CHAPTER 5

HYDROPHOBICITY AND THE LONG RANGE HYDROPHOBIC FORCE

5.1 INTRODUCTION

Hydrophobic interactions are the driving force for phenomena such as self-assembly of lipids, micelles, protein aggregates and biological membranes [1]. In biochemistry, they are the driving force for enzyme-substrate interactions [2]. It is also known that the hydrophobic attraction between macroscopic surfaces plays a crucial role in industrially important processes such as froth flotation [3,4], adhesion [5] and wetting [6].

Hydrophobic forces were first measured by Israelachvili and Pashley [7,8]. They found that the interaction forces between two mica surfaces in 1×10^{-5} M cetyltrimethylammonium bromide (CTAB) solutions are more attractive than those described by the DLVO theory [9,10]. The extra attractive force ($F_h$) was represented by a single exponential function:

$$\frac{F_h}{R} = C_o \exp\left(\frac{-H}{D_o}\right)$$  \hspace{1cm} [1]

where $R$ is the mean radius of curvature of the interacting surfaces, $H$ the closest distance of separation, $C_o$ and $D_o$ are fitting parameters. Here, $D_o$ is known as the decay length. The hydrophobic forces measured by Israelachvili and Pashley [7,8] were fitted with $C_o = -30$ mN/m and $D_o = 1.0$ nm.

When stronger hydrophobic forces were measured, a double exponential function [11-13]:

$$\frac{F_h}{R} = C_1 \exp\left(\frac{-H}{D_1}\right) + C_2 \exp\left(\frac{-H}{D_2}\right)$$  \hspace{1cm} [2]
was found to better fit the experimental data. In effect, $C_1$ and $D_1$ represent the short range attraction, while $C_2$ and $D_2$ represent the long range attraction.

Some investigators prefer to fit the measured hydrophobic forces using a power law [12,14-16]:

$$F_h = -\frac{KR}{6H^2} \quad [3]$$

in which $K$ is the only fitting parameter. Eq.[3] is the of the same form as the van der Waals force. Therefore one can directly compare $K$ with the Hamaker constant $A$.

Over the past few years, long-range hydrophobic forces have been measured using surfaces prepared by a variety of methods. These include in situ equilibrium adsorption from aqueous solution [7,8,], Langmuir-Blodgett (LB) deposition of monolayers [11,12], chemical modification of surfaces [15-18] and equilibrium adsorption of surfactants from non-aqueous solvents [19-21]. The measurement of hydrophobic forces between macroscopic hydrophobic surfaces has now become a routine affair. One would, therefore, imagine that with the active research being done in this field, the initial mystery surrounding the hydrophobic force would be slowly unraveled. Unfortunately, as things stand today, the topic of hydrophobic forces is one filled with controversies with a great deal of confusion.

To begin with, controversy exists regarding the effect of certain experimental parameters on the magnitude of the hydrophobic force. For example, the effect of electrolyte addition on the hydrophobic force has been quite controversial. It has been shown that the magnitude of the hydrophobic force reduces [20], increases [22] or remains unaffected with increasing electrolyte concentration [23]. Similarly, there are conflicting reports concerning the effect of temperature on the magnitude of the hydrophobic force [20, 22]. It is also quite disconcerting that the same experiment conducted for the same system by different investigators produce different results. Take for example the forces measured between glass surfaces in CTAB solutions. Earlier
measurements by Parker et al [24] suggested that there existed a weak hydrophobic force that was discernible only at separation distances (H) less than 20 nm. However, recent measurements for the same system [25-27] suggest that the hydrophobic force is a few orders of magnitude stronger (D₂=20 nm) than those reported by Parker et al [24] and is discernible at distances (H) of approximately 80 nm.

Controversy also exists regarding the molecular origin of the hydrophobic force. Theoreticians have been struggling to come up with a model that can satisfactorily explain the long-range forces reported in literature; as a result a diverse number of theories have been proposed. These include: water structural effects [28], hydrodynamic fluctuations [29,30], an anomalous electrostatic response of the adjacent liquid layer [31], charge correlation due to adsorbed counter ions [32], dipole moments associated with hydrophobic domains [19,33], cavitation [34-36], subcritical density fluctuations [37,38], bridging of an air bubble [39] and change in the adsorption-desorption equilibrium of surfactants [40, 41], has gained universal acceptance.

An interesting aspect of the hydrophobic forces that has often been either proved [13, 16, 42] or disproved [41, 43] is the effect of the hydrophobicity of the interacting surfaces on the measured forces. Earlier measurements [7,8,44] indeed did suggest that the water contact angle exhibited by a surface was directly related to the magnitude of the hydrophobic force. In particular, the work done in this laboratory over the past few years has consistently shown a trend between the advancing contact angle (θₐ) and the magnitude of the hydrophobic force. The work of Yoon and Ravishankar[13, 42] 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. They plotted the D₂ values obtained from their study along with the D₀ and D₂ values obtained by other investigators as a function of the advancing contact angle (θₐ). Their conclusions were: i) short range hydrophobic forces (D₂<3 nm) are observed at θₐ < 90⁰, ii) long range hydrophobic forces (D₂ >10 nm) are observed at θₐ >90⁰, 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 contact angle exhibited by a surface.

However, the idea that the water contact angle can be related to the hydrophobic force is not universally agreed. For example, Woods and Sharma [45] conducted force measurements between polymerized octadecyltriethoxysilane (OTE) coated mica surfaces ($\Theta_a \approx 111^\circ$) and found only a short range attractive force. By the same token, forces of interaction between bulk hydrophobic polymer surfaces such as polystyrene ($\Theta_a = 109^\circ$) [46], polypropylene ($\Theta_a = 103^\circ$) [47] or teflon [19] do not show a long range attraction. In this regard, the work of Kurihara and Kunitake [48], 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 $\Theta_a$ increased to $105^\circ$, no attractive forces were measured and yet the surfaces jumped into primary contact at separation distances of approximately 24 nm. In other words, for the same system, as $\Theta_a$ increased, the magnitude of the hydrophobic force was found to decrease.

An interesting aspect of the above discussion is that most of the investigators assume the water contact angle, $\Theta_a$, as a measure of a surface’s hydrophobicity. Although such an assumption is perfectly valid, its applicability to force measurements needs to be questioned. This is because $\Theta$ is a parameter that is measured at the three phase (solid, liquid and vapor) contact line, while the measured forces are a result of the interaction between two phases only, i.e., solid and liquid phases. A better approach, therefore, would be characterizing hydrophobicity in terms of the fundamental surface free energy parameters of the interacting phases (solid and liquid) alone.
In this regard the work that came out of Kitchener’s group [49, 50] about thirty years back may be useful. To the best of our knowledge, they were the first ones to: i) show that the interaction between macroscopic hydrophobic surfaces should be long ranged [50], and ii) define macroscopic hydrophobicity in terms of the fundamental surface free energy parameters [49].

