

CHAPTER 1

INTRODUCTION

1.1 General

The process of flotation critically relies on the successful attachment of the mineral particle to the bubble surface [1]. However, due to the complex nature of the bubble-particle interaction the process is extremely difficult to model. In the past some models were developed by considering only the hydrodynamic parameters, e.g., bubble size, particle size, turbulence, energy dissipation, viscosity etc [2,3]. These parameters were used to predict bubble-particle collision.

It is important to point out that, however, knowing the probabilities of collision is not sufficient to predict flotation rates. There are two other sub-processes other than collision that affect flotation rate. These include the probabilities of adhesion and detachment, both of which are dictated largely by the surface forces involved in bubble-particle interactions [4,5]. In fact mineral processing engineers have long known the importance of surface chemistry parameters such as zeta potential and hydrophobicity of the mineral particle (as measured by the contact angle θ) in maximizing flotation efficiency. As mentioned earlier, none of these parameters were considered in the earlier flotation models.

Derjaguin and Dukhin [6] were probably the first to consider the role of surface forces in bubble-particle interactions. They suggested that a particle should pass through three distinct zones, i.e., hydrodynamic, diffusio-phoretic and wetting zones, before bubble-particle attachment can occur. Once the particle is in the wetting zone, three different surface forces, namely, the van der Waals force, the double layer force and the structural forces dictate its attachment to the bubble surface. Derjaguin and Dukhin [6] originally believed that the structural force was hydrophilic in origin and had to become zero for successful bubble-particle attachment. In

essence these authors did not consider that an attractive force, related to the hydrophobicity of the mineral surface, could play a major role in bubble-particle interactions.

The earliest evidence for the existence of an attractive force in bubble-particle interactions was probably given by Blake and Kitchener [7] who conducted film stability measurements for the methylated quartz-air bubble system. These investigators reported that both the electrostatic and dispersion forces were repulsive for the methylated quartz-air bubble; yet, film rupture occurred at distances greater than 60 nm. Therefore, Blake and Kitchener [7] suggested that there must be an additional attractive force, not known at the time, playing a role in determining the stability of wetting films.

It was not until 1982 that the exact nature of this attractive force became quite clear. In a landmark paper, Israelachvili and Pashley [8] reported the surface force measurements conducted between cylindrical mica sheets in 1×10^{-5} M CTAB solutions. They found that the measured attractive force was an order of magnitude higher than that predicted by the continuum van der Waals force. Since the publication of this paper, many investigators conducted similar measurements and confirmed that the additional attractive force is the hydrophobic force.

Although it is now generally agreed that the hydrophobic force may play a role in bubble-particle interactions, its exact role in flotation has not been accurately quantified. A major problem has been that most of the surface force measurement techniques available today are not amenable to conduct direct force measurements for bubble-particle interactions. As a result, the force measurements conducted using air bubbles are quite controversial and in many cases the results reported are not consistent with flotation literature [9-12].

In order to alleviate the problems associated with using an actual bubble, surface force measurements were conducted at Virginia Tech between a hydrophobic glass sphere and mineral surfaces [13]. The hydrophobic glass sphere may simulate the behavior of air bubbles during flotation. This technique is based on the assumption that air bubbles are inherently hydrophobic and their hydrophobicity decreases with increasing surfactant concentration. Indeed the force

measurements conducted using a hydrophobic glass sphere as a simulated air bubble gave results that are consistent with flotation results.

It is the objective of the present work to study the role of hydrophobic forces in flotation in general. To meet this objective, an atomic force microscope was used to measure the surface forces between different mineral surfaces and a hydrophobic glass sphere. The minerals used for the measurements included covellite, activated sphalerite and hornblende. Another objective of the present work was to study the origin of the hydrophobic force. To meet this end, force measurements were conducted using silanated silica surfaces as model hydrophobic surfaces. The results were used to develop a model for the origin of the hydrophobic force.

In what follows a review of literature is presented with an aim to provide a relevant background to the research presented in this work.

1.2 Review of Literature

1.2 (a) Flotation

The process of froth flotation is used to separate minerals suspended in aqueous media by attaching selected constituents of the minerals to gas bubbles. There is some evidence that the process was practiced in the East as early as the 15th century, but it was not well established until after the Industrial Revolution [14]. Credit should probably be given to William Hayes who patented a process in 1860, in which a large amount of oil was used to float metal sulfides [14]. A similar process was also patented in Germany by the Bessel brothers in 1877 to recover graphite [15]. The first flotation plant in America was set up in the year 1911 at Basin Mill, Montana, to recover metal sulfides. Soon the process was extended to a wide number of minerals including non-sulfide minerals. Today, it is responsible for recovering different types of metallic and non metallic minerals and has wide applications in a number of areas other than minerals processing [16]. These include technologies such as deinking, oil recovery, and waste water treatment [16].

The process of flotation critically relies on the successful attachment of the mineral particle to the bubble surface [4]. However due to the complex nature of the bubble-particle interaction the process is extremely difficult to model. Some models were developed by considering only the hydrodynamic parameters involved in flotation [2,3]. Such models do not describe flotation behavior adequately since they completely ignore the role played by surface chemistry parameters [4,5].

Derjaguin and Dukhin [6] were probably the first to consider the role of surface forces in bubble-particle interactions. They suggested that a particle should pass through three distinct zones, i.e., hydrodynamic, diffusio-phoretic and wetting zones, before bubble-particle attachment can occur. Once the particle is in the wetting zone, three different surface forces, namely, the van der Waals force, the double layer force and the structural forces dictate its attachment to the bubble surface. Derjaguin and Dukhin [6] originally believed that the structural force was hydrophilic in origin and had to become zero for successful bubble-particle attachment. However, recent advances made in the field of surface force measurements clearly suggest that it is the attractive hydrophobic force rather than the disappearance of the repulsive hydrophilic force that actually drives bubble particle interactions.

The earliest evidence for the existence of the hydrophobic force was probably given by Blake and Kitchner [7], who conducted film thickness measurements between a gas bubble and a methylated silica surface in aqueous solutions. They showed that for a bubble-particle interaction both the double layer and the van der Waals forces are repulsive, in which case the intervening liquid film should be stable at all separation distances. On the contrary, film rupture occurred at distances greater than 60 nm. Blake and Kitchener [7] suggested therefore, that an additional attractive force may be at play. They considered that the additional attractive force may be due to the perturbation of water molecules adjacent to the hydrophobic surface. Over the years, this additional attractive force has been recognized as the hydrophobic force.

Hydrophobic forces were first measured by Israelachvili and Pashley [8] between cylindrical mica sheets in 1×10^{-5} M CTAB solutions. They found that the measured attractive force was an order of magnitude higher than that predicted by the van der Waals force based on

continuum theory. Over the years, the hydrophobic force has been measured for a diverse number of systems. However, it is only in the last ten years that its role in flotation been accurately quantified.

