution. The results were obtained at an approach velocity ($V$) of $1.5$ µm/s. In a $10^{-6}$ M CTAB solution, the negative charge at air/water interface was reversed due to an adsorption of the CTAB molecules at interface, while the charge at the solid/water interface remained negative. The oppositely charged double layers in a TLF created a long-range electrostatic attraction. Both the interaction force ($F(t)$) and the spatiotemporal thickness profiles ($h(r, t)$) of the TLF were recorded simultaneously. Over the period of the
bubble approach, the piezo elevated the bubble towards the silicon surface at $V = 1.5 \, \mu\text{m/s}$. At $t \approx 2.98 \, \text{s}$, the film ruptured. The spatial profiles of the TLF were shown in correspond to the interference fringes. They were obtained by analyzing the temporal thickness profiles at each pixel along the radial direction. It was shown that the film thinned continuously with a minimum film thickness occurred at a symmetric axis. The shape of the film remained the same at the outer region with a significant pinning occurred at the center, where the film thickness locally at the

![Image](image_url)

**Figure 9.2** Interaction forces and spatiotemporal thickness profiles of the thin liquid film between an air bubble and a silica surface in a $10^{-6} \, \text{M} \, \text{CTAB}$ aqueous solution. A long-range attractive force was created by the electrostatic double-layer force between a positive charged air bubble and a negative charged silica surface. The results were obtained at bubble approach velocity ($V$) of $1.5 \, \mu\text{m/s}$. (a) time evolution of the interference fringes of the thin liquid film; (b) spatiotemporal thickness profiles of the thin liquid film in correspond to the interference fringes; (c) drive of the piezo, i.e., the approach distance of the hemispherical air bubble at the bottom; (d) $h \, \text{vs.} \, t$ for the minimum thickness; (e) raw experimental data and simulated results of the forces, e.g., hydrodynamic, surface and total forces acting in a thin liquid film.
center was below 200 nm. A zoom look at the thickness profiles prior to the film rupture was shown in Fig. 9.3. The pinning occurred where the local film thickness was significantly thinner than the thickness for a spherical-curved film.

The interaction force between an air bubble and a silicon surface in a 10^-6 M CTAB solution was shown in Fig. 9.2(c) and Fig. 9.3(a). The green curve represents the force data experimentally obtained. The red, blue and black curves are the simulated results for hydrodynamic forces, surface forces and total forces. The spatiotemporal thickness profiles are used to calculate the hydrodynamic force using the eqs. (9.2)-(9.3). The surface force is determined by integrating the disjoining pressure over the area of the film. The total force is a sum of the hydrodynamic and surface forces. From a best fit of the experimental data with the simulation results, one can obtain the disjoining pressure in a TLF. In the present work, the film thickness was above 50 nm, in which the van der Waals dispersion force was negligible. Therefore, the electrostatic double layer force was only considered for calculating the disjoining pressure. A best fit was found using $\kappa = 60$ nm, $\psi_1 = -43$ mV and $\psi_2 = 70$ mV, as shown in table 9.1. The fitted values were close to the values reported by Churaev [28, 29].

At a low approach velocity ($V = 1.5$ $\mu$m/s), the thickness profiles of the deformable air/water interface remained closely spherical before the disjoining pressure played a role. As the film drainage continued to $h < 200$ nm, the film thinning accelerated, resulting in the formation of a pin-shaped film (or called a “pimple”) at the center. At a higher approach speed (6 $\mu$m/s), however, the thickness profiles of the TLFs looked very different. Figure 9.4 shows a set of film profiles obtained in a 10^-6 M CTAB solution. The initial distance before the approach of the bubble was approximately 14 $\mu$m. As shown in the drive ($D$) vs. $t$ plot of Figure 9.4, the bubble approach stopped at $t = 0.6$ s. Afterwards, the film was allowed to drain on its own (or spontaneously). The excess pressure in the film was higher than at the lower approach speed; therefore, the initial drainage rate was higher. Both the interference fringes and the spatial thickness profiles presented in Figure 9.4 show that the radii of the TLFs developed at $V = 6$ $\mu$m/s were larger than at $V = 1.5$ $\mu$m/s despite the fact that the bubble approach stopped at $h_{\text{min}} = 600$ nm. The film radii became larger as the film thinned. When an attractive disjoining pressure began to play a role, the film thinned faster at the edge of the film. As a result, the film profiles showed a dimple at the center. The film eventually ruptured when the film thickness reached the critical rupture thickness.
The interaction force obtained at $V = 6 \, \mu\text{m/s}$ is shown in Fig. 9.4(c). As shown, it increased when the bubble was approaching the cantilever surface. As the bubble approach stopped, the interaction force remained constant until the film ruptured. The interaction force stayed more or
less constant as the hydrodynamic force was balanced by the attractive surface force. The attractive force due to double-layer interaction was calculated with the following information: $\kappa^{-1} = 43$ nm, $\psi_1 = -70$ mV and $\psi_2 = 70$ mV. It was found that the Debye length obtained at a higher approaching velocity was smaller than that obtained at a lower approaching velocity.

It was found that the formation of either a pimpled or a dimpled film was the resulted from a coupling effect of the hydrodynamic pressure and disjoining pressure. A detailed comparison of film thickness ($h$), hydrodynamic pressure ($p$), disjoining pressure ($\Pi$) and curvature (or total) pressure ($p_{\text{cur}}$) are shown in Fig. 9.5. A pimple was formed at a lower approach velocity, while a
dimple was formed at a higher velocity. A $p$ vs. $r$ plot shows that the hydrodynamic pressure increased from the edge ($r = \infty$) to the center of the film ($r = 0$). As the film thinning continued, the hydrodynamic pressure increased with time. Note that the hydrodynamic pressure was created from a mix of the mechanical approach of the bubble and the curvature pressure gradient due to the changes in local curvatures at interface. At a high approach speed, the contribution from the mechanical approach disappeared at $t > 0.6$ s as the approach velocity was zero. Only the curvature pressure drove the film thinning.

The $\Pi$ vs. $r$ plot shows the temporal evolution of the disjoining pressure along the radial direction. As shown, the disjoining pressure became more negative as film thinned. It was found that an attractive disjoining pressure developed at the center of the film at a lower approach speed, while such attraction occurred at the edge at a higher approach speed.

The $p_{\text{cur}}$ vs. $r$ plot shows the temporal evolution of the curvature (or total) pressure along the radial direction. The $p_{\text{cur}}$ was calculated as a sum of the hydrodynamic pressure and the disjoining pressure. The profiles of $p_{\text{cur}}$ vs. $r$ plots correlated well with the local curvature and the shape of the TLF. It was found that $p_{\text{cur}}$ increased from $r = \infty$ to $r = 0$, indicating that the spherical bubble deformed when subjected to a hydrodynamic pressure. The hydrodynamic repulsion prevented the film thinning by flattening the film. As the bubble became flattened, the curvature in the thin film increased, resulting in an increase of the curvature pressure.

When a long-range attractive $\Pi$ played a role, the $p_{\text{cur}}$ behaved differently. At a low approach speed, the bubble remained closely spherical at the outer region of the film, while the center of the film was pulled to be pinned. The pimpled profiles were created by an attractive disjoining pressure, the curvature pressure at the center decreased. In case of a dimpled profile, the peak and valley values of $p_{\text{cur}}$ were developed at the center and at the edge, respectively.

9.3.2 Short-range Attractive Disjoining Pressure

Above we have shown both the interaction force and spatiotemporal profiles of the TLF between an air bubble and a silicon surface when a long-range attractive surface force was present in the film. Two types of the film profiles were obtained at different approach speed. A pimple was formed due to the long-range attractive surface force at a lower approach speed. When the bubble approached a solid surface at a higher approaching speed, a dimple was formed.
Figure 9.5  Effect of approach speed on the changes in spatial profiles of the film thickness ($h$), hydrodynamic pressure ($p$), disjoining pressure ($\Pi$) and curvature pressure ($p_{\text{cur}}$) in a thin liquid film. The $p_{\text{cur}}$ was obtained from a sum of $p$ and $\Pi$. A comparison was made between the approaching speeds of 1.5 µm/s and 6 µm/s.