Laskowski and Kitchener [49] suggested that the work of adhesion ($W_a$) of a liquid on a solid surface is given by:

$$W_a = W_{ad} + W_{an}$$  \[4\]

where $W_{ad}$ represents the contributions from dispersion interactions and $W_{an}$ represents the same from non dispersion (polar and ionic ) interactions. These authors suggested that all solids would be hydrophobic if $W_{an}$ =0, i.e., if the surface is free of polar groups on which water molecules can be bonded.

In the last twenty years, significant advances have been made in the thermodynamic treatment of surface free energy components, largely due to the pioneering work of Fowkes et al [51-53] and Van Oss, Chaudhary and Good (VCG) [54-57]. According to these approaches the surface free energy (SFE) of a phase $i$ is given by:

$$\gamma_i = \gamma_{iLW} + \gamma_{iAB}$$  \[5\]

where $\gamma_{iLW}$ represents the contributions from the Lifshitz Van der Waals (LW) interactions and $\gamma_{iAB}$ represents the same from acid-base interactions. The LW interactions include contributions from London dispersion ($\gamma_i^d$), Debye induction ($\gamma_i^I$), and Keesom dipole-dipole ($\gamma_i^\mu$) interactions. Thus $\gamma_{iLW}$ represents the entire Lifshitz Van der Waals contribution to the SFE. However, Van Oss et al found that in most cases [54-57] the contributions from $\gamma_i^d$ and $\gamma_i^\mu$ to $\gamma_{iLW}$ is negligible. It needs to be pointed out that some authors still prefer to use $\gamma_{Sd}$ instead of $\gamma_{SLW}$. Therefore, in the rest of this communication $\gamma_{Sd}$ may be taken to represent $\gamma_{SLW}$ effectively.
According to the VCG approach [54-57], the $\gamma_i^{AB}$ in Equation 5 for phase $i$ is given by:

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+ \gamma_i^-} \quad [6]$$

where $\gamma_i^+$ and $\gamma_i^-$ refer to the electron acceptor (Lewis Acid) and electron donor (Lewis Base) contributions to the total surface free energy of phase $i$.

When two phases, say solid $S$ and liquid $L$, are interacting, then based on the VCG approach, one can derive the following equation:

$$(1 + \cos \Theta)\gamma_L = 2((\gamma_S^{LW} \gamma_L^{LW})^{1/2} + (\gamma_S^+ \gamma_L^-)^{1/2} + (\gamma_S^- \gamma_L^+)^{1/2}) \quad [7]$$

where $\gamma_L$ refers to surface tension of the liquid $L$, $\gamma_L^+$ and $\gamma_L^-$ refer to the electron donor and acceptor contributions to the surface tension of the liquid ($\gamma_L$), $\gamma_S^+$ and $\gamma_S^-$ refer to the electron acceptor and donor contributions to the solid surface free energy ($\gamma_S$), $\gamma_S^{LW}$ and $\gamma_L^{LW}$ refer to the Lifshitz van der Waals contributions to the surface free energy of the solid and liquid phases, respectively and $\Theta$ refers to the contact angle exhibited by liquid $L$ on solid $S$.

If the contact angle values of three liquids (whose $\gamma_L$, $\gamma_L^{LW}$, $\gamma_L^-$ and $\gamma_L^+$ are known) on a solid $S$ are known, then we have three simultaneous equations. They can be solved for the three unknown parameters of the solid ($\gamma_S^{LW}$, $\gamma_S^+$ and $\gamma_S^-$). This means that by a simple measurement of three contact angles using three appropriate liquids one can determine all the relevant SFE parameters of the solid surface. In the present work a non polar liquid such as diiodomethane and two polar liquids such as water and glycerol have been used [57].

It was the primary objective of the present work to explore the relation between hydrophobicity and the hydrophobic force. In order to meet this objective, AFM force measurements were conducted between: i) silanated silica surfaces of varying hydrophobicities in water, and ii) silanated silica surfaces in ethanol/water mixtures. The results of the force
measurements were related to the SFE parameters obtained using the VCG approach. It is hoped that such a treatment will not only help understand the relationship between hydrophobicity and the hydrophobic force, but will also throw more light regarding the molecular origin of the hydrophobic force.

5.2 EXPERIMENTAL

5.2 (a) Materials

Optically smooth fused silica plates were obtained from Heraeus Amersil, Inc., and cleaned by boiling in a nitric acid solution for 12-15 h before use. Glass spheres obtained from Duke Scientific were used as received. HPLC-grade cyclohexane, glycerol and diiodomethane were obtained from Aldrich Chemical Company at 98% purity, and used as received. Octadecyltrichlorosilane (OTS) was also obtained from Aldrich Chemical Company at 95% purity and used without further purification. Absolute 200-proof (USP grade; >99.2% pure) ethanol was obtained from Aaper Alcohol and Chemical Company and used without further purification. All experiments were conducted using conductivity water produced from a Barnstead Nanopure II water treatment unit.

5.2 (b) Apparatus and Procedure

Surface force measurements between a silanated glass sphere and an OTS-coated flat silica plate were conducted using a Digital Instruments Nanoscope III atomic force microscope (AFM). The glass sphere was glued to the end of an AFM cantilever spring by means of Epon R Resin 1004F obtained from Shell Chemicals Company in a manner described by Ducker et al [58]. The AFM was equipped with a standard liquid cell. All AFM force measurements were carried out in a manner described by Rabinovich and Yoon [15]. For the measurement of weak repulsive forces standard triangular silicon nitride (Si₃N₄) cantilevers (0.1<k<0.32 N/m) were used while rectangular TESP cantilevers (25<k<35 N/m) were used to measure strong attractive
forces. The cantilevers were calibrated using the technique described by Cleveland et al [59].

5.2(c) Silanation

Fused silica plates were silanated in OTS-in-cyclohexane solutions in a nitrogen atmosphere. The cyclohexane was dried overnight over 3-12 mesh Davidson 3-Å molecular sieves before use. Flinn et al [60] described the process of silanation in detail. The hydrophobicity of the silica plates could be varied by choosing appropriate concentrations of OTS and by changing the immersion times [60]. For force measurements, glass spheres were silanated along with the silica plates in the same batch, so that the plates and the spheres exhibited identical hydrophobicities.

5.2 (d) Contact Angle Measurements

Contact angle measurements were made using a Rame Hart Model 100 Goniometer. The test liquids used to measure contact angle include Nanopure water, diiodomethane and glycerol. The sessile liquid drop technique was used to measure the advancing contact angle in a manner described by Good [61]. Since the glass spheres and the silica plates were hydrophobized in the same batch, it is implicitly assumed that they exhibit the same contact angles ($\theta_a$).