Perhaps the first measurement that related hydrophobic forces to flotation was done by Rutland et al [17] who conducted force measurements between mica surfaces in solutions of a hydrolyzable surfactant such as dodecylammonium hydrogenchloride (DAHCl). These measurements were conducted as a function of pH. Rutland et al [14] observed long range hydrophobic forces in alkaline solutions (pH 8-9) of 10^{-4} M DAHCl; however no changes in decay length were reported. These authors attributed the presence of long range hydrophobic force to the coadsorption of neutral amines (DA) along with the dodecylammonium ions (DAH^+). This suggestion is consistent with the work of Gaudin and Fuerstenau [18] who showed that the flotation recovery of quartz reaches a maximum at this pH where DAHCl hydrolyzes to form DA.

In the last decade or so the Center for Coal and Minerals Processing (CCMP) at Virginia Tech has pioneered in the study of hydrophobic forces in flotation. Yoon and Ravishankar [19-21] conducted force measurements between cylindrical mica sheets in solutions of DAHCl. Their work can be divided into two parts. In the *first* part, force measurements were conducted in DAHCl solutions at pH 5.7 in the presence of neutral surfactants such as octanol or dodecanol. Addition of neutral surfactants was found to increase the magnitude of the hydrophobic force. Furthermore, the magnitude of hydrophobic forces measured in the presence of dodecanol were higher than those measured with the addition of octanol. Yoon and Ravishankar [19,20] attributed the increase in the magnitude of the force to the formation of a well-ordered compact layer of hydrocarbon chains formed due to the addition of neutral molecules. Furthermore, their results are in good agreement with the results reported by Smith [22] who found that the contact angle exhibited by quartz in amine solutions substantially increased with the addition of dodecanol. In the *second* part of their work, Yoon and Ravishankar [20] conducted force measurements in DAHCl solutions alone as a function of pH. The decay lengths of the measured hydrophobic forces could be related to the flotation behavior of quartz. A significant difference between the work of Yoon and Ravishankar [18] and those of Rutland et al [17] is the

concentration of DAHCl employed. Yoon and Ravishankar conducted their force measurements using DAHCl solutions in a range of concentrations ($=10^{-7}$ to 5×10^{-6} M) while Rutland et al [17] used a fixed concentration of 10^{-4} M. This is significant because the concentration of amine used by Rutland et al [17] is higher than the p.c.r ($=10^{-5}$ M) for mica, where DAH^+ ions are known to form flip flop layers. As a result, the hydrophobic forces measured by Rutland et al [17] were significantly weaker than those measured by Yoon and Ravishankar [19-21]. Furthermore, the concentration of DAHCl used by Yoon and Ravishankar [19,20] is also more realistic when compared to what is commonly employed in the industrial flotation circuits.

One of the drawbacks of all the measurements cited above is that they were conducted between two symmetrical solid surfaces. Therefore, the measurement essentially represented particle-particle interactions and not bubble-particle interactions. To study the surface forces relevant to flotation, it would be ideal to conduct force measurements between an air bubble and a mineral surface. However, AFM force measurements conducted using a bubble and a particle so far have been quite controversial. In some cases the results reported are not consistent with flotation literature. For example, Ducker et al [9] used an AFM to conduct force measurements between air bubble and hydrophilic silica sphere and observed net attractive forces. In fact, the magnitude of the attractive force was greater than that measured between OTS-coated silica and an air bubble in water. Such a result would suggest that hydrophilic particles are naturally floatable, which is contrary to flotation practice. Similarly, Butt [10] conducted force measurements between an air bubble and a particle. Contrary to Ducker et al's [9] results, he showed that the interaction forces between an air bubble and a hydrophilic silica particle in water are net repulsive. However, some of the results reported by Butt cast severe doubts on the efficacy of the technique itself. For example, force measurements conducted between a water droplet and a hydrophobic particle in air showed the presence of a long-range attractive force!

More recently, Fielden et al [11] and Preuss and Butt [12] have revisited the topic of force measurements between a bubble and a particle. While Preuss and Butt [12] showed a net attractive force between a hydrophobic particle and an air bubble, Fielden et al [11] showed a net repulsive force for the same system. In short, none of the above mentioned works can claim to represent the bubble-particle interactions occurring during flotation. It is also not clear as to why

these measurements should show such discrepancies. It is possible that at least some of the error might lie in the fact that the actual separation distance between the bubble surface and the particle is masked by the deformation of the bubble surface resulting in erroneous force vs. distance curves.

In order to alleviate the problems associated with using an actual bubble, surface force measurements were conducted at CCMP using a hydrophobic glass sphere as a simulated bubble [13]. The underlying assumption here was that an air bubble is inherently hydrophobic [23-25]. Recently, Yoon and Aksoy [25] have shown that the hydrophobic force between air/water interfaces in surfactant solutions increases with decreasing concentration of the surfactant. Furthermore, recent spectroscopic studies show that the orientation of water molecules adjacent to a silanated solid/water interface is identical to those at water/vapor interface [26].

Using the above mentioned approach, Flinn [13] conducted force measurements between a hydrophobic glass sphere and a hydrophilic silica plate in 4×10^{-5} M DAHCl solutions as a function of pH. He observed that the magnitude of the hydrophobic force, as represented by the hydrophobic force constant K , varied as a function of pH. Figure 1.1 shows the K values obtained by Flinn [13] plotted as a function of pH. Also shown in Figure 1.1 is the flotation recovery of quartz as a function of pH [27]. As seen, the changes in K can be readily related to the flotation behavior of quartz. Note that the strongest K values observed by Flinn [13] corresponds to the pH at which the flotation recovery of quartz reaches a maximum. In other words, the assumption that a hydrophobic glass sphere may simulate air bubbles during flotation is perfectly justified. More recently, a similar approach was also used by Nalkowski et al [28] to conduct force measurements between a polyethylene sphere ($\theta=110^\circ$) and a colemanite surface. The force data were found to be in good agreement with the colemanite flotation data.

Until now, almost all the force measurements conducted related to flotation have been done using oxide mineral surfaces while very little work has been done using sulfide minerals. Among the sulfides only sphalerite (ZnS) has been studied extensively using force measurements, but such studies were not conducted from a strictly flotation perspective [29-31]. This is rather unfortunate since the sulfide ores are the largest group of ores treated by the

flotation process. Approximately 225 million metric tons of sulfide ores are treated annually [32]. Therefore, a fundamental study regarding the flotation behavior of sulfides is warranted.

