A new angle on the coalescence of drops

By

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Submitted in fulfilment of the requirements for the degree of

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Institute for Frontier Materials
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July, 2016
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# Table of contents

List of figures ...................................................................................................................... iv  
List of tables ......................................................................................................................... xiv  
List of symbols ...................................................................................................................... xiv  
List of abbreviations ........................................................................................................... xvi  
Abstract ................................................................................................................................... xvii  
Acknowledgement ................................................................................................................ xvi  

**Chapters**

Chapter 1 Introduction ........................................................................................................... 1  
1.1 Background ....................................................................................................................... 1  
1.1.1 Drop collision ............................................................................................................... 2  
1.1.2 Bubble collision ........................................................................................................... 2  
1.2 Research significance ...................................................................................................... 3  
1.3 Research aims .................................................................................................................. 4  

Chapter 2 Literature review .................................................................................................. 5  
2.1 Experimental measurements .......................................................................................... 5  
2.1.1 Surface force apparatus .............................................................................................. 5  
2.1.2 Rising and sliding bubble experiments ...................................................................... 11  
2.1.3 Coalescence experiments ......................................................................................... 16  
2.1.4 Rolling and sliding arguments .................................................................................. 21  
2.1.5 Interference pattern observation for drops or bubble. .............................................. 23  
2.2 Theoretical models ......................................................................................................... 25  
2.2.1 Surface forces ........................................................................................................... 25  
2.2.2 Hydrodynamic force .................................................................................................. 33  
2.2.3 Surface deformation .................................................................................................. 38  
2.2.4 Theoretical modelling of a deformable body with an inclined surface.......... 39  

Chapter 3. Research Methodology ....................................................................................... 41  
3.1 Experimental set-up development .................................................................................. 42  
3.2 Hydrophobic treatment ................................................................................................. 46  
3.3 Newton’s rings and their analysis method ..................................................................... 47  

Chapter 4 Results and discussion for a hydrophilic surface ............................................ 59
A new angle on the coalescence of drops

Ninghui Han  Sep 2016

4.1 Baseline experiment ................................................................. 62
  4.1.1 Description of baseline experiment ........................................ 62
  4.1.2 Fringe shape profile and 3D map .......................................... 66
  4.1.3 Maximum and minimum film thickness against sliding time and distance .......... 77
  4.1.4 Sliding speed related to fringe shape and film 3D profile .................. 78
4.2 Effect of salt concentration .......................................................... 80
4.3 Effect of viscosity ...................................................................... 83
4.4 Effect of inclined angle ............................................................... 90
4.5 Effect of bubble size .................................................................. 94
4.6 Discussion .................................................................................. 98
  4.6.1 The dynamics of thin film drainage at an inclined angle into the ‘toboggan shape’. 98
  4.6.2 Evolution of toboggan thin film and its final shape ......................... 105
  4.6.3 The effect of viscosity on the thin film shape ............................... 108
  4.6.4 Sliding vs rolling .................................................................... 112
Chapter 5 Results and discussion for hydrophobic surfaces .................. 116
  5.1 Results at 0.5º ........................................................................ 116
  5.2 Results at 1º ........................................................................... 124
  5.3 The critical parameter that triggers the thin film rupture ..................... 125
  5.4 Thin film rupture progression ...................................................... 127
  5.5 Discussion .............................................................................. 130
    5.5.1 New geometry for thin film rupture ........................................ 130
    5.5.2 Sideways displacement of the bubble ..................................... 132
Chapter 6. Comparison between hydrophilic and hydrophobic collision experiments .................................................. 134
  6.1 Results .................................................................................... 134
  6.2 Discussion .............................................................................. 141
    6.2.1 The sliding speed difference of air bubble under inclined hydrophilic and hydrophobic surface ........................................ 141
    6.2.2 The relationship between the sliding speed and bubble’s surface deformation 144
Chapter 7. Summary and future work .................................................. 147
  7.1 Summary ................................................................................ 147
A new angle on the coalescence of drops

List of figures

Figure 2.1 Conventional SFA for solid-solid interactions. (a) Two cylindrically curved solid surfaces are positioned in a crossed-cylinder geometry; the lower solid is attached to a spring. (b) As the upper solid is driven towards the other surface, the spring (with a spring constant, $k$) gets deflected. The SFA gives the actual surface separation, $h$.

Figure 2.2 Schematic diagram of the SFA of Connor and Horn.

Figure 2.3 Special names of surface deformation of a deformable body: (a) ‘dimple’ shape, (b) ‘wimple’ shape.

Figure 2.4 Schematic diagram of Parkinson’s rising bubble experiment.