Here, we showed a set of results between an air bubble and an opposite charged silicon surface in a $10^{-4}$ M NaCl aqueous solution containing $10^{-6}$ M CTAB. In a $10^{-4}$ M NaCl solution, the Debye
length ($\kappa^{-1}$) was 30 nm. In a solution with a 30 nm Debye length, the electrostatic double-layer attraction is screened at a large separation distance.

Figure 9.6 shows the results of the force measurements between an air bubble and a silicon surface in a $10^{-4}$ M NaCl solution containing $10^{-6}$ M CTAB at $V = 1.5 \ \mu$m/s. The bubble approach stopped at $t = 6$ s. At $t = 8.6$ s, the bubble jumped onto the solid surface causing the film to
rupture. It was found that the time spent for rupturing the film in the $10^{-4}$ M NaCl solution was longer than the film in the absence of NaCl. An inspection of the interference fringes revealed that a larger film was formed as the bubble was pushed toward a rigid silicon surface. It was found that the bubble remained spherical initially at thick film. As the bubble approach continued to a thickness below 300 nm, a concave-shaped, or dimpled film began to form. At $t = 8.6$ s, the film became metastable and ruptured at the edge where a critical rupture thickness was reached. It was shown in Fig. 9.6(b) that a dimple was formed at $t = 6$ s, when the kinetics for the minimum film thickness was no longer following the kinetics at the center of the film. The difference between the minimum film thickness and the film thickness at the center was becoming significant as the film thinned.

Figure 9.6(c) shows both the measured and simulated interaction forces at low approach velocity. As shown, the interaction force increased when the piezo drove the air bubble towards the cantilever surface. As the piezo stopped, the force reached a constant value before the film ruptured. Once the film ruptured, the bubble began to spread on the solid surface, and at the same time the force jumped to negative values. The overall hydrodynamic force obtained from the temporal profiles was larger than the total force measured when $h < 200$ nm. The difference was attributed to the attractive surface force between the oppositely charged surfaces.

Figure 9.7 shows a comparison of the spatial profiles of $h$, $p$, $\Pi$ and $p_{\text{cur}}$ in a TLF under both a long-range attraction and a short-range attraction at $V = 1.5$ µm/s. It was found that a pimple was formed when the TLF was subjected to a long-range disjoining pressure, causing the film to rupture at the center. When the TLF was subjected to a shorter-range attraction, the film becoming larger (or flatter) as the piezo extended. Only when $\Pi$ played a role in the TLF with the film thickness below 100 nm in a $10^{-4}$ M NaCl solution, the film thinning accelerated at the edge of the film. A dimple was formed when a high pressure gradient was developed at the edge. The $\Pi$ vs. $r$ plot showed that a negative $\Pi$ developed in consonance to the film profiles. The $\Pi$ became increasingly attractive as the film thinned. The $p_{\text{cur}}$ vs. $r$ plot shows the curvature pressure caused by the curvature changes along the radial direction. As discussed earlier, a decrease of $p_{\text{cur}}$ in a pimpled film was due to the smaller curvature developed at the center than at the edge. Different patterns was found when a short-range attractive force was present. When the dimple was developed, the curvature pressure reached a plateau at the center and jumped to a near zero value at the edge. At the outer region, the curvature pressure had a secondary peak.
The temporal value at the outer region, and it decayed along the radial position of the film. The temporal

Figure 9.7 Effect of acting range of the attractive surface force on spatial profiles of the thickness ($h$), hydrodynamic pressure ($p$), disjoining pressure ($\Pi$) and total pressure ($p_{\text{cur}}$) in a wetting film. The results were obtained at $V = 1.5 \, \mu\text{m/s}$. The force measurements for both long- and short-range attractions were compared. A pimple was formed when the film was subjected to the long-range attraction. Contrarily, a dimple was developed when subjected to the short-range attraction.
variance of the pressures showed that the shape of the film was long-range correlated with the pressure distribution across the entire film.

Figure 9.8 shows the results obtained at $V = 6 \, \mu m/s$ when the TLF formed between the air bubble and the solid surface was subjected to a short-range attraction. It was shown that the bubble was rising at $V = 6 \, \mu m/s$ before the film reached the minimum thickness ($h_{\text{min}}$) of 400 nm. At $t = 1.2 \, s$, the bubble rising stopped. The film was allowed to drain spontaneously by the curvature pressure in the TLF. As shown from the spatial profiles, a flat film was initially formed.
When a short-range attractive force began to play a role, a subtle dimple was formed. Figure 9.8(c) shows the interaction forces obtained experimentally and simulated using the Reynolds lubrication theory. The interaction force remained constant when the piezo driving stopped. A short-range attraction was found at $t > 4.5$ s, when the film thickness was below 100 nm. The oscillation of the hydrodynamic force was partially due to the fluctuating spatiotemporal thickness profiles of the TLF. The fluctuation signal was attributed to the unstable output of the mercury light source. In the present work, the hydrodynamic force was determined in cylindrical coordinate, assuming the film was axis-symmetric. A detailed investigation on the non-uniform thinning profiles will be carried out in the future for accurate estimation of the hydrodynamic force.

9.4 Discussion

Above, we have shown both the film profiles and interaction forces between an air bubble and a solid surface when the film drainage was affected by the long- or short-range attractive surface forces. It was found that the interaction force increased only when the piezo drove the air bubble towards the cantilever surface. The interaction force remained constant when the mechanical drive stopped and film was allowed to drain spontaneously.

In a TLF, a normal force balance at air/water interface is always satisfied for pressures acting in a TLF with accounting of the surface tension pressure due to the changes in local curvatures. Mathematically, the relation is given by

$$ p_{cur} = p + \Pi $$  \hspace{1cm} (9.5)

In a thick film, $\Pi$ is negligible. The hydrodynamic pressure developed by the external force is translated into the deformation of the air bubble. As a result, an increase of the curvature pressure was observed when the bubble was pressed against the cantilever surface. As shown previously, the overall interaction force can be calculated from an integral of the curvature pressure over a thin liquid film. When the curvature pressure was developed by the external motion of the bubble, we have seen an increase of the interaction force with time.

The film thinned spontaneously by converting the hydrodynamic pressures into the curvature pressures, when the piezo stopped or the external force disappeared. In a case of a stable TLF,
the repulsive disjoining pressure was partially counter balanced the curvature pressure. As a result, the hydrodynamic pressure in the film decreased in accordance to the normal stress balance at the air/water interface. However, energies coming from the curvature pressures was conserved during the transformation of the pressures in the TLFs. In a similar manner, it is also applied for the case when the TLF was subjected to an attraction. Although we have seen that the curvature pressure developed at the center of the film right before the film rupture, the overall interaction force (or energy) between the air bubble and the cantilever surface remained constant. The constant force achieved by the reconstruction of the film profiles so that a lower curvature near the edge was created in order to maintain the constant energy.

We have shown in Fig. 9.5 that the curvature pressure was low in the thin liquid film where the film was pulled to be ruptured. In a case of the pimpled films, the curvature pressure was low at the center while high nearby the center. In a case of dimpled films, the curvature pressure became close to zero at edge, while a bump was found for the curvature pressure at the center of the film. Various configurations of the film profiles were found to satisfy the constant energy during the film drainage. This is why the overall interaction force was constant even when the TLFs were subjected to a long-range attractive force. The attractive force in the TLF was translated in the form of the curvature pressure, and thus, the energy of the thin liquid film remained constant.