Collector adsorption on sulfides are very different when compared to oxide minerals. The collectors used for sulfide flotation go by the generic name of thiol (sulfhydryl) collectors. Roughly about 70% of the thiol collectors used belong to the family of xanthates [33]. The commercial xanthates used are alkali metal salts (e.g., ROCSSNa) of the monoalkyl esters of dithiocarbonic acid. It is now well established that the interaction between sulfide minerals and thiol collectors take place by a corrosion type mixed potential mechanism [34,35]. According to this mechanism the process rendering the surface hydrophobic is an anodic reaction that transfers electrons from the collector to the mineral. These electrons are returned to the solution phase by a cathodic reaction such as the reduction of oxygen:



The corresponding anodic reactions can form a number of different oxidation products of the collector at the mineral surface such as:

1) Chemisorption of the thiol ion (X^-)



2) Oxidation of the thiol ion to corresponding dithiolate:



3) Reaction of the thiol with the mineral to form metal thiol compound:



Two important aspects need to be stressed. *One*, all the xanthate oxidation products produced as a result of Eqs. [2] to [4] render the surface hydrophobic [34-36]. *Two*, all the above reaction mechanisms suggest that thiol adsorption is an electrochemical reaction. Therefore, there exists a unique thermodynamic equilibrium potential value for each reaction. An anodic process can occur only if the potential across the solid-solution interface is higher than the reversible

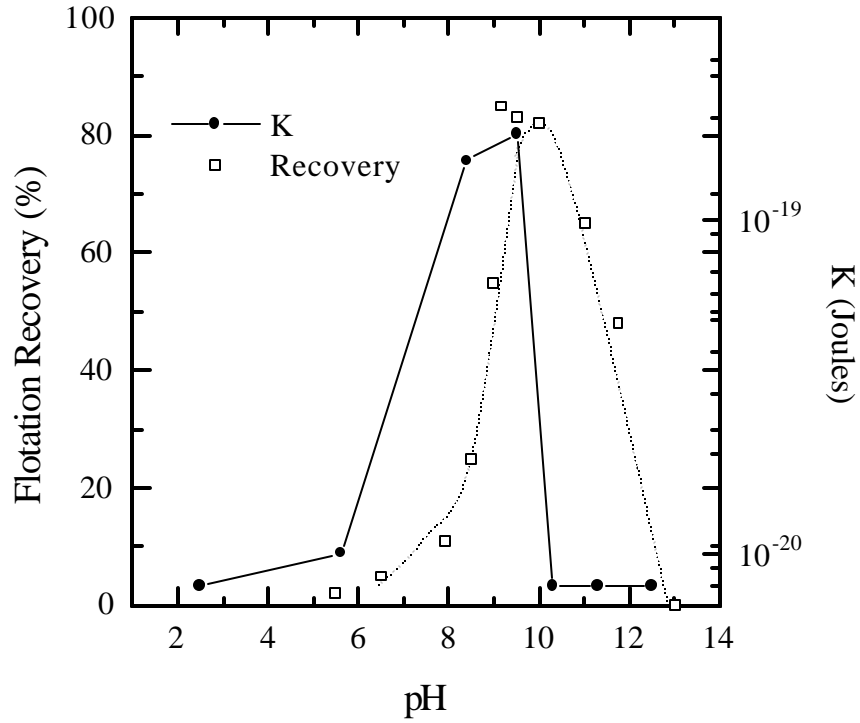


Figure 1.1. The hydrophobic force constant (K) obtained for the interaction of a hydrophobic glass sphere ($\theta=109^\circ$) and a hydrophilic silica plate in 4×10^{-5} M DAHCl solutions, plotted as a function of pH [13]. Also shown for comparison is the flotation recovery () of quartz as a function of pH [27].

potential value. This is probably the most significant difference between oxide collector adsorption and sulfide collector adsorption, i.e., for sulfides, collector adsorption is critically dependent on the electrochemical potential across the solid/solution interface.

1.2 (b) DLVO Theory

The classical DLVO theory named after its proponents Derjaguin, Landau, Verwey and Overbeek was proposed in the 1940s to primarily explain colloidal stability [37,38]. The DLVO theory states that the total force of interaction (F) between two particles suspended in aqueous media is given by:

$$F = F_e + F_d \quad [5]$$

where F_e is the ion electrostatic force and F_d is the London van der Waals force.

For the interaction of a sphere and a flat surface F_e is given by:

$$F_e \approx 4\pi R \epsilon \epsilon_0 \kappa \psi_0^2 e^{-\kappa H} \quad [6]$$

where ϵ is the dielectric constant of the medium, ϵ_0 is the permittivity of free space, κ is the reciprocal of the Debye length, ψ_0 is the surface potential of the interacting surfaces, R is the radius of the sphere and H is the separation distance [39]. Note that Eq.[6] is only an approximation and is recommended only for surfaces with low potentials (i.e., $\psi_0 \leq 25$ mV).

A similar expression for F_d is given by:

$$F_d = -\frac{AR}{6H^2} \quad [7]$$

where A is a constant called the Hamaker constant and is an intrinsic property of the material and the intervening medium [39]. The Hamaker constant (A) is always positive in magnitude for two identical bodies interacting across any medium. However for dissimilar surfaces the value of A

may take negative values depending on the refractive indices of the interacting bodies and the medium. For example, for the interaction of a bubble and a particle in aqueous media the value of A is actually negative suggesting that the van der Waals forces are net repulsive [40].

Figure 1.2 shows a schematic representation of the interaction between two surfaces in a polar liquid based on the DLVO theory. As it can be seen, at small separation distances (H), the dispersion force dominates, whereas, at larger separations, the double layer repulsion dominates. The net interaction gives rise to an energy barrier (E_1), which needs to be overcome before the two surfaces can come into primary adhesive contact.

1.2 (c) Measurement of Surface Forces

The earliest surface force measurements were conducted by Derjaguin and Abrikosovva [41] in 1954 who measured the van der Waals attraction between a flat quartz plate and a spherical quartz cap in air and in vacuum. Separation between the surfaces (H) was monitored optically by Newton's rings using monochromatic light. Though these techniques could detect forces with a lot of precision, separation distances could be measured only up to ~ 100 nm. Soon the development of a new instrument by Tabor and Winterton allowed forces to be measured at separation distances less than 100 nm [42]. These investigators measured the van der Waals force between mica sheets in air. The important technical advances made by these investigators include: (i) use of cleaved muscovite sheets glued to glass half cylinders, thereby eliminating problems caused by roughness of the surfaces encountered by previous researchers, (ii) use of Fringes of Equal Chromatic Order (FECO) to detect separations with much greater accuracy (~ 0.8 nm), and (iii) using a piezoelectric crystal to control surface separation. The changes incorporated by Tabor and Winterton [42] are being used largely unchanged even to this day.