5.3 RESULTS

Figure 5.1 shows a series of force curves obtained for the interaction between symmetric silanated surfaces, i.e., the silica plates and the glass spheres were silanated under identical conditions. This would give the two surfaces the same degree of hydrophobicity and, hence, the same contact angle ($\theta_a$). The measured forces $F$, normalized by the radius of the sphere $R$, are plotted versus the separation distance $H$. It needs to be mentioned that this experiment is a repetition of an earlier work done by Yoon et al [16]. This was necessary since the results from these measurements will play a central role in the argument presented in this work.
As the figure shows, there are seven different force curves that represent force measurements conducted between surfaces exhibiting $\Theta_a$ of 109, 105, 100, 92, 83, 75 and 0°. Note that at $\Theta_a=0$, 75 and 83° the measured forces are repulsive. However, with increasing values of $\Theta_a$ the forces become net attractive. Since the attractive forces measured using $\Theta_a=109$, 105, 100 and 92° are much larger than those measured at lower contact angles, they are plotted separately in the inset.

The dotted line in Figure 5.1 represents a theoretical DLVO fit of the data obtained for $\Theta_a=0°$. The ion electrostatic force ($F_e$) was calculated using the constant potential model developed by Oshima et al [62]. $F_e$ was calculated using the following parameters: surface potential of silanated silica $\Psi_1=-60$ mV and Debye length $\kappa^{-1}=94$ nm. The Lifshitz Van der Waals force ($F_d$) was calculated using a value of $A_{131}=8\times10^{-21}$ J taken from literature [63]. Note that silanation is not known to change the surface potential of silica [50]. Therefore, the dotted line (Figure 5.1) may be taken as a theoretical DLVO prediction for all the conditions employed in Figure 5.1.

There are two striking features about the force curves presented in Figure 5.1. One, all the forces measured cannot be fitted to the DLVO theory. Two, the strength of the attractive force increases with increasing $\Theta_a$ of the surfaces. While the measurements conducted between surfaces exhibiting $\Theta_a=0°$ show an extraneous repulsive force, all the other forces measured suggest an extra attractive force not accounted for by the DLVO theory. Derjaguin and Churaev [64] suggested that the DLVO theory is only applicable to weakly hydrophobic colloids exhibiting contact angles of 20-45°. The repulsive force measured at $\Theta_a=0°$ is probably due to the hydration of the silica surface and is of little relevance to the present work. We shall, therefore, concentrate on the attractive hydrophobic forces measured between the silanated silica surfaces.

When hydrophobic forces are measured it is often necessary to extend the DLVO theory so that:
\[ F = F_c + F_d + F_h \]  

[8]

where \( F_h \) represents the contributions from the hydrophobic force. It has been shown that \( F_h \) can be conveniently represented by a power law:

\[ F_h = \frac{-K}{6H^2} \]  

[9]

where \( K \) is called as the hydrophobic force constant and represents the magnitude of the hydrophobic force.

The hydrophobic forces measured have been fitted using a power law (Eq.9) with \( K=2\times10^{-16}, 6\times10^{-17}, 2\times10^{-17}, 5\times10^{-18}, 8\times10^{-20} \) and \( 5\times10^{-20} \) J for force measurements conducted using silanated silica surfaces exhibiting \( \Theta_h \) of 109, 105, 100, 92, 83 and 75° respectively (The values of \( F_c \) and \( F_d \) used were the same as that mentioned earlier). The data is also summarized in Table 5.1 which shows the \( K \) values obtained at different values of \( \Theta_h \). In essence, Figure 5.1 and Table 5.1 clearly suggest that the magnitude of the hydrophobic force is indeed related to the \( \Theta_h \) exhibited by a surface. Table 5.1 also shows the \( K \) values obtained by Yoon et al [16]. It is noteworthy that the \( K \) values reported here agree well with those reported by Yoon et al [16].

Figure 5.2 shows the SFE parameters \( \gamma_{SL}^{LW}, \gamma_{SL}^+, \gamma_{SL}^- \) and \( \gamma_{SL}^{AB} \) obtained for silanated silica surfaces, plotted as a function of \( \Theta_h \) exhibited by these surfaces. For a given hydrophobicity of the silica plate, advancing contact angles were measured using three test liquids, i.e., Nanopure water, glycerol and diiodomethane. Based on the values of \( \Theta_h \) obtained for these liquids, Eq. [7] was solved simultaneously to obtain the values of the relevant SFE parameters. Table 5.2 gives the values of \( \gamma_{SL}^+, \gamma_{SL}^- \) and \( \gamma_{SL} \) from literature [57] and are given in Table 5.2. The contact angles obtained and the values of the SFE parameters \( \gamma_{SL}^{LW}, \gamma_{SL}^+, \gamma_{SL}^- \) and \( \gamma_{SL}^{AB} \) are given in Table 5.3.

The results given in Figure 5.2 and Table 5.3 show four important trends that need to be discussed. One, the value of \( \gamma_{SL}^- \) is much higher than the value of \( \gamma_{SL}^+ \) for surfaces with lower
hydrophobicities. For example, at \( \Theta = 50^\circ \), \( \gamma^\S_\S^- = 21.63 \text{ mN/m} \) where as \( \gamma^\S_\S^+ = 1.59 \text{ mN/m} \). The results presented here agree well with those reported in literature [65-67]. This finding suggests that the silica surface, a well known acidic oxide, is essentially more basic than acidic. This seemingly odd observation can be rationalized if we consider the possibility that there is always a layer of water molecules adsorbed on the surface of silica [65,66]. Since the polarizability of \( \text{Si}^{4+} \) ions is so high it would be difficult to get rid of water from the surface of silica. According to the molecular dynamic simulations carried out by Grivtsov et al [68], water can adsorb on to surface silanol groups (\( \equiv \text{Si-OH} \)) in two different ways as shown in Figure 5.3. According to Grivtsov et al [68], the orientation shown in Figure 5.3 (a) is the more likely of the two. Hence, the basic nature of the silica surface reported here and in literature should be attributed to the basic oxygen molecule that is exposed as a result of the orientation shown in Figure 5.3 (a).

Two, the values of \( \gamma^\S_\S^- \), \( \gamma^\S_\S^+ \) and \( \gamma^\S_\S^{AB} \) decrease with increasing \( \Theta \). The decrease in \( \gamma^\S_\S^{AB} \) is a direct consequence of the decrease in both \( \gamma^\S_\S^- \) and \( \gamma^\S_\S^+ \) as suggested by Eq. [6]. Tagawa et al [69] reported the \( \gamma^\S_\S^{AB} \) values for silanated silica surfaces exhibiting \( \Theta = 72 \) and 89\(^\circ\) were 5.49 and 4.40 mN/m, respectively. According to Figure 5.2, the \( \gamma^\S_\S^{AB} \) values obtained at \( \Theta = 72 \) and 89\(^\circ\) are approximately 5.7 and 2.9 mN/m, which agree reasonably well with those of Tagawa et al [69]. Note that an increase in \( \Theta \) is achieved primarily due to an increase in the adsorption density of the OTS molecules on silica surface. Flinn et al [60] studied the adsorption of OTS on silica and found that with increased adsorption, the OTS molecules become well ordered thereby exposing their terminal methyl groups to the aqueous solution. Therefore, with increased OTS adsorption, the surface changes from one bearing polar silanol groups that can readily participate in acid-base interactions with water molecules to a hydrocarbon surface (exposing its terminal methyl groups) that shows little tendency to interact with the water molecules.