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<th>$\kappa^{-1}$ (nm)</th>
<th>$\psi_1$ (mV)</th>
<th>$\psi_2$ (mV)</th>
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<tr>
<td>Long-range Attraction</td>
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<tr>
<td>V= 1.5 $\mu$m/s</td>
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<td>-70</td>
<td>43</td>
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<tr>
<td>Long-range Attraction</td>
<td></td>
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<tr>
<td>V= 6 $\mu$m/s</td>
<td>43</td>
<td>-70</td>
<td>70</td>
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<tr>
<td>Short-range Attraction</td>
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<tr>
<td>V= 1.5 $\mu$m/s</td>
<td>27</td>
<td>-30</td>
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<td>V= 6 $\mu$m/s</td>
<td>16</td>
<td>-30</td>
<td>-60</td>
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In the present work, we have shown that the Debye length in the TLF decreased as the approach velocity increased. The results were in agreement with the results obtained in Chapter 8. Table 9.1 shows a summary of the fitting parameters for the double-layer force between a positively charged air bubble and a negatively charged silicon surface separated by a thin film of water at varying approach speeds. We found that the decay lengths decreased with an increase of the approaching speeds. The results obtained in the present work between two oppositely charged surfaces were in consistent with the observations in a TLF between two similar charged surfaces. The decrease of the Debye length in a TLF of the high shear-rate flow was attributed to the preferential drainage of the bulk liquid in a TLF containing less electrolyte than the electrostatic double layers near the surface. As a consequence, the electrolyte was accumulated in a TLF when the film was squeezed. The detailed discussion on the decrease of the Debye length was made in Chapter 8.

9.5 Summary

Dynamic interaction between a positively charged air bubble and a negatively charged silicon surface was studied by monitoring both the interaction forces and the spatiotemporal thickness profiles of the film simultaneously. It has been shown that the interaction force increased when an air bubble was mechanically driven towards a silicon surface. As the piezo stopped, the interaction force remained constant during the period when the wetting film was allowed to drain spontaneously. The interaction force became attractive after the film ruptured and allowed to expand on the flat surface.

We have shown two different patterns of TLF profiles when attractive surface forces were present. A pimple is a funnel-shaped film whose thickness is the thinnest at the center. It created a higher thickness gradient along the radial direction (dh/dr), resulting in a lower curvature pressure. Pimples were formed when the surface force is strongly attractive and the curvature pressure is weak. A dimple is a convex film with an inverted curvature at the center. It was observed when a film was subjected to a higher hydrodynamic force, or a weak surface force, or a combination of the two.

Measured forces increased with increasing speed of the bubble approaching a flat surface. When the mechanical force moving the bubble toward the surface stopped, the measured forces
stayed constant until the force became negative due to the attractive surface force and the film ruptured. While the measured forces stayed constant, the film thinning process continued due to the curvature pressure.

9.6 References


ABSTRACT

The effect of surface hydrophobicity on bubble-particle interaction has been studied using the force apparatus for deformable surfaces (FADS). Both the interaction forces and bubble deformation measured with and without hydrophobization with potassium ethyl xanthate (KEX) were analyzed on the basis of the Reynolds lubrication theory and the extended DLVO theory. Regardless of the surface hydrophobicity, the interaction force is controlled initially by the hydrodynamic force and subsequently by the surface force at a separation distance approximately below 300 nm. The results obtained without the hydrophobization showed that the major contribution to the positive interaction force, or the kinetic barrier to film thinning, came from the double-layer repulsion.

When the gold surface was hydrophobized in a $10^{-5}$ M KEX solution for 10 min, the interaction force became less repulsive due to the presence of an attractive hydrophobic force. As the gold surface became more hydrophobic due to an increase of the immersion time, the disjoining pressure became more negative and the film thinning kinetics increased. Thus, the results obtained in the present work suggest that the role of collector in flotation is to create a negative disjoining pressure and thereby increase the film thinning kinetics and promote the film rupture. Once the film rupture occurred, the wetting film receded rapidly to form a finite contact angle.
10.1 Introduction

Hydrophobic coagulation occurs when two hydrophobic bodies in water agglomerate together to form larger clusters, or when one hydrophobic body engulfs the other. Air bubbles coagulate with hydrophobic particles spontaneously to lower the free energy when they are in contact [1]. There are many industrial processes that can be considered hydrophobic coagulation, e.g., pickering emulsion [2, 3], froth flotation [4, 5], microfluidics [6, 7], etc. Among all the applications, bubbles exhibit a unique feature that they coagulate with hydrophobic matters by collapsing the liquid film in between.

During the course of bubble-particle interaction, a thin liquid film (or wetting film) is formed. Thermodynamically, hydrophobic coagulation occurs when the changes in the free energy is less than zero, or the contact angle is greater than zero in accordance to the Young’s relation. It is well documented that the wetting film is stable on a hydrophilic surface [8-10]. When an air bubble approaches a hydrophilic solid surface, such as mica or silica, a β-film is formed by balancing the disjoining pressure with the Laplace pressure. As solid surfaces became hydrophobic, the wetting films become metastable. The film ruptures spontaneously at a critical rupture thickness, followed by an expansion of the three-phase contact line.

The bubble interacting with hydrophobic surfaces across a thin film of water has been intensively studied over the decades. In the late 1930s, Derjaguin and his co-workers designed an optical system to observe wetting films directly [11, 12]. Later in 1969, Laskowski and Kichener measured the water contact angles on methylated silica surfaces, and found that a rise of the contact angle on the solid surface might be related to the hydrophobic effect [13]. The study was further continued by Blake and Kitchener [14]. In their work, they experimentally monitored the thickness of the wetting films formed on a hydrophobic solid surface. They suggested the presence of hydrophobic force in the wetting film. Many follow-up experiments were conducted to study the stability of the wetting films on hydrophobic surfaces. However, the cause for the instability of wetting films on the hydrophobic surface was debated for decades without a consensus.

The possibility of the hydrophobic force being present in wetting films has been discussed since the initial discovery of the disjoining pressure. Laskowski and Kitchener [13] showed that the development of the contact angle on the solid surface was accompanied by an increase of the
attraction force between an air bubble and a hydrophobic surface. Later, Tchaliovsk et al. [15] studied the stability of the wetting films formed on a mica surface treated by dodecylammonium hydrochloride (DAH). They found that both the hydrophobic force and double-layer force played significant roles in destabilizing the wetting films. Mahnke et al. [16] showed a long-range hydrophobic force with a decay length of 13 nm in the wetting film formed on the methylated glass. However, the consensus on the presence of the hydrophobic force in the wetting film was never reached. Varying origins were proposed, including nanobubbles, nucleation, and double-layer attraction.

The nanobubble theory has received most attentions among the researchers to explain the film rupture with a combination of the capillary wave mechanism. Stockelhuber et al. [17] suggested that the rupture of the wetting film was caused by the van der Waals dispersion attraction between the nanobubbles present on the solid interface and the air bubble in the wetting film. The capillary wave brought the film to be touched locally by the dispersion attraction between two vapor/water interfaces. Hampton and Nguyen [18] suggested that the rupture of the wetting films formed on hydrophobic surface is due to the nanobubbles nucleating on the solid surfaces. However, recent evidences collected by the state-of-the-art spectroscopy techniques showed that the nanobubbles were not inherently present on the hydrophobic solid surfaces [19, 20]. The nanobubbles might be present on hydrophobic surfaces during the solvent exchanges or pressure changes. Some investigators [21] showed that the rupture of the wetting film formed on the hydrophobic surface was attributed to a formation of the gas channels. The hole expanded over time, resulting in the film rupture. However, Sharma [22] suggested that the hole formation might be due to the hydrophobic attraction.