Direct measurements to investigate the DLVO theory were first conducted by Derjaguin and co-workers [43] who used an apparatus similar to the one used by Derjaguin and Abrikosova [41]. This modified apparatus was used to measure the forces between two crossed platinum wires in salt solutions. In 1978 Israelachvili and Adams [44] published a landmark manuscript dealing with force measurements between mica surfaces in solutions. Good

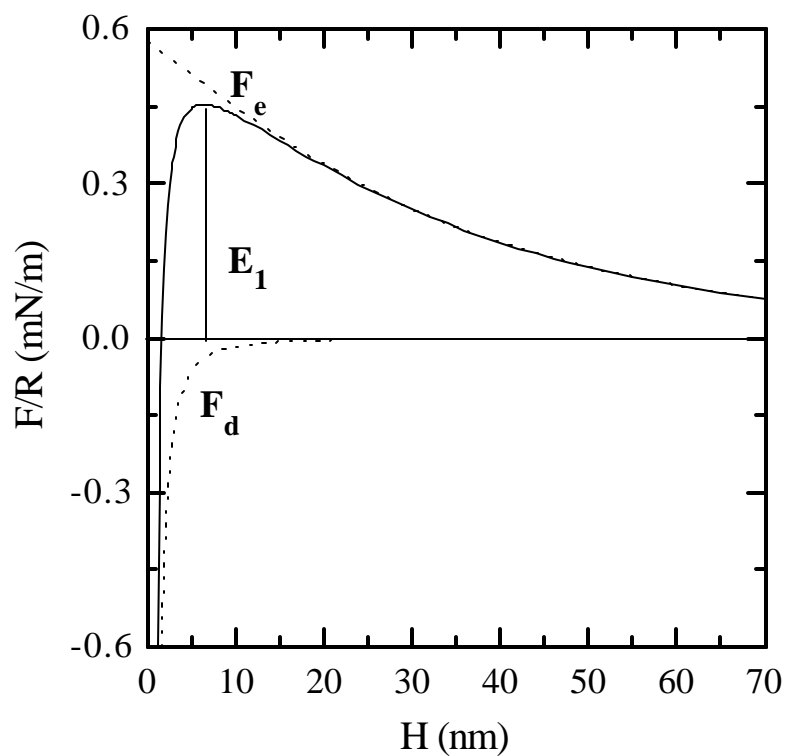


Figure 1.2. A typical DLVO force curve. The upper dotted force curve represents the double layer force curve (F_e) and the lower dotted curve represents the van der Waals force (F_d). The solid line represents the total force of interaction (F), which according to the DLVO theory, is an algebraic sum of F_e and F_d .

agreement with the DLVO theory was found down to a separation distance of few nanometers. Below this separation an additional repulsive force was observed which was ascribed to either steric interactions or the hydration force. The apparatus used by these investigators was similar to the one used by Tabor and Winterton [42] for the measurement of van der Waals forces. However, several modifications were introduced, most notably the use of a tubular piezoelectric crystal. This apparatus has come to be known as the Surface Forces Apparatus (SFA) and has served as a very important tool for measuring surface forces between colloidal particles for the past twenty years.

The apparatus used for force measurements in the present work is of a relatively newer origin and is called the Atomic Force Microscope (AFM). The AFM was invented by Binnig et al [45] and was designed originally to image the topography of surfaces with atomic resolution. Figure 1.3 (A) shows a schematic representation of its working principle. A pyramidal tip (a), attached at the end of the cantilever spring (b), is placed over a sample (c) to be examined. The sample is scanned in x- and y-directions by means of a Piezo-electric crystal, while the pyramidal tip remains stationary. As the tip moves over the ‘mountains’ and ‘valleys’ of the surface, the pyramidal tip (and the cantilever spring) is deflected by the forces between the atom at the end of the tip and those on the surface. The cantilever deflection is monitored by the laser beam, which is emitted from a source (e), deflected off the cantilever, and enters a detector (f). The cantilever deflection gives the z-coordinate of the pyramidal tip, which is used to obtain, in conjunction with the x- and y-coordinates of the sample, a 3-D map of the surface. If the surface is molecularly smooth, it is possible to see the atoms of the surface.

Over the years the AFM has been successfully converted into a force measuring device. Initial force measurements conducted using the AFM were between the cantilever tip and a flat substrate [46,47]. Unfortunately, since the geometry of the tip was not known, comparison with theory proved difficult. This drawback was soon overcome by Ducker et al [48,49] who glued a sphere of known radius R , to the cantilever as shown in Figure 1.2 (B). As a flat plate, placed on top of the Piezo-crystal, moves toward the sphere in the z-direction, the cantilever may deflect

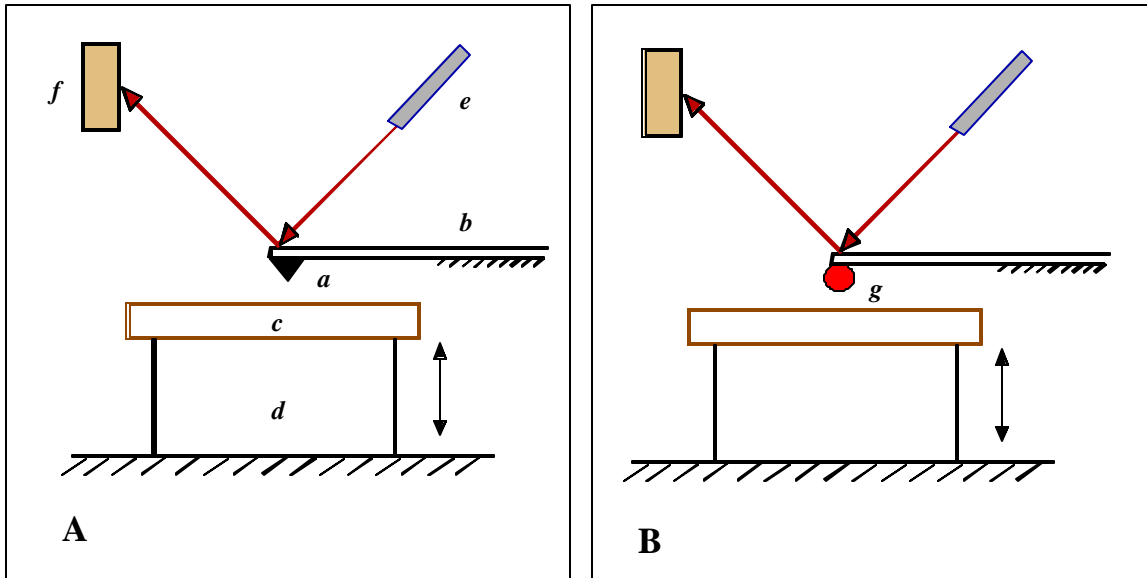


Figure 1.3. A) A schematic representation of the working principle of the atomic force microscope (AFM) used for surface force measurements: a) pyramidal tip; b) cantilever; c) mineral plate; d) piezo-electric crystal; e) laser source; f) photo diode. The measurement is conducted in aqueous solutions. B) A modified AFM used for force measurements by attaching a colloidal sphere (g) to the cantilever (b).

depending on the surface forces acting between the sphere and the plate. From the cantilever deflection and the piezo movement, one can determine: i) the closest distance (H) between the two surfaces, and ii) the surface force (F) if the spring constant of the cantilever is known.