Figure 2.5 Shape change of coalescence bubble from left to right, line by line to the bottom.

Figure 2.6 Time resolved shape evolution of the head-on collision of (a) two sheared equal-size drops and (b) two drops with size ratio 0.5.

Figure 2.7 Depiction of the two types of droplet–droplet encounter: (a) head-on-head and (b) shear-induced.

Figure 2.8 3D picture of a gravity driven moving droplet on a solid surface, black arrow: moving direction; red arrow: side view direction; blue arrow: vertical (top) view direction.

Figure 2.9 Simulation results from A: Parkinson et al. and B: Poliščuk.

Figure 2.10 Non-retarded van der Waals interaction free energies between bodies of different geometries calculated on the basis of pair-wise additivity (Hamaker summation method).
Figure 2.11 (a) A schematic representation of the electrical double layer based on the Helmholtz model. (b) Corresponding potential distribution across the interface. $\psi_M$ is the surface potential of the metal and $\psi_S$ is the potential of the solution.

Figure 2.12 (a) A schematic representation of the electrical double layer based on the Gouy-Chapman model. (b) Corresponding potential distribution across the interface.

Figure 2.13 (a) A schematic representation of the electrical double layer based on the Stern model. (b) Corresponding potential distribution across the interface.

Figure 2.14 Geometry of thin film drainage problem where a bubble approaches a solid surface in liquid with a velocity $dD/dt$, where $D$ is the distance of closest approach between the two surfaces; $h(x,y)$ is the local distance between the surfaces.

Figure 2.15 The analysis of any curved surface's extending work.

Figure 2.16 Simulation results of Griggs's study for Simulation results for oblique angle 15 degree and Bond number 3 as well as its contour map.

Figure 3.1 Experimental apparatus schematic diagram of Parkinson et al..

Figure 3.2 Schematic diagram of the experimental set-up used.

Figure 3.3 The tilting table.

Figure 3.4 The optical system.

Figure 3.5 Structure of custom-designed bubble chamber.
A new angle on the coalescence of drops

Figure 3.6 Image of contact angle of glass slide after hydrophobic treatment.

Figure 3.7 (a) Schematic drawing of a hemispherical lens placed on a plane surface. Newton's rings of (b) viewed with monochromatic light and (c) with white light.

Figure 3.8 Image of asymmetric Newton's ring obtained in our experiment. A, original image we obtained, B, image after treatment and C, original image with stripes on it.

Figure 3.9 Schematic diagram of (a) single bubble under a watch glass in distilled water experiment, and (b) the thin film between bubble and watch glass.

Figure 3.10 Top image of single bubble collided with watch glass in distilled water with green light.

Figure 3.11 Top images of single bubble of 1.5mm in diameter collided with watch glass in distilled water with (a) blue light $\lambda=465$nm, $n=1.339$, (b) green light $\lambda=521$nm, $n=1.335$ and (c) red light $\lambda=630$nm, $n=1.331$.

Figure 3.12 Absolute film thickness against fringe radius. Bubble radius = 0.75mm, red symbols for red light ($N_0$ value from 1 to 5), green symbols for green light ($N_0$ value from 1 to 5) and black/white symbols for blue light ($N_0$ value from 1 to 8).

Figure 3.13 Whole profile of the dimple formation of the bubble.

Figure 4.1 Single air bubble approaching tilted hydrophilic solid surface.

Figure 4.2 Important parameters in rising bubble/solid surface system.

Figure 4.3 Important parameters in sliding bubble/solid surface system.
Figure 4.4 Brief procedure of a sliding bubble interacting with a flat hydrophilic microscope glass slide at 0.5° (view from left to right, top to bottom). The central bright spot is caused from the reflection of our microscope and it is present in every image of our original experiment data, it can be removed by image processing as shown in Figure 4.10 and Figure 4.14 later in this chapter. The image brightness and bubble orientation is not the same for every picture because each of them comes from an independent experiment.

Figure 4.5 Number of visible bright fringes we observed as a function of (a) sliding time and (b) distance, both referenced to the bubble’s first approach to the surface.

Figure 4.6 Image of bubble’s top surface in the small bouncing stage (sliding distance 7.5 mm).

Figure 4.7 Contour map of the bubble’s top surface from Figure 4.6 (for all the contour maps the fringe orders are linked to a particular color of data points in the Figure, the correspondence between fringe order number and film thickness is Chapter 3. Sliding distance 7.5 mm).

Figure 4.8 3D map of the thin film plotted from Figure 4.7 (the solid surface is at the bottom in this map and the blue arrow is the bubble’s sliding direction, red symbols in picture A are the original data points in Figure 4.7. Sliding distance 7.5 mm).