It was hoped that the puzzles surrounding the wetting film rupture would be answered when the surface force measurement techniques such as SFA and AFM were developed. The hydrophobic force was first measured between two hydrophobic mica surfaces in an aqueous solution using the surface force apparatus (SFA) in 1982 [23]. A hydrophobic force with a decay length of 1.1 nm was measured between the CTAB-coated mica surfaces. The use of atomic force microscope (AFM) allowed the measurements of forces between opaque solid surfaces. Rabinovich and Yoon [24, 25] were the first to measure the hydrophobic force with an AFM. A hydrophobic force with a decay length of 21.7 nm was found between two OTS-treated hydrophobic surfaces with advancing contact angle of 116°.
The first attempt to measure the interaction forces between an air bubble and a hydrophobic solid surface was done by Ducker et al. [26]. They observed a repulsive force during the approach of an air bubble towards a hydrophobic particle. The force jumped to a negative value when the liquid film in between ruptured. Fielden et al. [27] also measured the interaction force between an air bubble and an OTS-treated silica particle in aqueous solution. It was found that the force jumped to a negative value at 10-20 nm. The repulsive force observed prior to the film rupture was predicted by the electrostatic double-layer force. Ishida [28] conducted the AFM force measurement between an air bubble and a hydrophobic particle with varying hydrophobicity. He found that the interaction force between the bubble and the hydrophobic particle was repulsive at a long separation distance due to the electrostatic double-layer force. An attraction was observed when the film in between collapsed. It was shown that a critical rupture thickness was not significantly influenced by the surface hydrophobicities.

However, the measurement of the surface forces between an air bubble and a solid surface using an AFM is not possible without considering the deformation of the air bubble. When AFM force measurement is conducted at a high frequency (or at a high approach speed), the piezo driving created a strong hydrodynamic repulsion, resulting in a significant deformation of the thin liquid film. Additionally, the zero separation distance between an air bubble and a solid surface is difficult to be determined with the AFM. Chan et al. [29, 30] derived a mathematical model to predict the spatiotemporal thickness profile of the thin liquid film between an air bubble and a solid surface. The overall interaction force obtained experimentally was successfully simulated from the Reynolds lubrication theory.

Recently, we have developed and constructed a novel surface force apparatus for a real-time measurement of both the interaction force and the spatiotemporal thickness profiles of the thin liquid film between an air bubble and a solid surface, as described in Chapter 7. The interaction force between an air bubble and a solid surface was obtained by monitoring the deflection of a custom-fabricated cantilever using the fiber optic interferometry, while the spatiotemporal thickness profiles of the thin liquid films were obtained using the microinterferometry technique. The surface force was extracted from a fit of the simulation results with the experimental data.

In the present work, we studied the effect of solid hydrophobicity on the interaction force between an air bubble and a gold surface. The hydrophobicity of the gold surfaces was
controlled by varying the immersion time in a potassium ethyl xanthate (KEX) solution. Disjoining pressure was determined from a fit of the overall interaction force obtained experimentally with the simulated results, in which the information on disjoining pressure was required as an input. The numerical simulation was carried out on the basis of the Reynolds lubrication theory and extended DLVO theory. The overall interaction force composes both the hydrodynamic force and surface force. We compared the results on both the bare gold surfaces and the hydrophobic gold surfaces.

10.2 Mathematical Model

When an air bubble collides with a solid surface in water, a thin liquid film (TLF) (or a wetting film) is formed. In wetting films, the characteristic thickness scale \( h \) is negligible compared to the characteristic length scale \( r \). Thus, fluid drainage in a wetting film is simplified to a 2D flow by considering the radial flow only. Here, the governing equation for the film drainage is given in cylindrical coordinate.

\[
\frac{\partial h}{\partial t} = \frac{1}{12 \mu r} \frac{\partial}{\partial r} \left( r h^3 \frac{\partial p}{\partial r} \right) \tag{10.1}
\]

where \( \mu \) is the viscosity of liquid and \( p \) is the pressure in film relative to the bulk. Equation (10.1) is derived under the non-slip boundary conditions. The non-slip boundary condition in a wetting film has been recently confirmed experimentally [31-34], showing that the slippage was retarded in a thin film of a low shear rate liquid. It might be attributed to the adsorption of the aerobic particles and organic matter at the interface.

The \( p \) is the driving pressure for the film thinning. When the pressure gradient \( (\partial p/\partial r) \) is developed in the thin film, the film thins spontaneously. From eq. (10.1), \( p \) can be obtained by integrating eq. (10.1) twice,

\[
p = 12 \mu \int_{r=\infty}^{r} \frac{1}{r h^3} \left[ \int_{r=0}^{r} r \frac{\partial h}{\partial t} \right] dr \tag{10.2}
\]

Equation (10.2) is derived under the conditions of \( p(r = \infty) = 0 \) and \( \partial p/\partial r|_{r=0} = 0 \).

As the film thins to a thickness below 300 nm, the disjoining pressure begins to play a role. It has been well documented that the film drainage is retarded when a repulsive disjoining pressure
is present in a wetting film formed on a hydrophilic surface. As the solid surfaces become hydrophobic, the hydrophobic interaction brings the film to thin faster and eventually to rupture catastrophically.

In a wetting film formed on a hydrophobic gold surface, the disjoining pressure may be composed of three components,

\[
\Pi = \Pi_d + \Pi_e + \Pi_h
\]

\[
= -\frac{A_{132}}{6\pi h^3} - \frac{\varepsilon \varepsilon_0 \kappa^2}{2 \sinh(\kappa h)} \left[ \psi_1^2 + \psi_2^2 \right] \cosh(\kappa h) - 2\psi_1 \psi_2 \coth(\kappa h) \frac{K_{132}}{6\pi h^3}
\]

(10.3)
in which \(\Pi_d, \Pi_e\) and \(\Pi_h\) represent the disjoining pressures due to the van der Waals dispersion force, electrostatic double-layer force, and hydrophobic force, respectively. In eq. (10.3), \(A_{132}\) is the Hamaker constant for the wetting film formed on a solid surface. In general, \(A_{132}\) is negative in wetting films and therefore the van der Waals dispersion force is always repulsive. In the present work, \(\Pi_e\) is obtained using the Hogg–Healey–Fuerstenau (HHF) approximation [35], in which \(\varepsilon_0\) is the permittivity in vacuum, \(\varepsilon\) is dielectric constant of water, \(\psi_1\) and \(\psi_2\) are the double-layer potentials at the solid/water and air/water interfaces, respectively, and \(\kappa\) is the reciprocal Debye length. The hydrophobic disjoining pressure is represented by a power law, in which \(K_{132}\) is the hydrophobic force constant for the bubble-solid interaction in water. Hydrophobic forces have been represented by both the exponential [24, 36, 37] and power laws [38, 39] interchangeably. In the present work, the power law is used to represent the hydrophobic disjoining pressure as shown in Eq. [10.3]. The subscripts 1, 2, and 3 represent solid, gas, and liquid, respectively. Unlike the solid-solid interaction, the bubble-particle interactions involve deformation of bubbles. A normal stress balance is in a wetting film shows the following relation,

\[
p = \frac{2\gamma}{R} - \frac{\gamma}{r} \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) - \Pi
\]

(10.4)
in which \(\gamma\) is the interfacial tension and \(R\) is the radius of the bubble in the far field. As shown in Eq. (10.4), a sum of \(p\) and \(\Pi\) is related with the curvature at vapor/water interface.

The overall interaction force exerting on the cantilever surface can be obtained by integrating the excess pressure \((p)\) over the film area from \(r = 0\) to \(r = R\). Thus, the overall interaction force is given by,
By substituting the eq. (10.4) to eq. (10.5), one can derive an equivalent expression for the overall interaction force between air bubble and solid surface from the profiles of the thin liquid film,

$$F(t) = 2\pi \int_{r=0}^{\infty} \left[ p(r, t) + \Pi(r, t) \right] dr$$

Eq. (10.6) is useful when the high-resolution spatial profiles of the thin liquid films are available. However, the use of eq. (10.6) for a prediction of the overall interaction force is not accurate for the thickness profiles with low spatial resolution. In the present work, eq. (10.5) was used to calculate the overall interaction force for bubble-particle interactions.