The advantage of using the AFM for force measurements is that it does not use optical interferometry to determine the surface separation distances (unlike the SFA). Hence the substrates used are not restricted to transparent materials only. As a result the AFM has been successfully used for force measurements for a variety of surfaces. These include gold [50], alumina [51], rutile [52], sphalerite [29], silica [48], iron oxide [53], zirconia [54], and polymer surfaces [55,56]. However the AFM has two distinct disadvantages as compared to the SFA. These include: i) the zero separation distance between the two surfaces cannot be determined absolutely, and ii) the adhesion force cannot be measured reliably due to the torsion of the springs before separation [57].

1.2 (d) Hydrophobic Forces

The advent of sophisticated techniques to measure colloidal forces has aided in the discovery of a number of surface forces that were not accounted for in the original DLVO theory. These include the hydration force [58], hydrophobic force [11], depletion force [59], solvent mediated oscillatory force [60], steric repulsion forces [61] and ion correlation forces [62]. In the present work, the entire focus will be on the hydrophobic force (F_h). As mentioned earlier the hydrophobic force is the driving force for bubble-particle interactions occurring during flotation.

Apart from its central importance in flotation, the hydrophobic force is crucial to a wide range of phenomena, such as wetting [63], adhesion [64] and interactions of biological membranes [65]. Consequently understanding the nature of the hydrophobic force is currently the subject of much experimental and theoretical interest.

Finally it needs to be mentioned that when hydrophobic forces are measured it is often necessary to extend Eq. [5] so that:

$$F = F_e + F_d + F_h \quad [8]$$

where F_h refers to the hydrophobic forces. Eq.[8] is often referred to as the extended DLVO theory. As we shall see there are a number of convenient mathematical representations that can be used to represent F_h .

1.2 (e) Direct Measurement of Hydrophobic Forces

In the early 1980s, Israelachvili and Pashley [8,66] conducted direct measurements of forces (using a SFA) between macroscopic hydrophobic surfaces in aqueous solutions and observed the existence of attractive forces much stronger than those expected from van der Waals attraction. The surfaces used were cylindrical mica sheets, which were rendered hydrophobic by equilibrium adsorption of cetyltrimethylammonium bromide (CTAB). The surfaces exhibited an advancing contact angle $\theta_a=64^\circ$. It was noted that the hydrophobic force could be represented by a single exponential function such as:

$$F_h = C_0 \exp\left(\frac{-H}{D_0}\right) \quad [9]$$

where F_h represents the hydrophobic force, R is the radius of curvature of the interacting bodies, C_0 is a preexponential factor, H is the separation between the mica surfaces and D_0 is referred to as the decay length. The hydrophobic force observed between CTAB monolayers on mica could be represented by Eq.[9] using $C_0 = -140$ mN/m and $D_0 = 1.0$ nm. Israelachvili and Pashley [8] also found that this hydrophobic attraction was quite insensitive to changes in electrolyte addition, temperature and pH.

It needs to be noted that subsequent experiments conducted by Pashley et al [67] and Kekicheff et al [68] have shown that the contact angle of pure CTAB monolayers on mica is over 90° . It seems likely that the CTAB used in the original experiments was contaminated. Nevertheless, the original experiments conducted by Israelachvili and Pashley [8] are very

significant since they were the first to give a qualitative indication to the interactions expected between macroscopic hydrophobic surfaces across thin films.

One of the initial causes for skepticism regarding the results of Israelachvili and Pashley [11, 66] was the suggestion that the attractive force may be due to a bridging of the surfaces by surfactant molecules [69]. In order to resolve this issue Claesson et al [70] prepared hydrophobic surfaces by Langmuir-Blodgett deposition of dioctadecyldimethylammonium bromide (DDOABr) on mica. Surfaces thus prepared were weakly charged, formed a closed packed monolayer of DDOA and exhibited θ_h of 94°. The force measurements revealed the presence of a strong attractive force suggesting that the hydrophobic force was for real and not just an artifact. However, a representation in a form such as Eq. [9] was found to be inadequate; therefore a double exponential function such as:

$$\frac{F_h}{R} = C_1 \exp\left(\frac{-H}{D_1}\right) + C_2 \exp\left(\frac{-H}{D_2}\right) \quad [10]$$

was used to fit the observed hydrophobic force data. The values of the parameters used were, $C_1 = -360$ mN/m, $D_1 = 1.2$ nm, $C_2 = 6.6$ mN/m and $D_2 = 5.5$ nm. Note that the larger decay length (D_2) in this case is stronger than the D_0 values ($=1.0$ mN/m) reported by Israelachvili and Pashley. Christenson and Claesson [71] subsequently conducted force measurements using neutral LB deposited monolayers of hydrocarbon and fluorocarbon surfactants on mica. The attraction was now discernible at separation distances of ~ 70 nm with hydrocarbon surfactants and ~ 90 nm with fluorocarbon surfactants. The corresponding D_2 values required to fit the hydrophobic force data were 12 and 15 nm respectively.

Another popular mathematical representation for the hydrophobic force is the power law [72-75]. Some authors suggest that the force can be better described by a force law such as:

$$F_h = \frac{-KR}{6H^2} \quad [11]$$

where K is a constant. The advantage of using a power law is that it requires only one parameter that needs to be fitted and the value of K can be directly compared to the Hamaker constant A .

Over the past few years a variety of methods have been used to form hydrophobic surfaces. These include (i) equilibrium adsorption of soluble cationic surfactants on negatively charged surfaces [11,66], (ii) equilibrium adsorption of surfactants from non aqueous solvents onto mica [76-78], (iii) LB deposition of insoluble double chain surfactants on mica [70,71], (iv) chemical modification of surfaces by reacting with silanating agents [74,79], and (v) the use of bulk polymer surfaces or thin polymer films [55,80].

The measurement of hydrophobic forces has now become a routine affair. Yet the field is one filled with controversies and conflicting opinions. In what follows a brief description of the currently debated issues regarding the hydrophobic force have been summarized.