Figure 4.9 Inverted 3D picture with faint blue lines indicating the curvature of the bubble outside the dimpled region. The vertical scale exaggerates the apparent curvature of the bubble and its deformation (sliding distance 7.5 mm).

Figure 4.10 Image of bubble’s top surface after it finished bouncing (sliding distance 14 mm).

Figure 4.11 Contour map of the bubble’s top surface from Figure 4.10 (sliding distance 14 mm).

Figure 4.12 3D map of the thin film plotted from Figure 4.11 (the solid surface is at the bottom in
this map and the blue arrow is the bubble’s sliding direction, sliding distance 14 mm).

**Figure 4.13** Inverted 3D picture with faint blue lines indicating the curvature of the bubble outside the dimpled region. The vertical scale exaggerates the apparent curvature of the bubble and its deformation (sliding distance 14 mm).

**Figure 4.14** Images of a later stage of bubble’s top surface after Figure 4.10 (sliding distance 30 mm).

**Figure 4.15** Contour map of the bubble’s top surface from Figure 4.14 (sliding distance 30 mm).

**Figure 4.16** 3D map of the thin film plotted from Figure 4.15 (the solid surface is at the bottom in this map and the blue arrow is the bubble’s sliding direction. Sliding distance 30 mm).

**Figure 4.17** Maximum and minimum film thickness against sliding time and distance.

**Figure 4.18** Bubble’s sliding speed as a function of sliding time.

**Figure 4.19** Bubble’s sliding speed links with thin film profile and bubble’s 3D surface map.

**Figure 4.20** Bubble’s sliding speed as a function of sliding time at different salt concentrations.

**Figure 4.21** Thin film shape of bubbles in different salt concentration liquid with the same sliding speed.

**Figure 4.22** Overview of a sliding bubble/hydrophilic solid surface in 0.5 mol/L sucrose solution whose viscosity is just over twice that of water (view from left to right, top to bottom).

**Figure 4.23** Sliding speed as a function of sliding distance with different viscosities.
Figure 4.24 Image of bubble's top surface in 0.5 mol/L sucrose solution after it finished bouncing (sliding distance: 12 mm).

Figure 4.25 Contour map of the bubble’s top surface from Figure 4.24 (sliding distance 12 mm).

Figure 4.26 3D map of the thin film plotted from Figure 4.25 (the solid surface is at the bottom in this map and the blue arrow is the bubble's sliding direction. Sliding distance 12 mm).

Figure 4.27 Image of bubble's top surface in 0.5 mol/L sucrose solution at a later stage (sliding distance: 25 mm).

Figure 4.28 Contour map of the bubble’s top surface from Figure 4.27 (sliding distance 25 mm).

Figure 4.29 Maximum and minimum film thickness against sliding distance in 0.5 mol/L sucrose solution.

Figure 4.30 Sliding speed as a function of sliding time of bubble in 0.25°.

Figure 4.31 Brief overview of a sliding bubble/hydrophilic solid surface at 0.25° (view from left to right, top to bottom).

Figure 4.32 Image of bubble’s top surface of the longest time we can reach (17 s). The inset shows the same image, rotated and with background intensity subtracted.

Figure 4.33 Contour map of the bubble’s top surface from Figure 4.32.

Figure 4.34 3D map of the thin film plotted from Figure 4.33 (the solid surface is at the bottom in this map and the blue arrow is the bubble’s sliding direction).
A new angle on the coalescence of drops

Figure 4.35 Sliding speed as a function of sliding time of different radii of bubble at 0.5° in water.

Figure 4.36 Sliding speed as a function of sliding distance of different sizes of bubble at 0.5° in water.

Figure 4.37 Interference patterns as a function of sliding distance of different sizes of bubble at 0.5° in water (the vertical stripes in the right-hand series of images are caused by an intermittent fault with our high-speed camera, see Chapter 3 for details).

Figure 4.38 Maximum and minimum film thicknesses against sliding distance for different bubble radii at 0.5° in water.

Figure 4.39 Example of interference patterns and 3D surface map.

Figure 4.40 Dimpling phenomenon of regular (symmetric) Newton’s rings and its cross section shape in the perpendicular collision system.

Figure 4.41 Mirror-symmetric Newton’s rings from our experiment results, and different cross section cuts.

Figure 4.42 Different cross section shapes of the thin film in Figure 4.41 (parallel to x-axis).

Figure 4.43 Cross section shape of the thin film parallel to y-axis in Figure 4.41. Insert picture is the image of cross section of drop shape from Griggs et al..

Figure 4.44 Thin film deforming process for the toboggan profile.