### 10.3 Materials and Methods

The gold surfaces were prepared by depositing a thin layer of gold on the cantilever surface. The cantilevers were made from 50 µm thick glass sheets (SCHOTT, Inc.) with a dimension of 15 x 4 x 0.05 mm. The glass cantilevers were cleaned carefully prior to the metal deposition. They were immersed in a boiling Piranha solution (H₂SO₄:H₂O₂ by volume 7:3) at 125 °C for 5 minutes, rinsed with amounts of ultrapure water and dried with the ultrapure nitrogen gas. Both the upper and lower cantilever surfaces were deposited by a 60 nm thick gold layer with a 5 nm thick titanium adhesion layer. The deposition was operated using the E-beam physical vapor deposition (PVD) technique in class-100 cleanroom. The ultrapure water was obtained from Direct-Q water purification system (Millipore). The produced water has a resistance of 18.2 MΩ•cm and < 10 ppb of total organic carbon. The water is used as obtained without degassing and any further purification. The pH of pure water is 6.9 - 7.1.

Prior to the force measurement, the gold cantilevers were treated in UV-Ozone environment for one hour to remove the adsorbed organic compounds from the atmosphere. The cleaning procedure was followed by flushing with methanol (99.9 %, Sigma-Aldrich) to remove the oxide and the partial residues on the cantilever surface. The treated bare gold surfaces have the water equilibrium contact angle of less than 20°. The hydrophobic gold surfaces were prepared using the ex-situ method. They are hydrophobized in a 10⁻⁵ M potassium xanthogenate (KEX) aqueous
solution for 10 minutes up to 120 minutes. The KEX (90%, TCI America) was purified twice before use by dissolving the technical grade KEX in acetone (HPLC grade, Fisher Sci.) and recrystallized in diethyl ether (99.999%, Sigma-Aldrich).

The force measurements were conducted between an air bubble and a gold-coated cantilever surface in water. The experiments were carried out using the force apparatus for

![Figure 10.1 (a) Interaction force (F) vs. time (t) in wetting films between air bubbles and gold surfaces with receding contact angles (θ_r) of < 20° and 50°; (b) spatotemporal thickness profiles of the wetting films between air bubbles and gold surfaces. The measurements were conducted at bubble approach velocity (V) of 0.75 μm/s. The left figure in (b) shows the profiles of the thin liquid film (TLF) formed on a bare gold surface with θ_r < 20°, and the right figure shows the profiles of the TLF formed on the xanthate-treated gold surface with θ_r = 50°.](image-url)
deformable surfaces (FADS). Detailed designs and operational methods were described in Chapter 7. The cantilever was glued onto the upper quartz surface using a medical-grade epoxy. The top quartz plate was connected with a 5-axis translational stage, allowing the cantilever move in x, y, z, $\theta_x$, $\theta_y$ directions. The water was then injected through the bottom quartz plate using a 20 mL glass syringe. The water was allowed to flush the cell for at least two times to guarantee the minimal amount of the trace particles in the fluid cell. An air bubble of 2 mm in radius was created by slowly injecting the gas into the cell using an air-tight gas syringe. The measurement was conducted by elevating an air bubble towards the cantilever surface using a piezo actuator. The interaction force was obtained by monitoring the deflection of the cantilever using the fiber optical interferometry technique. A single-mode fiber was sitting at 100 $\mu$m above the cantilever. A cavity was created between the end face of the fiber and the upper surface of the cantilever, allowing an interference of the returning laser light. Meanwhile, the spatiotemporal profiles of the thin liquid films between the air bubble and the lower surface of the cantilever were in real-time monitored by the high-speed imaging of the interference patterns of the TLF. The analysis of the interference patterns were allowed to reconstruct the spatial and temporal thickness profiles of the TLF.

10.4 Results and Discussion

Figure 10.1(a) shows the interaction force in water between an air bubble and a gold surface

![Before contact](image1)

![After contact](image2)

Figure 10.2 Snapshot of an air bubble and a gold substrate in water before and after the three-phase contact. The receding contact angle was measured at liquid phase of the three-phase contact point. $\theta_r = 50.1^\circ$ for a gold surface treated in a $10^{-5}$ M KEX solution for 10 minutes.
with and without KEX treatment. The force measurements were conducted at an approach speed \( V \) of 0.75 \( \mu \text{m/s} \). The gold surfaces having a receding contact angle \( (\theta_r) \) of 50° were obtained by immersing them in a 10\(^{-5}\) M KEX solution for 10 minutes. The \( t = 0 \) was when the minimum film thickness was 4 \( \mu \text{m} \). It was shown that the interaction force in a wetting film formed on the bare gold surface increased with time, as the bubble approached towards the cantilever surface. The overall interaction force increased slowly at \( t < 7 \text{ s} \), subsequently in a linear function with time, and became constant when the film was allowed to drain spontaneously to the equilibrium. For a wetting film formed on the hydrophobic gold surface, however, the interaction force was less repulsive than the force obtained on the hydrophilic gold surface. The interaction force became net attractive at \( t = 6.604 \text{ s} \), when the film ruptured.

Figure 10.1(b) shows the spatial and temporal thickness profiles of the TLFs formed on both the hydrophilic and hydrophobic gold surfaces. On a bare gold surface, a thick equilibrium film was formed when the disjoining pressure in the film was balanced by the curvature pressure. It was shown that at \( t = 8.33 \text{ s} \), the film reached equilibrium at \( h_e = 105 \text{ nm} \). As the bubble continued pressing towards the cantilever surface by the piezo actuator, the flat film became larger. At \( t = 10 \text{ s} \), the film thickness at the center of the film remained constantly.

In a wetting film formed on a hydrophobic gold surface, the bubble remained spherical during the wetting drainage. As the film thickness was reduced below 300 nm, the film thinning accelerated at the center. As shown, the spherical bubble bulged at the center of the film, leading
to the formation of a convex-shaped film. When the film reached a critical rupture thickness, the film ruptured catastrophically.

Once the film was ruptured, the bubble began to dewet on the solid surface by receding the liquid along the three-phase contact line. Figure 10.2 shows a series of the interference fringes after the film ruptured. At $t = 6.6$ s, the film reached a critical rupture thickness, and became metastable. The film rupture was followed by an expansion of the three-phase contact line. The bright spot shown in the interference fringes represents the contact area where the bubble touches the gold surface. It was shown that at $t = 6.604$ s, the radius of the three-phase contact was greater than 400 μm. The contact area kept increasing, until a maximum receding contact angle was formed in equilibrium. The angle was determined from the side-view image of the three-phase contact. The value was obtained by measuring the angle between the base line of the solid surface and the tangent line of the liquid/air interface at a three-phase contact point. Figure 10.3
showed a snapshot of the air bubble and the cantilever surface before and after the film ruptures and the three phase contact. It was shown that $\theta_r = 50.1^\circ$ on the gold surface treated in a $10^{-5}$ M KEX solution for 10 minutes.

The measured forces between the air bubble and the solid surface were simulated using eqs. (10.2)-(10.4). Figure 10.4 shows both the measured and simulated interaction forces between an air bubble and a bare gold at $V = 0.75$ µm/s. The black, blue and red lines represent the hydrodynamic, surface and total forces, respectively. The total force is a sum of the hydrodynamic force and surface force. A close fit was obtained between the experimental data and the simulation results, in which the surface forces according to the DLVO theory were included. In a wetting film formed on a bare gold surface, the hydrophobic force was negligible for its water contact angle was less than 40$^\circ$. Thus, the disjoining pressure was calculated from the van der Waals dispersion and the electrostatic double-layer force only using eq. (10.3). In eq. (10.3), $A_{132} = -14.8 \times 10^{-20}$ J, $\psi_1 = -40$ mV, $\psi_2 = -36$ mV and $\kappa^{-1} = 84$ nm.