Three, the values of \( \gamma^\S_\S^{LW} \) decrease as the surface becomes more hydrophobic. For example, \( \gamma^\S_\S^{LW} \) changes from 41.04 mN/m at \( \Theta = 50^\circ \) to 22.9 mN/m at \( \Theta = 109^\circ \). It needs to be pointed out that the \( \gamma^\S_\S^{d} \) values reported in literature for hydrophilic silica range from 43-79 mN/m [70,71] while the \( \gamma^\S_\S^{d} \) value reported for silanated silica is approximately 22-25 mN/m [69,
Furthermore, the trend reported here is also in excellent agreement with those reported by Yoon and Xu [73] who calculated the $\gamma_S^{d}$ values for silica and methylated silica. Hence, the decrease in $\gamma_S^{LW}$ values with increased silanation reported here agree well with what has been published in literature. Furthermore, the value of $\gamma_S^{LW}=22.9$ mN/m obtained at $\Theta_a=109^\circ$ is very close to the value of $\gamma_S^{d}=23$ mN/m [74] reported for a terminal methyl group (-CH$_3$). This indeed does suggest that at $\Theta_a=109^\circ$, the silica surface is essentially covered with a well ordered monolayer of octadecyl silane chains, exposing their terminal methyl groups to the aqueous solution. Note that unlike $\gamma_S^{AB}$ the values of $\gamma_S^{LW}$ do not become zero. This is because dispersion forces are universal and therefore should exist even in inert gases such as argon and neon [75].

Finally, it may be questioned as to what really causes an increase in $\Theta_a$ with increased silanation. Is it due to a decrease in $\gamma_S^{LW}$ or is it due to a decrease in $\gamma_S^{-}$ and $\gamma_S^{+}$? After all, with increased silanation, the change in $\gamma_S^{LW}$ as it reduces from 41.04 to 22.9 mN/m is comparable to the decease in $\gamma_S^{-}$ from 21.63 to 0.001 mN/m. In fact a simple calculation can be made using Eq. 7 to show the effects of $\gamma_S^{LW}$, $\gamma_S^{+}$ and $\gamma_S^{-}$ on the changes in $\Theta_a$. For example, when $\gamma_S^{LW}$ decreases from 41.04 to 22.9 mN/m, while keeping $\gamma_S^{+}$ and $\gamma_S^{-}$ constant at 21.6 and 1.59 mN/m, respectively, $\Theta_a$ changes only by 12$^\circ$. On the other hand, a decrease in $\gamma_S^{+}$ and $\gamma_S^{-}$ from 21.6 and 1.59 mN/m, respectively, to zero while keeping $\gamma_S^{LW}$ constant at 41.04 mN/m changes $\Theta_a$ by 57$^\circ$. In other words, out of the 69$^\circ$ change in $\Theta_a$ (from 50 to 109$^\circ$) observed in the present case, only 12$^\circ$ is due to a decrease in $\gamma_S^{LW}$ while the rest 57$^\circ$ is due to a decrease in $\gamma_S^{-}$ and $\gamma_S^{+}$.

Figure 5.4 represents a series of $F/R$ vs $H$ curves obtained for the interaction of a silanated plate and glass sphere in ethanol/water mixtures of varying concentrations. The silica plate and glass sphere silanated under identical conditions exhibited $\Theta_a=109^\circ$ in Nanopure water. For the sake of brevity, the phrase “fully-silanated silica” will refer to the silica plates and spheres that exhibit $\Theta_a=109^\circ$ in water.
It can be seen from Figure 5.4 that the hydrophobic force is strongest when measured in Nanopure water and decreases with increasing ethanol concentration. The measured forces have been fitted to a power law with $K=2\times10^{-16}$, $5\times10^{-17}$ J, $2\times10^{-17}$, $1\times10^{-17}$ and $4\times10^{-18}$ J for ethanol concentrations of 0, 10, 20, 40 and 60 \% by volume respectively. The values of $F_e$ and $F_d$ used for all the conditions are the same as that used in Figure 5.1. It can be argued that $F_e$ and $F_d$ should in fact change with increasing concentration of ethanol and therefore the $K$ values obtained by assuming constant $F_e$ and $F_d$ values would be incorrect. However, since the hydrophobic forces measured here are very strong, it was found that changing the values of $F_e$ and $F_d$, say even to zero, would have made little difference in the $K$ values.

The $K$ values obtained from the force measurements are reported in Table 5.2 along with the $\Theta_\Theta$ values obtained for a given ethanol/water mixture. Again, the same trend as in Figure 5.1 can be seen, i.e., as $\Theta_\Theta$ decreases progressively; so does the magnitude of the hydrophobic force. The decrease in the magnitude of the hydrophobic force with increasing ethanol concentration observed here is similar to the results reported by Parker et al [22], who conducted force measurements between silanated glass surfaces in aqueous solutions as a function of ethanol concentration.

More recently, Kokolli and Zukoski [76] conducted force measurements between hexadecanethiol-coated gold surfaces in ethanol/water mixtures. These authors found that both the contact angle and the hydrophobic attraction decreased with increasing ethanol concentration. They argued that the decrease in the magnitude of the hydrophobic force should be directly related to the decrease in contact angle with increasing ethanol concentration and, hence, the hydrophobicity of the surface.

It needs to be pointed out that Figure 5.4 represents a situation where the solid surface is maintained at constant hydrophobicity, while the liquid properties are being varied by increasing the ethanol concentration. Recall that in the present case, fully-silanated silica surfaces have been used. Figure 5.2 shows that these surfaces have no acidic or basic sites that can interact
with the water/ethanol molecules. A decrease in hydrophobicity is primarily due to a decrease in the surface tension of ethanol/water mixtures with increasing concentration of ethanol (shown in Table 5.4) [77]. Note that this is in complete contrast to the measurements made in Figure 5.1 where the hydrophobicity of the solid surface was varied while keeping the liquid properties constant.

Comparison of the $K$ values obtained in Figures 1 and 3 reveals an interesting trend. Table 5.4 shows that in solutions containing 50% ethanol by volume $\Theta_h = 75^0$ and $K = 1 \times 10^{-17}$ J. This is a few orders of magnitude higher than the value of $K = 5 \times 10^{-20}$ J observed for the same $\Theta_h = 75^0$ in Nanopure water. This result, as we shall see later, may have significant implications.