(a) Effect of Surface Preparation

Does the method of preparation of a surface affect the magnitude of the hydrophobic force? Earlier force measurements seemed to suggest that the magnitude of the force is directly related to the method of preparation of the surface [8,66]. It was generally accepted that equilibrium adsorption of surfactants from solution gives rise to forces with a range of less than 30 nm [8]. Surfaces prepared by LB deposition give rise to forces extending up to 90 nm [70]. Chemically modified surfaces give rise to similarly long range forces [74], while polymer surfaces exhibit either no hydrophobic force or at best a weak attractive force discernible at distances less than 20 nm [54,55].

However, such a notion was dispelled by the results of Kekicheff and Spalla [81] who found that equilibrium adsorption of CTAB on glass surfaces can result in extremely long range attractive forces. These results have been verified by Craig et al [82,83] and their measurements suggest that the hydrophobic force ($D_2=45\text{nm}$) exhibited can be as large as that produced by any other method of surface preparation. However, it needs to be mentioned that earlier measurements for the same system showed only a weak attractive force 2-3 times stronger than the van der Waals force [84]. It is not clear why the magnitude of the force has suddenly increased by a few orders of magnitude within a few years.

(b) Effect of Electrolyte Addition

As mentioned earlier, Israelachvili and Pashley [8] in their very first measurements noted that the magnitude of the hydrophobic force was independent of electrolyte concentration and temperature. Christenson et al [85] after a reanalysis of previous work, using L-B deposited monolayers, concluded that the magnitude of the attraction was reduced, but the exponential decay of the long-range attraction was not substantially reduced even after the addition of electrolyte concentrations up to 0.01M. On the other hand, the work of Tsao et al [77] suggested that electrolyte addition decreases both the magnitude and the range of the attraction. These authors conducted force measurements between double chain surfactant monolayers (DDOA) adsorbed on to mica from an organic solvent. The measured force was strongly dependent upon electrolyte concentration. The effect of 2:2 electrolyte was found to be larger than that of 1:1 electrolyte, but no simple correlation with the Debye length was found.

An important aspect that needs to be addressed is the effect that the addition of electrolyte has on the stability of the hydrophobic surface. Thus, increasing salt concentrations may lead to a reduction in attraction due to direct effects on the hydrophobic surfaces, rather than the screening of an electrostatic force. Such effects may be particularly true for surfaces rendered hydrophobic by equilibrium adsorption of surfactants. For example addition of 0.1M salt typically lowers the critical micelle concentration of an ionic surfactant by approximately an order of magnitude [82]. Therefore, the surfactant concentration at which a hydrophobic monolayer is formed on a surface (say silica) may also be expected to be reduced by an order of magnitude. Similarly, addition of high concentrations of salt may also raise the Krafft temperature well above the room temperature resulting in precipitation of the ionic surfactant [82]. Therefore, any results claiming an effect of electrolyte using surfaces rendered hydrophobic by ionic surfactants should be treated with caution.

In the opinion of this author, the only way to avoid ambiguity is to use surfaces that are inert to electrolyte. An investigation of the hydrophobic attraction between polypropylene surfaces and chemically fluorinated glass surfaces, which are inert to electrolyte, suggests that

the interaction is independent of salt concentration [55,86]. In fact for the case of chemically fluorinated surfaces addition of 5 M NaCl was found to actually increase the range of the attraction!

(c) Hydrophobic Effect and the Hydrophobic Force

Is there a connection between the hydrophobic effect observed between nonpolar solute molecules and the hydrophobic interaction between macroscopic surfaces? There are two schools of thought on this matter. The first line of argument is by Israelachvili and coworkers [8,66] who argue that the hydrophobic effect and the hydrophobic force are indeed related. In fact in their very first measurements of the hydrophobic force, these authors showed that the free energy of interaction obtained for the CTAB covered monolayers was comparable to the free energy of dimerization of non polar molecules such as methane, cyclohexane and benzene [8].

The second line of argument is the one proposed by Christenson [69] who emphatically denies any such relation. Christenson [69] argues that the thermodynamics involved with a non polar solute and that of a macroscopic hydrophobic surface are completely different. His line of defense begins by considering the free energy change (ΔG) for a system

$$\Delta G = \Delta H - T\Delta S \quad [12]$$

where ΔH and ΔS represent the change in enthalpy and entropy respectively. According to Christenson [69], the enthalpy of transfer of a non polar solute molecule from bulk to water is negative. This is due to the formation of additional hydrogen bonds around the solute resulting in cagelike dynamic structures or “clathrates” of water [87,88]. However, the change in entropy term (ΔS) is also negative resulting in an unfavorable contribution to the free energy. At normal temperatures the entropy term dominates, resulting in a positive free energy of transfer, which leads to the low solubility of non polar molecules in water. With increase in temperature, the solubility of non polar molecules in water actually decreases. On the other hand, for a macroscopic hydrophobic surface the absence of clathrate formation and a lack of hydrogen bonding result in positive values for both ΔH and ΔS respectively. Therefore, with increase in

temperature, the interfacial energy across a hydrophobic solid/liquid interface actually decreases. In other words the energetics involved with a non polar solute molecule and that of a macroscopic hydrophobic surface in water are completely different.

(d) Contact angle and Hydrophobic Force

Earlier measurements suggested that the macroscopic hydrophobicity of a surface (as measured by the contact angle θ) and the magnitude of the hydrophobic force are uniquely related [11,66]. The work of Yoon and Ravishankar [19,20] should be specially addressed in this regard. These investigators conducted force measurements between mica surfaces in dodecylammonium hydrogen chloride (DAHCl) solutions containing neutral surfactants such as octanol or dodecanol. Figure 1.4 shows a plot taken from the work of Yoon and Ravishankar [19,20] where the D_2 values obtained from their study along with the D_0 and D_2 values obtained by various investigators are plotted as a function of the advancing contact angle (θ_a). According to Figure 1.4: i) short range hydrophobic forces ($D_2 < 3$ nm) are observed only between surfaces that exhibit $\theta_a < 90^\circ$, ii) long range hydrophobic forces ($D_2 > 10$ nm) are observed only between surfaces that exhibit $\theta_a > 90^\circ$, and iii) the magnitude of the hydrophobic force sharply increases around $\theta_a = 90^\circ$ suggesting a transition from short ranged to long ranged attraction. In essence Yoon and Ravishankar argued that the magnitude of the hydrophobic force was critically dependent on the θ_a exhibited by a surface.