As shown in Fig. 10.4, the total force was initially dominated by the hydrodynamic force and subsequently by the surface force. The contribution from the surface forces to the total force was
Figure 10.6 Force vs. time measured between an air bubble and a hydrophobic gold surface in water. The hydrophobic gold surfaces were prepared in a $10^{-5}$ M potassium ethyl xanthate solution for 10 minutes. A best fit was obtained between the measured force and simulation results with considering the attractive hydrophobic force. The hydrophobic force was represented as a power law with force constant $K_{132} = 7.6 \times 10^{-18}$ J.

Figure 10.5 shows a plot of the hydrodynamic, surface and total forces vs. minimum film thickness in a wetting film formed on a bare gold surface. As shown, the total force was dominated by the hydrodynamic force when the film thickness was above 300 nm. As the film thinned to a thickness below 300 nm, the surface force due to electrostatic double-layer interaction became significant in contributing the overall interaction force. However, the hydrodynamic force remained constant during the drainage of the wetting film. It decreased equivalent to that from the hydrodynamic force at $t = 8$ s. The results showed that the hydrodynamic force initially increased slowly, reached a plateau at $t > 7$ s, and decreased when the piezo stopped. At $t > 7$ s, the surface force became dominating in contributing to an increase of the total force. As shown, the surface force increased linearly with time, and reached a plateau when the piezo stopped at $t \approx 15$ s. In an equilibrium, the hydrodynamic force became zero and the overall total force was contributed by the surface force only.
when the bubble approach stopped and became zero when the film reached equilibrium. The present results suggested that the drainage of the wetting film was initially controlled by the curvature pressure due to the initial impacting energy at the film thickness above 300 nm, and subsequently by the surface force.

In a wetting film of water formed on the bare gold surface, the surface force was mainly controlled by the electrostatic double-layer force. We have shown that the surface force played an important role when the film thickness was below 300 nm. It has been shown that the role of the surface force became increasingly significant as the film thickness decreased. The film thinning continued when the pressure gradient was non-zero that drove the liquid out of the film. As the disjoining pressure became equivalent to the surface tension pressure (or curvature pressure) created by the changes in curvature, the excess pressure for film thinning became zero. As a consequence, the film became stabilized by the repulsive disjoining pressure.

Unlike a stable film formed on the hydrophilic surface, a wetting film formed on the hydrophobic surfaces became metastable. An example is the wetting films formed on the gold surfaces treated by the hydrophobizing chemicals, such as xanthate and thiol. As shown in Fig.

Figure 10.7 Changes in hydrodynamic, surface and total forces vs. minimum film thickness in a TLF between an air bubble and a hydrophobic gold surface treated in $10^{-5}$ M KEX solution for 10 minutes.
10.1, the wetting films formed on the gold surfaces treated by KEX ruptured spontaneously at a critical rupture thickness. Figure 10.6 shows both the experimental and simulated results of the interaction force in water between an air bubble and a gold surface with $\theta_r = 50.1^\circ$. The hydrophobic gold surface with $\theta_r = 50.1^\circ$ obtained by immersing it in a $10^{-5}$ M KEX solution for 10 minutes. A close fit was obtained between the experimental data of the interaction force and the simulated results, in which the hydrophobic force was included. It was shown that the hydrophobic interaction between the air bubble and the hydrophobic gold surface treated in a $10^{-5}$ M KEX solution for 10 minutes was attractive with hydrophobic force constant ($K_{132}$) of $7.6 \times 10^{-18}$ J. As shown, the overall interaction force was repulsive, and it increased gradually with time during the approach of the air bubble towards the cantilever surface. As the film thinning continued, the attractive surface force brought the film thinning acceleratedly. Consequently, the hydrodynamic pressure increased dramatically when the attractive surface force played a role. The overall interaction force, however, increased slowly even when the hydrodynamic repulsion was large due to the accelerated film drainage. A slow increase of the overall interaction was
attributed to an exponential increase of the attractive surface force that counter balanced the hydrodynamic force.

Figure 10.7 shows the forces vs. minimum film thickness for hydrodynamic, surface and total forces in a wetting filmed formed on a hydrophobic gold surface, treated in a manner as Fig. 10.6. It showed that the overall interaction force increased slowly when the film thinned from 600 to 100 nm. The profiles of the hydrodynamic and surface forces showed that the overall interaction force was initially dominated by the hydrodynamic force at $h > 400$ nm. The surface force played a role in accelerating the film drainage until the wetting film ruptured. We have shown that the hydrophobic force played a significant role in destabilizing the wetting film.

When the gold surfaces were treated in a $10^{-5}$ M KEX solution for a longer immersion time, the water contact angle on the gold surfaces became slightly increased. Figure 10.8 shows the interaction force between an air bubble and a gold surface treated in the KEX solution for 30
minutes. The receding contact angle of the hydrophobic gold surface in water is $53.5 \pm 2.0^\circ$. A close fit was obtained between the experimental data and numerical results, in which the hydrophobic interaction was included in the extended DLVO theory with $K_{132} = 12 \times 10^{-18}$ J for the estimation of the surface forces. A comparison of the results obtained at 10 minutes and at 30 minutes hydrophobization time showed that the hydrophobic force became more attractive when the gold surfaces were immersed in a $10^{-5}$ M KEX solution for a longer immersion time. It was shown in the green line that the overall total force increased slowly and became attractive when the film ruptured. Note that, the deviation was found at $t > 2$ s between the experimental data and the theoretical prediction. The result showed that the theoretical prediction with an inclusion of the hydrophobic interaction of a power law overestimated the overall interaction force. At $t > 2$ s, the film thickness was below 100 nm. It appears that the hydrophobic force of a power law might overestimate the force at a short-range distance.

Figure 10.9 shows the interaction force in wetting films formed on the gold surfaces hydrophobized in the $10^{-5}$ M KEX solution for 120 minutes. At 120 minutes, the contact angle of water on the gold surface decreased slightly, and $\theta_r = 51.0 \pm 1.2^\circ$. We have shown that the force constant ($K_{132}$) for the hydrophobic force decreased to $10.4 \times 10^{-18}$ J at a hydrophobization time of 120 minutes. It is clearly shown that the use of a power law for the hydrophobic interaction might overestimate the hydrophobic interaction at short-range separation distance. However, it quantitatively predicted the surface force at a long-range distance.

Figure 10.10 shows the disjoining pressure in a wetting film between an air bubble and a hydrophobic gold surface treated in a $10^{-5}$ M KEX solution for different immersion time. The black curve shows the van der Waals dispersion force ($\Pi_d$) in a wetting film formed on a gold surface with the Hamaker constant ($A_{132}$) of $-14.8 \times 10^{-20}$ J. The curve labeled “0 min” represents the disjoining pressure between an air bubble and a bare gold surface. A repulsion was found at a long-range distance, while an attraction was found at a short-range distance as predicted by the HHF theory. When the gold surfaces were rendered hydrophobic in the $10^{-5}$ M KEX solutions, the disjoining pressure became increasingly attractive. It was shown that the hydrophobic force constant ($K_{132}$) in wetting films increased when the gold surfaces were rendered hydrophobic in KEX solutions from 10 minutes to 30 minutes, and decreased at 120 minutes. An increase of the hydrophobic force at short hydrophobization time might be attributed to a formation of the hydrophobic monolayer on gold surfaces, while a decrease of the
hydrophobic force at longer time might be attributed to the formation of multilayers above the monolayers. The adsorption of the multilayers might render the hydrophilic head group of xanthate towards the water phase, resulting in a decrease of solid hydrophobicity. As shown from the contact angle measurement, the contact angle decreased slightly when leaving the gold surfaces in a KEX solution for a longer hydrophobization time.