Figure 5.5 shows the results of force measurements conducted between fully-silanated silica and glass sphere in 70, 80 and 100% by volume alcohol solutions. Note that virtually no surface forces are observed and the results look identical to one another. However, the surfaces jump into primary contact at separation distances ($H$) of approximately 8.0 nm. The absence of an attractive force profile for the van der Waals force may be due to the insensitivity of the cantilever ($k = 0.1$ N/m) used in the present work [78, 79]. The absence of a repulsive ion-electrostatic force suggests that the hydrocarbon coated silica surfaces remain uncharged in ethanol solutions. The trend observed here is similar to those obtained by Kokolli and Zukoski [76] who found that the forces measured between hexandecanethiol coated gold surfaces could be well described by van der Waals force alone when the mole fraction of ethanol/water mixtures was higher than 0.75.

The solid line in Figure 5.5 shows a theoretical van der Waals prediction for two silanated surfaces interacting in 100% ethanol solutions. The Hamaker constant was calculated using the relation [75]:

$$A_{131} = \frac{3}{4} kT \left( \frac{e_1 - e_3}{e_1 + e_3} \right)^2 + \frac{3h\nu_r}{16\sqrt{2}} \left( \frac{n_1^2 - n_3^2}{n_1^2 + n_3^2} \right)^2$$  [10]
where \( k (=1.38 \times 10^{-23} \text{ JK}^{-1}) \) is the Boltzmann constant, \( T (=298 \text{ K}) \) is the absolute temperature, \( \varepsilon_1 (=2.06) \) is the dielectric constant for silanated silica (it is assumed to be similar to that of octadecane) [77], \( \varepsilon_3 (=26) \) is the dielectric constant of ethanol [75], \( h (=6.63 \times 10^{-34} \text{ Js}) \) is the Planck’s constant, \( \nu_e (=3 \times 10^{15} \text{ s}^{-1}) \) is the UV absorption frequency [74], \( n_1 (=1.43) \) is the refractive index of octadecane [77] and \( n_3 (=1.361) \) [75] is the refractive index of ethanol. The \( A_{131} \) value calculated using Eq. [10] for silanated silica in 100% ethanol solutions is equal to \( 3.52 \times 10^{-21} \text{ J} \). It may be mentioned that the \( A_{131} \) value calculated using Eq [10] for two silanated surfaces in 70% ethanol solutions is \( 3.79 \times 10^{-21} \text{ J} \), i.e., \( A_{131} \) changes from \( 3.52 \times 10^{-21} \text{ J} \) in 100% ethanol solutions to \( 3.79 \times 10^{-21} \text{ J} \) in 70% ethanol solution. However, all the measured forces look identical and can be fitted to the same value of the Hamaker constant (=\( 3.52 \times 10^{-21} \text{ J} \)). It is possible that these small changes in surface forces are well within the sensitivity of the cantilever \( (k=0.1 \text{ mN/m}) \) used in the present work [78,79].

The contact angle values (\( \Theta_a \)) obtained on fully silanated-silica using 70, 80 and 100% ethanol solutions are also shown in Table 5.4. The contact angle values are 35, 20 and \(<10^\circ\) respectively for 70, 80 and 100% ethanol solutions by volume respectively. The absence of a hydrophobic force at these concentrations of ethanol can be directly related to the low contact angles. As mentioned earlier the colloidal behavior of weakly hydrophobic colloids can often be well described by the DLVO theory [64].

### 5.4 DISCUSSION

The results presented in the foregoing section suggest that the magnitude of the hydrophobic force is intricately dependent on the hydrophobicity (\( \Theta_a \)) of the surface. The central idea of this work is summarized in Figure 5.6, where the \( K \) values obtained from Figure 5.1 and the values of \( \gamma^+_S, \gamma^-_S, \gamma^{\text{LW}}_S \) and \( \gamma^\text{AB}_S \) given in Figure 5.2 are plotted vs. \( \Theta_a \) (water). The plot also includes a comprehensive set of \( K \) values obtained from the research in our laboratory in the past.
seven years. The plot is similar to the one published by Yoon and Ravishankar [42] and differs by the facts that: i) $K$ values, rather than $D_2$ or $D_0$ values are used to represent the magnitude of the measured force, and ii) additional experimental data since the previous work was published have been included. The data obtained from references 13 and 42 are for force measurements conducted using the SFA between mica surfaces in DAHCl solutions in the presence of a neutral species such as octanol or dodecanol; references 15 and 16 are for the force measurements conducted between silanated silica surfaces using an AFM; reference 80 are for the force measurements conducted using the SFA between mica surfaces in solutions of dioctadecylammonium hydrogen chloride (DOAHCl). With the exception of Reference 80, all the other references shown in Figure 5.6 are published data and the reader is referred to the original publications for more information.

Figure 5.6 shows that $K$ increases as $\Theta_s$ increases. As has already been pointed out, the increase in $\Theta_s$ is essentially due to a decrease in $\gamma_s^-$ and $\gamma_s^+$ and, hence, a decrease in $\gamma_s^{AB}$. An important point needs to be made here. Suggesting that the increase in $\Theta_s$ is due to a decrease in $\gamma_s^{AB}$ may be quite misleading since according to Eq. [6] $\gamma_s^{AB}$ is actually given by:

$$\gamma_s^{AB} = 2\sqrt{\gamma_s^+\gamma_s^-}$$  \hspace{1cm} [11]$$

so that $\gamma_s^{AB}$ will take zero values for three conditions: i) when $\gamma_s^-=0$ and $\gamma_s^+\neq0$, or ii) when $\gamma_s^-=\neq0$ and $\gamma_s^+=0$, or iii) when $\gamma_s^-=\gamma_s^+=0$. However, according to conditions (i) and (ii), although $\gamma_s^{AB}$ may be zero, the solid surface will still not be hydrophobic to water, since either $\gamma_s^+$ or $\gamma_s^-$ have finite values respectively. This is because water being an amphoteric solvent can still effectively bond with either the acidic or the basic sites of the solid surface respectively. On the other hand, according to condition (iii), a zero value of $\gamma_s^{AB}$ is attained since both $\gamma_s^-$ and $\gamma_s^+$ are zero. This is exactly what has been observed in the present work where $\Theta_s$ increases with decrease in the values of both $\gamma_s^+$ and $\gamma_s^-$ and a maximum of $10^9\theta$ is reached when both $\gamma_s^+$ and $\gamma_s^-$ are approximately zero.
It is now popularly believed that the inability of water molecules to bond with a hydrophobic surface makes the aqueous film adjacent to a hydrophobic surface metastable [29-31, 34-37]. Furthermore, it is also agreed that the metastability of the aqueous film can lead to a long range attraction. However, controversy exists as to whether such metastability manifests itself as cavitation [36], hydrodynamic fluctuations [30], subcritical density fluctuations [37] or an anomalous electrostatic response [31]. Of all the mechanisms based on metastability, the formation of a vapor cavity or the cavitation phenomenon has received the most attention. The theory is based on the thermodynamic argument that for surfaces exhibiting $\Theta > 90^\circ$, the line tension becomes negative, i.e.,

$$\gamma_{SV} - \gamma_{SL} < 0$$

which suggests that the formation of a vapor cavity should occur spontaneously since it is energetically favorable to replace the solid/liquid interface by the solid/vapor interface. It needs to be mentioned that the formation of a vapor cavity between macroscopic hydrophobic surfaces has often been either observed directly [36, 44] or inferred [22] from experiment.