However the idea that the water contact angle exhibited by a surface can be related to the magnitude of the hydrophobic force is not universally agreed. For example, Woods and Sharma [89] conducted force measurements between polymerized octadecyltriethoxysilane (OTE) coated mica surfaces ($\theta_a \sim 111^\circ$) and found only a short range attractive force. By the same token, forces of interaction between bulk hydrophobic polymer surfaces such as polystyrene ($\theta_a = 109^\circ$) [90], polypropylene ($\theta_a = 103^\circ$) [55] or teflon [76] do not show a long range attraction. In this regard, the work of Kurihara and Kunitake [91], who conducted force measurements between LB deposited polymeric ammonium amphipile on mica, needs to be mentioned. These authors found that when the amphipile was deposited in the down stroke mode the surface exhibited $\theta_a = 94^\circ$ and the hydrophobic force ($D_2 = 72$ mN/m) was net attractive and discernible at separation

distances (H) of 300 nm. However, when they deposited the same amphipile in the up stroke mode, the θ increased to 105° , no attractive forces were measured and the surfaces jumped into primary contact at separation distances of approximately 24 nm. In other words, for the same system, as θ increased, the magnitude of the hydrophobic force was found to decrease.

(e) Origin of the Hydrophobic Force

Perhaps the most intensively debated aspect of the hydrophobic force is its molecular origin. Although a diverse number of mechanisms have been suggested so far, none of them have gained universal acceptance. Since experimental observations made so far are fraught with uncertainty, numerous contradictions to the predictions of a particular model can easily be found. The sections described below give a brief explanation of the mechanisms proposed thus far.

(i) Water Structural Effects

As mentioned earlier Blake and Kitchener [7] originally suggested that the long range attraction was due to the perturbed structure of the water molecules adjacent to the hydrophobic surface. This explanation was based on an earlier finding by Laskowski and Kitchener [92] that the film adjacent to a hydrophobic surface is unstable due to a deficiency in hydrogen bonding with the surface. More recently, Eriksson et al [93] proposed a phenomenological model that the hydrophobic force originates from the hydrogen-bond-propagated ordering effects in the water layer between two hydrophobic surfaces. Their model is based on the square gradient approximation used by Marcelja and Radic [94] for the treatment of repulsive hydration forces. Besseling [95] suggested that the hydrophobic surface may alter the local density of water molecules in the adjacent layers and this may lead to an attractive force. Ruckenstein [96,97] considered that fluctuating gaps generated by thermal perturbations between a hydrophobic solid and water may be responsible for the long-range hydrophobic attraction. However, computer simulations and refractive index measurements seem to show that there is hardly an extended variation in the water structure adjacent to hydrophobic surfaces [98,99]. Water seems to attain its bulk structure within a few molecular layers. Hence it is inconceivable that a long range force extending several hundred nanometers could emerge due to water structuring effects.

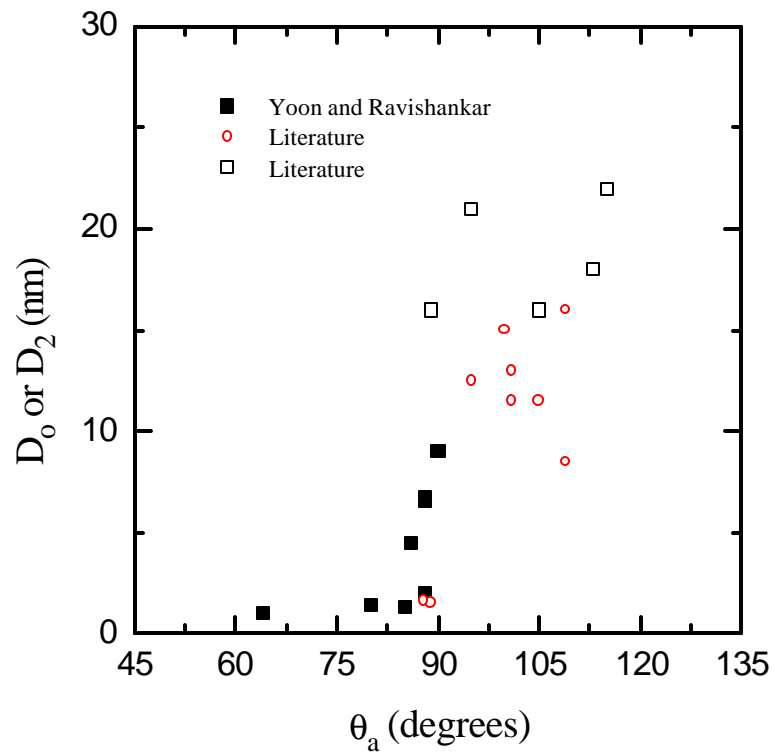


Figure 1.4. A decay length (D_0 or D_2) vs advancing contact angle (θ_a) plot taken from the work of Yoon and Ravishankar [19,20].

(ii) *Metastability of the film*

It is well known that an aqueous film adjacent to a hydrophobic surface is metastable, i.e., it is in a state ready to undergo a phase transition. It can be readily shown that for a surface exhibiting $\theta > 90^\circ$ the line tension becomes negative, i.e.,

$$g_{SV} - g_{SL} < 0 \quad [13]$$

i.e., it becomes thermodynamically favorable to replace the solid/liquid interface by the solid/vapor interface. Yuschenko et al [100] have theoretically shown that the formation of a vapor cavity can result in long range attraction. Cavitation has also been investigated between surfaces in a poorly wetting liquid using Monte Carlo simulations [101]. The results predict a monotonically increasing attractive force. Furthermore, cavitation has either been observed directly [102,103] or inferred [104] between hydrophobic surfaces, but the precise conditions under which cavities form vary. In some cases cavitation occurs only after the separation of the hydrophobic surfaces from contact [103], in some cases it occurs at contact [103] and in one particular case it was shown to occur before contact [86]. Also the size and shape of the cavities observed directly have been shown to be consistent with predictions from the Laplace equation [103]. However, the formation of cavities requires a large activation energy that needs to be overcome, especially at large separation distances [100].

In some cases no cavitation has been observed, yet the measured forces are long ranged [104]. This has led some authors to suggest that although macroscopic cavitation may not occur, however submicroscopic cavitation or subcritical density fluctuations due to thermal fluctuations of the intermolecular voids can still occur and result in a long range attractive force [105,106]. Yoon and Ravishankar [20] calculated the attractive force due to subcritical fluctuations and concluded that an upper bound for such attraction is at most an order of magnitude larger than the van der Waals force. Hence this mechanism clearly cannot account for the long range attraction discernible at separation distances of 300 nm [91].

(iii) Electrostatic mechanisms for the hydrophobic force

Electrostatic mechanisms are capable of giving rise to forces of the range measured for the hydrophobic attraction. Attard [107] suggested that perturbations involved with the aqueous film adjacent to a hydrophobic surface results in large density fluctuations. This may result in an anomalous electrostatic response that may correlate with that of an opposing surface to result in a long range attraction. A similar mechanism using an electrostatic origin was proposed by Podgornik [108], who suggested that the lateral mobility of adsorbed counter ions induces large fluctuating electric fields that may correlate to produce a long range attraction.