10.5 Summary

The interaction forces between air bubbles and gold surfaces were studied in water using the force apparatus for deformable surfaces (FADS). The new apparatus is capable of directly measuring the interaction force between a solid surface and an air bubble across a thin liquid film, while monitoring the bubble deformation during the course of the interaction. In the present work, we have studied the effect of the solid hydrophobicity on the forces acting between an air
bubble and a gold surface. The results showed that the wetting film formed on a bare gold surface was stable due to the repulsive disjoining pressure created by the double layer force.

It has been found, on the other hand, that the wetting films formed on a hydrophobic gold surface was unstable and ruptured catastrophically at a critical thickness ($h_{cr}$). As a result of the film rupture, a three-phase contact line was formed with a finite contact angle ($\theta$). When a bubble approached a strongly hydrophobic surface, pimpled wetting films with a concave shape were obtained. The film ruptured at the center of the wetting film. The results obtained in the present work represent the first ever 3D images recorded in nano-scale for bubble-particle interactions. Further, the results presented here provided an unequivocal evidence for the presence of the hydrophobic force in the wetting films formed on hydrophobic surfaces.

10.6 References


Chapter 11. Conclusions and Recommendations for Future Research

11.1 Conclusions

The major findings and contributions from this work may be summarized as follows.

1. When an air bubble is pressed against a flat substrate immersed in water, the bubble flattens and creates a thin liquid film (TLF) of water between the bubble and the substrate. The curvature change associated with the formation of the wetting film creates an excess pressure ($p$) in the film, which in turn causes the film of water to drain. The film drainage continues until the excess pressure becomes equal to the disjoining pressure ($\Pi$) in the film. The TLF is stable when the disjoining pressure is positive (repulsive) and is unstable when the disjoining pressure is negative (attractive). One can readily determine the positive disjoining pressures when the wetting films are stable. However, no one has ever been able to measure the negative disjoining pressures as the films drain too fast to do meaningful measurements.

2. In the present work, the thin film pressure balance (TFPB) technique, originally developed for the study of foam films, has been modified to measure the negative disjoining pressures in wetting films. It is equipped with a high-speed video camera to record the interference patterns (Newton rings) of the fast-evolving wetting films. The interference patterns were then analyzed offline to reconstruct the spatial and temporal (spatiotemporal) profiles of the wetting films with a nano-scale resolution. The experimental data obtained in this manner were analyzed using the Reynolds lubrication theory to determine the changes in disjoining pressure ($\Pi$) with time and film thickness ($h$). The results showed that long-range hydrophobic forces were present in the wetting
films formed on the gold surfaces hydrophobized by short-chain alkylxanthates. According to the thermodynamic analysis based on the Frumkin-Derjaguin isotherm, the kinetics of film thinning is expedited by the long-range hydrophobic forces, while the short-range hydrophobic forces are responsible for the rupture of the wetting film formed on a hydrophobic surface.

3. The role of collector on flotation has been studied by measuring the disjoining pressures of the wetting films with and without hydrophobization of the substrate. The results showed that collector coating increases the hydrophobicity of minerals and thereby creates a negative disjoining pressure, so that wetting films thin faster and ruptures.

4. The kinetics of film thinning has been studied by using the different sizes of the bubbles to form wetting films. The results showed that the wetting films formed with smaller air bubbles thin faster due to the larger curvature pressures.

5. The negative disjoining pressures observed in the wetting films formed on hydrophobic surfaces are the consequence of asymmetric hydrophobic interactions between the air/water and solid/water interfaces in wetting films. It has been found that the hydrophobic force constant ($K_{132}$) for the asymmetric hydrophobic interactions can be predicted from the hydrophobic force constant ($K_{131}$) for the symmetric hydrophobic interactions between hydrophobic surfaces and the symmetric hydrophobic force constant ($K_{232}$) between air bubbles using the geometric mean combining rule. In view of the fact that the geometric mean combining rule is used for the van der Waals force, the hydrophobic force may be considered a molecular force.

6. It has been shown in the present work that wetting films can be destabilized by the attractive double-layer interactions in wetting films. In the presence of $3 \times 10^{-5}$ M Al$^{3+}$ ions, the silica/water interface is positively charged while the air/water interface is negatively charged. The double-layer interaction between the two oppositely charged surfaces created a negative disjoining pressure. As a consequence, the wetting film thinned fast
and ruptured with a finite contact angle. The measured contact angle is in agreement with the prediction from the Frumkin-Derjaguin isotherm.

7. It has been a challenge to directly measure the interaction forces involved in bubble-particle interactions. The main reason was that air bubbles deform during the interaction, which makes it difficult to determine the separation distances between the two macroscopic surfaces. As a result, much of the data reported in the literature are inconsistent with flotation practices. The force apparatus for deformable surfaces (FADS) developed in the present work is capable of measuring both hydrodynamic and surface forces involved in bubble-particle interactions. The system has two optical systems, one to directly measure the deflection of the cantilever spring using a fiber optic system, and the other to record the interference patterns (Newton rings) of the fast-evolving wetting films using a high-speed video camera. The former is used for direct force measurement, and the latter is used to reconstruct the spatial and temporal film profiles of the wetting films offline.

8. Analysis of the FADS data show that an air bubble approaching a solid surface deforms in response to both the hydrodynamic and surface forces in the system. In the presence of a strong repulsive disjoining pressure, the wetting film becomes flat. In the presence of a strong attractive force, a concave (pimpled) wetting film is formed when the approach speed is slow, while a convex (dimpled) wetting film is formed when the approach speed is high. An unstable, either pimpled or dimpled, film was developed under an attractive force. It has been shown in the present work that bubble-particle interactions are controlled initially by hydrodynamics, followed by surface forces. Unlike the interactions between rigid particles, the energy associated with bubbles (or other soft matter) is conserved by shape changes when subjected to an external force.

9. The direct force measurements conducted with the FADS showed that hydrophobic forces are present in wetting films. The measured hydrophobic forces increase with increasing surface hydrophobicity. This finding is consistent with the thermodynamic
prediction from the Frumkin-Derjaguin isotherm that a wetting film ruptures only when its disjoining pressure is negative.

11.2 Recommendation for Future Research

On the basis of the present work, future research directions under the topic of the wetting film are recommended as follows.

1. FADS developed in the present work is a scientific breakthrough for the study of the TLF formed on a solid surface. However, FADS requires the upgrades for better performances. First of all, the current design is capable of measuring the force in a thin liquid film formed on a solid surface with a resolution of 5 nN. A better mechanical design with low drift and background noise is essential. Secondly, the spatiotemporal thickness profiles of the liquid films were determined from the interference fringes of the fast-evolving wetting films by means of a high-speed camera. The reconstruction of the spatiotemporal profiles was done using the monochromatic interferometry technique. However, such technique naturally lacks of the capability of determining the order of the fringes. Additionally, the use of the monochromatic interferometry is particularly limited in determining the film thickness below 20 nm. Future research will focused on developing a multi-wavelength interferometry technique to monitor the separation distance with a sub-angstrom resolution. Thirdly, FADS was specifically designed for the force measurement between an air bubble and a solid surface, with a lack of the accessories to study other soft matters, such as oil droplets, supercritical CO₂. A multifunctional platform will be constructed with an environment chamber for dust control and pressure regulation.