Based on the results presented in Figure 5.6, it would seem that it is the metastability of the aqueous film that is responsible for the observed long range attraction at $\Theta_a > 90^\circ$. Two reasons may be given in support of this. One, as $\gamma_{S+}$ and $\gamma_{S-}$ decrease, the aqueous film adjacent to the hydrophobic surface should become increasingly metastable. In other words an increase in $K$ with decreases in $\gamma_{S+}$ and $\gamma_{S-}$ essentially suggests a mechanism driven by metastability. Two, the magnitude of the hydrophobic forces measured between all the different surfaces shown in Figure 5.6 increase drastically at $\Theta_a > 90^\circ$, suggesting a cavitation like mechanism at play.

However, a mechanism based on the metastability of the film alone cannot account for all the observations made in this work. This becomes abundantly clear if we look at Figure 5.7 where the $K$ values obtained using ethanol/water mixtures are plotted as a function of the advancing contact angle. Also shown in Figure 5.7 are the $K$ values measured in ethanol/water
mixtures. At lower contact angles these values are orders of magnitude higher than those obtained in Nanopure water. Furthermore, long range hydrophobic forces are observed in ethanol/water mixtures for $\Theta_a < 90^\circ$ (for example, $K = 4 \times 10^{-18}$ J for $\Theta_a = 60^\circ$). Therefore, based on Eq. [10], one can definitely rule out any mechanism based on macroscopic cavitation alone.

Furthermore, a number of arguments can be made against the theories based on metastability in general and against cavitation in particular. One, there are a number of cases where macroscopic cavitation has been observed, yet the measured forces are not long ranged [45,88]. Two, the aqueous films next to all hydrophobic surfaces exhibiting high $\Theta$ should be metastable and hence should result in long range attraction. This is clearly not the case since there are a number of cases reported in literature [45-48] where extremely hydrophobic surfaces do not exhibit long range attraction. Three, Eriksson et al [81] have recently proposed a thermodynamic argument suggesting that cavitation should not occur between homogeneous macroscopic hydrophobic surfaces. The fully silanated surfaces used in the present work exhibit contact angle hysteresis of less than $2^\circ$ indicating that the surfaces are chemically and physically homogeneous. Therefore, it is unlikely that cavitation should occur between the silanated surfaces used in the present work.

An alternative explanation to theories based on metastability was given by Tsao et al [19, 20], who argued that the formation of domains of well ordered crystalline hydrocarbon chains on a hydrophobic surface is crucial for the appearance of long range attraction. These authors suggested that well-ordered hydrocarbon chains with a tilted orientation generate in-plane dipole moments that can correlate with the in-plane dipole moments of an approaching surface to result in a long range attractive force. These authors suggested that when surfactant molecules adsorbed on a surface lose their ordering and crystallinity, the magnitude of the hydrophobic force is decreases. In fact this has been verified by Rabinovich et al [33] who showed that as the ordering of surfactant decreases, so does the magnitude of the hydrophobic force.
A similar conclusion can also be reached by considering the data presented in Figure 5.6. Consider the work of Yoon and Ravishankar [13, 42] who conducted force measurements between mica surfaces in DAHCl solutions. These authors found that the magnitude of the hydrophobic force increased only after the addition of a neutral species such as octanol or dodecanol. Furthermore, the magnitude of the hydrophobic force measured with the addition of dodecanol solutions was higher than those measured in octanol solutions. These authors argued that the neutral species: i) coadsorb with the DAH$^+$ ions, thereby forming a compact well ordered domains (or patch), ii) produces a homogeneous monolayer which exposes the more hydrophobic methyl groups to the aqueous solution, and iii) causes the hydrophobic force at $\theta_a=90^\circ$ to increase sharply due to domain formation. Since dodecanol and DAH$^+$ were of the same chain length, a more homogeneous well ordered surface was formed with dodecanol than with the addition of octanol.

A similar argument can also be made about the silanated silica surfaces used in the present work. Flinn et al [60] studied the adsorption of OTS on silica using transmission FTIR and atomic force microscopy. Figure 5.8 shows an AFM image obtained by Flinn et al [60] for a silanated silica surface which shows that OTS adsorption occurs in silica in the form of ellipsoidal patches. With increased silanation, the size of the patch did not increase but the adsorption density within each patch increased. Flinn et al [60] concluded that as $\theta_a$ increased from 84 to 101$^\circ$; a well ordered homogenous OTS monolayer is formed, thereby exposing the terminal methyl groups (-CH$_3$) to the aqueous phase. Such an explanation is also consistent from the SFE treatment used in the present work which suggests that the $\gamma_{SV}$ of fully silanated silica is equal to 22.9 mN/m (as shown in Table 5.3) which is close to the $\gamma_{SV}=23$ mN/m [74] of a terminal methyl group.

It would therefore seem that the mechanism suggested by Tsao et al [19, 20] may be valid in the present case. However, such an explanation still does not fully explain the large attractive force observed in ethanol/water mixtures. In fact the attractive force due to in-plane dipoles should increase with decreasing dielectric constant of the medium [19]. The results presented
here show the contrary, i.e., the measured forces actually with decreasing dielectric constant of the solvent (note that the dielectric constant of the ethanol/water mixture should actually decrease with increasing ethanol concentration [77]).

In order to explain the results obtained in ethanol/water mixtures it may be instructive to consider another phenomenon that is closely associated with domain formation. Rabinovich et al [33] suggested that domain formation could lead to the unipolar orientation of the adjacent water molecules resulting in giant dipoles, which in turn correlate with those of the approaching surface, to produce a long range attractive force. Molecular simulation studies of water molecules in the vicinity of a hydrophobic surface indeed suggest a parallel orientation of the water dipoles [82, 83]. More importantly, Tolstoi and coworkers [84, 85] have actually measured the orientation and the magnitude of water dipoles on lyophobic colloidal particles using electrooptical studies. Their measurements suggested that such dipoles can assume magnitudes as large as $3.7 \times 10^{-20}$ Cm (in comparison, dipole moment of one water molecule=$3.36 \times 10^{-30}$ Cm)

We, therefore suggest that there may actually exist two criteria for the appearance of long range hydrophobic forces. One, the solid surface should be unable to bond with the adjacent water molecules. Two, there should exist domains which may serve as parking spaces for the unidirectional orientation of water molecules. It is possible that the size of the domain may in fact dictate the decay length of the measured attractive force. Does the domain grow indefinitely and the hydrophobic force becomes infinitely large? It has been suggested, however, ordering of water molecules over infinitely large areas may eventually become energetically unfavorable [20].