Tsao et al [76,78] suggested that domain formation of ordered hydrocarbon chains plays a crucial role in the origin of the hydrophobic force. These authors suggested that well ordered hydrocarbon chains with a tilt in their molecular axis generate large in-plane dipole moments. The correlation of the in plane dipole moments between two surfaces results in a long range attractive force. These authors found that the long range attractive forces between DDOA coated mica surfaces reduced when the surfactants lost their crystallinity and assumed a fluid like state.

There are a number of experimental observations that seem to support the theory proposed by Tsao et al [76,78]. Rabinovich et al [109] quantitatively compared the ordering parameter (S) of DDOA coated silicon crystal surfaces and found that the magnitude of the hydrophobic force indeed increased with the ordering of DDOA on the surface. Flinn et al [110] studied the adsorption of octadecyltrichlorosilane (OTS) on silica. These authors found that i) OTS adsorbs in the form of patches or domains, and ii) as the q_1 exhibited by a surface increased so did the adsorption density of OTS within the domain. For silanated surfaces exhibiting $q_1 > 100^\circ$ it was found that the hydrocarbon chains within a patch/domain were well ordered and vertically oriented thereby exposing their terminal methyl groups to the aqueous solution.

Rabinovich et al [109] have suggested that the formation of domains may cause structural changes in the adjacent water molecules. As a result, the water molecules may be unidirectionally oriented. Molecular simulation studies indeed do show that the water molecules adjacent to a hydrophobic surface are oriented in a parallel fashion [98,111]. Such orientations

could result in large dipole moments [112,113]; the magnitude of which would be related to the packing density and the size of the surfactant domains [15]. Rabinovich et al [109] suggested that the correlation of such large dipoles between two approaching surfaces may result in long range attraction.

An important test of theories that invoke electrostatic mechanisms is the relationship between the measured force profile and the electrolyte concentration. The addition of electrolyte is expected to reduce the range of the interaction. Since the effect of electrolyte addition on the magnitude of the force is quite ambiguous, electrostatic mechanisms proposed thus far suffer from the same level of ambiguity.

(iv) Other Mechanisms

There are a number of other mechanisms that have been suggested which cannot be included in any of the earlier categories. Carambassis et al [114] suggested that the hydrophobic surface may actually capture a bubble which might then act as a bridge between the two surfaces resulting in long range attraction. This is based on the assumption that hydrophobic surfaces may anchor dissolved air bubbles more readily than, say, hydrophilic surfaces. According to this mechanism, different experimental runs should capture bubbles of different radii, resulting in varying ranges of attraction for a given experimental condition. However most of the experimental data presented in literature suggest that the results of hydrophobic force measurements are well reproducible for a given experimental condition.

A closely related mechanism is one that suggests that dissolved gases in water may nucleate to result in a long range attractive force [115]. However, recent force measurements by Craig et al [85] suggests that although deaerating the water reduces the magnitude of the force slightly, still the attraction remains sufficiently long ranged.

Finally, Yaminsky et al [116,117] proposed that the adsorption-desorption equilibrium of surfactants may result in long range attraction. While such a mechanism may occur for equilibrium adsorption of surfactants, it is quite difficult to conceive how it can apply for LB

deposited monolayers or chemically modified silane surfaces. Nevertheless, Christenson and Yaminsky [116] contend that the lateral mobility of surfactants in LB films or physisorbed silane molecules [*sic*] may adsorb/desorb to result in long range attraction.

1.3 Research Objectives

The specific goals of this research were:

- a) to conduct direct force measurements between a covellite (CuS) plate and a hydrophobic glass sphere in xanthate solution as a function of applied electrochemical potential,
- b) to conduct direct force measurements between copper-activated sphalerite (ZnS) plate and a hydrophobic glass sphere in xanthate solution as a function of pH,
- c) to study the phenomenon of inadvertent activation of rock minerals using an atomic force microscope,
- d) to explore a relation between the hydrophobicity of a surface as characterized by fundamental surface free energy parameters and the long range attractive force, and
- e) to propose and develop a theory for the molecular origin of the long range hydrophobic force in view of the results obtained in (d).

1.4 Report Organization

The results obtained in the present work have been reported in Chapters 2 to 6. Each chapter comprises of an introduction, experimental, results, discussion, and conclusion sections and may be considered as an article for publication. In Chapter 2 results of force measurements conducted between a covellite plate and a hydrophobic glass sphere ($\phi=109^\circ$) in xanthate solutions are reported. The xanthate adsorption on covellite was controlled by changing the electrochemical potential of the mineral electrode. It was found that the hydrophobic forces measured in KEX solutions at pH 9.2 are strongly dependent on the electrochemical potentials of the covellite electrode. The potential region at which strong hydrophobic forces are observed corresponds to that where the flotation of covellite reaches a maximum.

In Chapter 3 force measurements were conducted between sphalerite and a hydrophobic glass sphere in xanthate solutions. The sphalerite was activated in 10^{-4} M CuSO_4 solution prior to conducting force measurements. Force measurements were conducted at pHs of 4.6, 6.8 and 9.2. The results show the presence of strong hydrophobic forces at pH 4.6 and 9.2 and net repulsive forces at pH 6.8. The results are consistent with the flotation behavior of sphalerite.

Chapter 4 is a summary of work done for the International Nickel Company (INCO) in order to investigate the cause for the low grades obtained in the nickel recovery circuit at the Clarabelle Mill. The results of the work suggest that the low grades may be due to the inadvertent activation of rock minerals, i.e., rock minerals such as hornblende when in contact with heavy metal ions such as Cu^{2+} or Ni^{2+} get activated. It was found that xanthate readily adsorbs on these activated minerals thereby rendering the surface hydrophobic. Force measurements conducted between hornblende and a hydrophobic glass sphere in xanthate solutions showed: i) the presence of strong hydrophobic forces only when rock minerals were contacted with heavy metal ions such as Cu^{2+} or Ni^{2+} , and ii) the magnitude of the hydrophobic forces were critically dependent on the pH. A simple solution based on pH control has been proposed.

In Chapter 5 force measurements were conducted between silanated silica surfaces in water and in ethanol/water mixtures. The strength of the measured hydrophobic forces were compared with the advancing contact angles exhibited by these surfaces and the acid-base components of the surface free energy. Based on the results obtained, a mechanism for the molecular origin of hydrophobic force has been suggested. It is based on the premise that surfactants adsorb in patches forming domains, which in turn gives rise to large dipole moments. The correlation of the dipole moments results in long range attraction.

In Chapter 6, a mathematical model for the long range hydrophobic force has been developed. The model was used to fit the hydrophobic force data obtained from force measurements for silanated silica surfaces. The model provides a reasonably good fit to the experimental data.

Finally, Summary and Conclusions and Future work are given in Chapters 7 and 8 respectively.

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