2. The results in Chapter 10 showed that xanthate adsorption on gold surfaces in an open circuit created a strong hydrophobic attraction in a wetting film between an air bubble and a hydrophobic gold surface. The attraction might be the hydrophobic interaction due to a rise of the surface hydrophobicity. It has been well documented that xanthate
adsorption on gold surfaces is an electrochemical process. The effects of applied potentials on the interaction force in TLFs formed on gold surfaces are recommended.
Appendix A. Calibration of Spring Constant

Spring constant of the home-made cantilever is in-situ calibrated by monitoring the deflection of a cantilever when a small weight is applied. The weight is created by an air bubble against a cantilever surface across a thin liquid film. During the course of the bubble approaching against the cantilever surface, the cantilever is subjected to both the hydrodynamic pressure by the fluid motion and the disjoining pressure created by the intermolecular force. In a TLF between an air bubble and a hydrophilic surface, the air/water interface begins to deform in responding to the force created by a repulsive disjoining pressure due to the double-layer force. Mathematically, the deformation of the air/water interface satisfies the normal stress balance at air/water interface,

\[ p = p_{\text{cur}} - \Pi \]  

(A.1)

Figure A.1 Deflection vs. time obtained by elevating an air bubble in steps
where $p_{\text{cur}}$ is the curvature pressure due to the surface tension, $p$ the hydrodynamic pressure and $\Pi$ the disjoining pressure. By definition, the interaction force, $F(t)$, exerting on the cantilever surface can be obtained from the integral of the hydrodynamic pressure and the disjoining pressure,

$$F(t) = 2\pi \int_{r=0}^{\infty} \left[p(r,t) + \Pi(r,t)\right]rdr$$

(A.2)

in which $r = 0$ represents the symmetric axis in a cylindrical coordinate, i.e., the center of the film. By substituting eq. (B.1) to eq. (B.2), one can obtain an alternative expression for the interaction force between an air bubble and a solid surface,

$$F(t) = 2\pi \int_{r=0}^{\infty} p_{\text{cur}}(r,t)rdr$$

(A.3)

in which the interaction force, $F(t)$ is expressed in term of $p_{\text{cur}}$. In a thin film, the curvature pressure, $p_{\text{cur}}$, can be estimated from the profiles of the thin liquid film using the following equation.

$$p_{\text{cur}} = \frac{2\gamma}{R} r \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right)$$

(A.4)
where $R$ is the radius of the bubble in the far field, and $\gamma$ is the interfacial tension of air/water interface. In eq. (B.4), the second term of $p_{cur}$ is the local Laplace pressure evaluated at radial position of the film. At flat film, $\partial h/\partial r$ is equivalent to zero at flat film, and thus $p_{cur} = 72 \text{ N/m}^2$ for 2 mm radius of an air bubble. Thus, the interaction force can be determined when the spatial thickness profiles of the TLF is known.

The calibration is carried out by pressing an air bubble towards a hydrophilic cantilever surface using a piezo actuator. Initially, a manual micrometer was used to lower the position of the cantilever until an equilibrium film is formed. Afterwards, the position of a bubble is controlled by means of a piezo actuator. When the piezo actuator extends by applying the voltage, the thin film expands at equilibrium film thickness, resulting an increase of the total force. Thus, the spring constant can be calibrated from a linear fit between the interaction force and the deflection of the cantilever by increasing the size of the flat film.

Figure A.3 Curvature pressure vs. radial position of the film at $t = 1340$ ms. The profiles of the $p_{cur}$ was obtained from the numerical analysis of the thickness profiles shown in Fig. B.2 using the eq. (B.4).
Fig. (B.1) shows the deflection vs. time by manually elevating an air bubble towards a cantilever in steps. It was shown that the interaction force increased when the piezo extended, while remained constant when the piezo stopped. The film profiles were tracked simultaneously by capturing the interference fringes by means of a high-speed camera. Fig. (B.2) shows the spatial thickness profiles of the wetting film at $t = 1340$ ms. The profiles were fitted using a six-order polynomial fitting method. Using the eq. (B.4), the curvature pressure can be obtained, as shown in Fig. (B.3).

From the integral of curvature pressure using eq. (B.3), we obtained that $F = 525.5$ nN. In a same manner, we determined the force at other time. Table B.1 shows the force and deflection at different time. A plot of the force vs. deflection is shown in Fig. (B.4). From a best linear fit, we obtain that the spring constant $k = 3.24$ N/m.

Figure A.4 A linear fit between the interaction force and the deflection. It shows that spring constant $k = 3.24$ N/m.
Table A.1  Forces and deflections obtained at different time

<table>
<thead>
<tr>
<th>Time (10 ms)</th>
<th>Deflection (nm)</th>
<th>Force (nN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1340</td>
<td>71.5</td>
<td>525.5</td>
</tr>
<tr>
<td>2702</td>
<td>130.8</td>
<td>731.7</td>
</tr>
<tr>
<td>3860</td>
<td>177.3</td>
<td>886.7</td>
</tr>
<tr>
<td>4702</td>
<td>235.0</td>
<td>1055.2</td>
</tr>
</tbody>
</table>
Appendix B. Determination of Hydrodynamic Force

When a particle is approaching against a flat solid surface in water, the hydrodynamic pressure is arisen due to the viscous stress exerting on its interface. In a thin liquid film, the hydrodynamic force can be obtained by the Reynolds lubrication theory,

\[ F = 6\pi R^2 \frac{dh}{dt} \tag{B.1} \]

where \( R \) is the radius of the sphere, \( h \) the thickness and \( t \) the time. Eq. (B.1) is obtained by solving the lubrication equation in the cylindrical coordinate. Eq. (B.1) assumes that the geometry of the sphere is not changed during the course of the interaction. In a thin liquid film between an air bubble and a solid surface, the bubbles deform in responding to the arising interaction force from both the viscous stress and intermolecular interaction. Thus, the determination of the hydrodynamic force in a thin liquid film needs to be done by integrating the hydrodynamic pressure over the film areas numerically. The governing equation in a thin liquid film is given by,

\[ \frac{\partial h}{\partial t} = \frac{1}{12\mu r} \frac{\partial}{\partial r} \left( rh^3 \frac{\partial p}{\partial r} \right) \tag{B.2} \]

where \( \mu \) is the viscosity of the liquid and \( p \) is the hydrodynamic pressure. The \( p \) is obtained from the integral of the velocity \( (\partial h/\partial t) \) over the film area,

\[ p = \int_{r=\infty}^{r} \frac{1}{rh^3} \left[ \int_{r=0}^{r} 12\mu r \frac{\partial h}{\partial r} dr - \frac{\partial p}{\partial r} \bigg|_{r=0} \right] dr - p(r=\infty) \tag{B.3} \]

Here, the vertical velocity is assumed to be constant along the radial position of the film. Thus, eq. (B.3) can be simplified as,

\[ p = \int_{r=\infty}^{r} 6\mu \frac{r}{h^3} \frac{\partial h}{\partial t} dr \tag{B.4} \]
where the hydrodynamic pressure was obtained by integrating the velocity from the infinity to the local radial position. By integrating the hydrodynamic pressure over the entire thin film, one can obtain an expression for the hydrodynamic force,

\[ F = 2\pi \int_{r=0}^{R} p r dr \]  

(B.5)

Fig. (B.1) shows the effect of approaching speed on the hydrodynamic force in a thin liquid film of water between two solid surfaces. The results were shown between a 2 mm sized liquid particle and a flat solid surface. It was found that the numerical results covering 300 and 500 \( \mu m \) radii of the film area were in a good agreement with the lubrication theory, while those covering 100 \( \mu m \) radii of area underestimated the hydrodynamic force. Thus, all the calculations for the hydrodynamic force in this work was done by the integral of the hydrodynamic pressure over the film areas at \( r = 0 - 300 \mu m \).

Figure B.1 Effect of approaching velocity on the hydrodynamic force exerting on the solid surface when a 2 mm radii particle is used. The solid lines and the circle points represent the hydrodynamic force predicted using the eq. (B.1) and the numerical analysis using the eqs. (B.2)-(B.5), respectively. The hydrodynamic forces obtained from the integral of the hydrodynamic pressure over the radial distance of (a) 100 \( \mu m \), (b) 300 \( \mu m \) and (c) 500 \( \mu m \) were compared.