If one subscribes to the mechanism presented above, then the large hydrophobic forces measured in ethanol/water mixtures shown in Figure 5.8 become explainable. Note that the force measurements conducted in ethanol solutions (Figure 5.4) are for fully-silanated silica surfaces, i.e., surfaces that contain well ordered domains. As a result, the domains on these surfaces are able to order the adjacent water molecules to result in large dipole moments. At higher ethanol
concentrations, ethanol may displace the water molecules from the parking lot, resulting in a decrease in the dipole moment and hence a decrease in the magnitude of the hydrophobic force.

On the other hand, the forces conducted in water using silanated surfaces (Figure1) exhibiting lesser contact angles reflect a situation where the hydrocarbon chains are not well ordered and are in a fluid like state [60]. As a result, there is very poor ordering of the water molecules and hence no giant dipoles are formed and no long range attraction is observed. In conclusion, it may be suggested that even though different solid/liquid pairs may exhibit the same contact angles, the magnitude of the hydrophobic forces exhibited may be different depending on domain formation and ordering of the water molecules.

The mechanism suggested here also provides a reasonable explanation for a number of experimental observations in the literature reported unexplainable. Consider the cases reported where extremely hydrophobic surfaces do not exhibit any long range attraction. Table 5.5 shows a comprehensive list of such cases reported in literature until now. As it can be seen, all the surfaces shown in Table 5.5 exhibit large contact angles, yet no long range attraction is observed. In fact for the case of OTE [45] and polymerized styrene [88] surfaces, macroscopic cavitation was observed, yet the measured hydrophobic forces are not long ranged. The fact that all these surfaces are polymer surfaces should not be dismissed as mere coincidence. It is possible that all these surfaces, although hydrophobic, do not contain well ordered hydrocarbon chains that can form domains. It is possible that this absence of domains and hence a resultant lack of ordering of the water molecules that denies these surfaces a long-range attractive force.

Finally, a few comments can be made about certain recent mechanisms suggested for the molecular origin of the hydrophobic force. Carambiss et al [39] suggested that a bridging air bubble captured on one of the surfaces may actually cause a long range attractive force. Such a mechanism would mean that different experimental runs should capture bubbles of different radii resulting in varying ranges of attraction for a given experimental condition. In the present work, all the measurements made were very reproducible and therefore one can rule out any suggestion
based on a bridging bubble. It is also unlikely that dissolved gases in water may play a part in the origin of this force. Recently, Craig et al [27] have shown that although removing the dissolved gases reduced the magnitude of the force slightly, the measured attraction remained considerably long ranged. Finally, Yaminsky et al [40,41] have recently suggested that the adsorption-desorption equilibrium of surfactants can result in a long range attraction. While this may be the case for equilibrium adsorption of surfactants it is not clear how this may be applicable in the present work where robust silanated surfaces have been used.

5.4 CONCLUSIONS

Force measurements were conducted to explore the relationship between the hydrophobicity of a surface and the magnitude of the hydrophobic force. To do this, force measurements were conducted: (i) between two silanated silica surfaces (of varying hydrophobicities) in Nanopure water, and (ii) between two fully-silanated silica surfaces (water contact angle=109°) in water-ethanol mixtures.

The results of the force measurements conducted for case (i) were compared with the $\gamma_S^+, \gamma_S^-, \gamma_S^{AB}$ and $\gamma_S^{LW}$ parameters obtained using the Van Oss, Chaudhary and Good thermodynamic approach. The results suggest that as $\gamma_S^+$ and $\gamma_S^-$ decrease, $\theta_a$ increases, and so does the magnitude of the hydrophobic force ($K$). However, when the $K$ values obtained in ethanol/water mixtures were plotted as functions of $\theta_a$, it was observed that in the range $60^\circ < \theta_a < 90^\circ$, the $K$ values were orders of magnitude higher than those obtained for case (i). This suggests that $\theta_a$ of the interacting surfaces alone does not uniquely determine the magnitude of the hydrophobic forces between them.

A possible parameter that needs to be considered is the ability of the surfaces to orient solvent molecules adjacent to them. It has been argued that the fully-silanated silica surfaces in case (ii) are very likely to contain domains of well-ordered surfactant chains. This may be very
effective in ordering the water molecules in the vicinity in a unidirectional manner, thus creating large dipole domains on the surface, which may correlate to give long-range forces. However, in case (i), the degree of ordering in the hydrocarbon domains decreases with decreasing $\Theta_a$. This reduces the effectiveness of such surfaces to orient solvent molecules in the vicinity, thereby reducing the range of the hydrophobic forces sharply. The mechanism suggested here can also provide an explanation as to why certain very hydrophobic surfaces do not exhibit a long range attractive force.
5.5 REFERENCES

Table 5.1. Force parameters obtained for symmetric interactions between silanated silica surfaces of varying hydrophobicities

<table>
<thead>
<tr>
<th>( \theta_{\beta} )</th>
<th>( K \times 10^{18} ) (Joules)</th>
<th>Present Work</th>
<th>Yoon et al ([16])</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>83</td>
<td>0.08</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>92</td>
<td>5</td>
<td>3.2</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>20</td>
<td>12.5</td>
<td>-</td>
</tr>
<tr>
<td>105</td>
<td>60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>109</td>
<td>200</td>
<td>270</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.2. Surface free energy components of the test liquids used in the present work \([57]\).

<table>
<thead>
<tr>
<th></th>
<th>( \gamma_{L} ) (mN/m)</th>
<th>( \gamma_{L}^{\text{LW}} ) (mN/m)</th>
<th>( \gamma_{L}^{\text{AB}} ) (mN/m)</th>
<th>( \gamma_{L}^{+} ) (mN/m)</th>
<th>( \gamma_{L}^{-} ) (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8</td>
<td>21.8</td>
<td>51.0</td>
<td>25.5</td>
<td>25.5</td>
</tr>
<tr>
<td>Glycerol</td>
<td>64</td>
<td>34</td>
<td>30</td>
<td>3.92</td>
<td>57.4</td>
</tr>
<tr>
<td>Diiodomethane</td>
<td>50.8</td>
<td>50.8</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 5.3. Surface free energy parameters obtained for silica surfaces of varying hydrophobicities

<table>
<thead>
<tr>
<th>( \theta_a^\ast )</th>
<th>( \theta_a^G )</th>
<th>( \theta_a^D )</th>
<th>( \gamma_S^+ ) (mN/m)</th>
<th>( \gamma_S^- ) (mN/m)</th>
<th>( \gamma_{SA} ) (mN/m)</th>
<th>( \gamma_{SL} ) (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>41</td>
<td>37</td>
<td>1.59</td>
<td>21.63</td>
<td>11.73</td>
<td>41.04</td>
</tr>
<tr>
<td>75</td>
<td>59</td>
<td>44</td>
<td>1.15</td>
<td>5.44</td>
<td>4.99</td>
<td>37.56</td>
</tr>
<tr>
<td>83</td>
<td>66</td>
<td>51</td>
<td>1.06</td>
<td>2.83</td>
<td>3.47</td>
<td>33.73</td>
</tr>
<tr>
<td>92</td>
<td>75</td>
<td>61</td>
<td>0.91</td>
<td>1.22</td>
<td>2.11</td>
<td>28.01</td>
</tr>
<tr>
<td>97</td>
<td>79</td>
<td>65</td>
<td>0.89</td>
<td>0.48</td>
<td>1.31</td>
<td>25.72</td>
</tr>
<tr>
<td>100</td>
<td>83</td>
<td>68</td>
<td>0.64</td>
<td>0.38</td>
<td>0.99</td>
<td>24.01</td>
</tr>
<tr>
<td>105</td>
<td>86</td>
<td>69</td>
<td>0.31</td>
<td>0.09</td>
<td>0.33</td>
<td>23.45</td>
</tr>
<tr>
<td>109</td>
<td>91</td>
<td>70</td>
<td>0.22</td>
<td>0.001</td>
<td>0.04</td>
<td>22.90</td>
</tr>
</tbody>
</table>

*\( \theta_a^\ast, \theta_a^G \) and \( \theta_a^D \) represent the advancing contact angles measured using water, glycerol and diiodomethane respectively.

Table 5.4. Force parameters obtained for symmetric interactions between silica surfaces in varying concentrations of ethanol/water mixtures.

<table>
<thead>
<tr>
<th>Ethanol (Vol. %)</th>
<th>( \theta_a ) (degree)</th>
<th>( K \times 10^{18} ) (Joules)</th>
<th>Surface Tension (mN/m)[^{[77]}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>109</td>
<td>200</td>
<td>72.6</td>
</tr>
<tr>
<td>10</td>
<td>97</td>
<td>50</td>
<td>51.1</td>
</tr>
<tr>
<td>25</td>
<td>86</td>
<td>20</td>
<td>38.9</td>
</tr>
<tr>
<td>50</td>
<td>75</td>
<td>10</td>
<td>30.1</td>
</tr>
<tr>
<td>60</td>
<td>60</td>
<td>4.0</td>
<td>28.1</td>
</tr>
<tr>
<td>70</td>
<td>35</td>
<td>-</td>
<td>27.3</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>-</td>
<td>25.9</td>
</tr>
<tr>
<td>100</td>
<td>&lt;10°</td>
<td>-</td>
<td>23.3</td>
</tr>
</tbody>
</table>
Table 5.5. Cases reported in literature of hydrophobic surfaces that do not exhibit long range hydrophobic force.

<table>
<thead>
<tr>
<th>Hydrophobic Surface</th>
<th>$\theta$</th>
<th>Range (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma polymerized polysiloxane</td>
<td>95</td>
<td>12</td>
<td>87</td>
</tr>
<tr>
<td>Polymerized ammonium amphipile</td>
<td>84</td>
<td>300</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>94</td>
<td>~30</td>
<td></td>
</tr>
<tr>
<td>Polymerized styrene</td>
<td>&gt;90</td>
<td>~28</td>
<td>88</td>
</tr>
<tr>
<td>Plasma polymerized hexamethyl disiloxane</td>
<td>109</td>
<td>-</td>
<td>89</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>111</td>
<td>9</td>
<td>47</td>
</tr>
<tr>
<td>Polymerized Octadecyl disiloxane</td>
<td>111</td>
<td>~20</td>
<td>45</td>
</tr>
<tr>
<td>Bulk polystyrene</td>
<td>89</td>
<td>&lt;7</td>
<td>46</td>
</tr>
<tr>
<td>Teflon</td>
<td>N/A</td>
<td>-</td>
<td>19</td>
</tr>
</tbody>
</table>
Figure 5.1. Results of the AFM force measurements conducted with silanated glass spheres and silica plates. The force, $F$, is normalized by the radius of the sphere, $R$, and plotted versus the separation distance, $H$. Each force curve was obtained using a sphere and silica plate silanated with octadecyltrichlorosilane (OTS) under identical conditions so that both exhibited the same contact angle: (o) 109°, (□) 105°, (♦) 100°, (●) 92°, (▲) 83°, (■) 75° and (●) 0°. The dashed line represents a DLVO fit of the data (for $\Theta_3=0°$) with $A_{131}=8\times10^{-21}$ J, $\psi_1= -60$ mV and $\kappa^{-1}= 94$ nm. A power law (Eq.3) has been used to include contributions from the hydrophobic force. The $K$ values are given in Table 5.1.
The surface free energy (SFE) parameters $\gamma^{-}_S$, $\gamma^{+}_S$, $\gamma^{LW}_S$ and $\gamma^{AB}_S$ obtained for silanated silica plates of varying hydrophobicities. The SFE parameters are plotted as a function of the advancing water contact angle $\theta_a$. The contact angles obtained using water, glycerol and diiodomethane and the individual SFE parameters are given in Table 5.2.
Figure 5.3. A schematic representation of the possible orientation of water molecules adsorbed on silica as suggested by Grivotsov et al [30]. The model shown in 3(a) imparts a basic character to the silica surface.
Figure 5.4. $F/R$ vs $H$ curves obtained for the interaction of silanated silica plates and glass spheres in ethanol/water mixtures. The silica plates and spheres were silanated under identical conditions and exhibited advancing water contact angles of 109°. Since the forces measured are net-attractive and cannot be fitted to the DLVO theory, a power law (Eq. 3) has been used to represent the contributions from the hydrophobic force. The $K$ values and the corresponding $\Theta_a$ obtained for the ethanol/water mixtures are given in Table 5.4. The values of $F_e$ and $F_d$ used are the same as in Figure 5.1.
Figure 5.5. F/R vs H curves obtained for the interaction of silanated silica plates and glass spheres in 70, 80 and 100 % ethanol/water mixtures by volume. The silica plates and spheres exhibited advancing water contact angles of 109°. The solid line represents a van der Waals force calculated using $A_{131}=3.52\times10^{-20}$ J.
Figure 5.6. The $K$ values obtained from Figure 5.1 and the SFE parameters obtained from Figure 5.2, plotted as a function of $\theta_a$. Also shown are the $K$ values obtained from References 13, 15, 16, 42, and 80.
Figure 5.7. The $K$ values obtained for silanated silica surfaces in ethanol/water mixtures as a function of the contact angle ($\theta_a$). Also shown for comparison are the $K$ values obtained from Figure 5.6.
Figure 5.8. An AFM image of a silanated silica surface taken from the work of Flinn et al [60].