Figure 4.45 Bubble’s final sliding speed we measured compared to Castillo’s results.
A new angle on the coalescence of drops

**Figure 4.46** Steady drop shape shown as cross-section in the plane of symmetry, drop-to-medium viscosity ratios =0 (dotted), 1 (solid) and 5 (dashed).

**Figure 4.47** Comparison of bubble’s top surface images between 0.5 mol/L sucrose solution (A) and water (B) at 0.5°.

**Figure 4.48** Cross section parallel to x-axis of bubble in 0.5 mol/L sucrose solution.

**Figure 4.49** Cross section shape of the thin film parallel to x-axis in Figure 4.48.

**Figure 4.50** A bubble at different stages in the same experiment running (hydrophilic solid surface, 0.5°, water). Image B is taken 0.16 seconds later than image A.

**Figure 4.51** Comparison of middle bright fringes (position) in Figure 4.50.

**Figure 4.52** Schematic picture of a rolling bubble.

**Figure 4.53** Comparison of edge bright fringes (shape and position) in Figure 4.50.

**Figure 5.1** Procedure of single air bubble colliding with hydrophobic glass slide in water at inclined angle of 0.5°.

**Figure 5.2** Bubble’s top image 5 ms before the film rupture started (sliding distance 3 mm).

**Figure 5.3** Contour map of the bright fringes in Figure 5.2 (sliding distance 3mm).

**Figure 5.4** 3D map of the thin film plotted from Figure 5.3 (the solid surface is at the bottom in this map and the blue arrow is the bubble’s sliding direction, sliding distance 3 mm).
Figure 5.5 Example of the first touch point.

Figure 5.6 First touch points spreading map of 0.5°, blue symbols refer to naturally coalescence, green symbols refer to the cause of dirt and black symbol refers to unexpected coalescence.

Figure 5.7 Bubble’s top image of the first touch point stage of 1°, and the points spreading map of 1°

Figure 5.8 Bubble’s top images of the stages a) 5 ms before thin film rupture happened, b) thin film completely ruptured and c) the two ‘contact’ areas before and after rupture has fully progressed, overlaid on the same scale (red dashed line: original interference area, red line: final contact area, blue dot: where thin film rupture started).

Figure 5.9 Schematic pictures of bubble’s contact area spreading process during the thin film rupture (dashed red line: original interference area, dotted arrows: spreading direction, dark area: contact area in the stages, dashed dark line: contact area of the previous stage, red line: final contact area).

Figure 5.10 Thin film geometry of a) plane, and b) dimple.

Figure 5.11 ‘Toboggan’ geometry of the thin film.

Figure 5.12 Possible rupture points for a) plane geometry and b) dimple geometry.

Figure 6.1 Bubble’s sliding speed versus sliding time along hydrophilic and hydrophobic solid surfaces at an inclined angle of 0.5° in water.

Figure 6.2 Bubble’s sliding speed versus sliding time along hydrophilic and hydrophobic solid surfaces at inclined angle of 1° in water.
A new angle on the coalescence of drops

Figure 6.3 Bubble’s sliding speed versus sliding time along hydrophilic and hydrophobic solid surfaces at inclined angle of 2° in water.

Figure 6.4 Bubble’s sliding speed versus sliding time along hydrophilic and hydrophobic solid surfaces at inclined angle of 0.5, 1 and 2 degrees in water.

Figure 6.5 Newton’s rings observed at points a), b), c) and d) in Figure 6.4. Inclined angle value a), b) and d) are 1°, c) is 2°. The sliding speeds are the same between a) and b), and also between c) and d). (The vertical stripes are an artefact resulting from an intermittent fault in the high speed video camera, which has been discussed in Chapter 3)

Figure 6.6 Bubble sliding speed versus sliding distance along hydrophilic and hydrophobic solid surfaces at inclined angle of 0.5, 1 and 2 degrees in water.

Figure 6.7 The speed profile for no-slip (a) and slip (b) boundary conditions.

Figure 7.1 Structure of the cylinder tube system.

Figure 7.2 The advantages of the cylinder tube compared with microscope glass slide.

Figure 7.3 Images of bubble’s top surface against cylinder tube surface (a, big bouncing step; b, sliding step).

Figure 7.4 Process of off-centre collisions air bubble with each other in water (viewing from left to right, top to bottom).
List of tables

Table 3.1 Fringe order number and the film thickness it represents (red light, wavelength 630 nm, refractive index 1.331)

Table 4.1 Standard experiment parameters (light source: red light, 630 nm wavelength).

Table 5.1 Sliding time, contact spreading time (i.e., the time between initial film rupture and air-solid contact area reaching its maximum size) and sliding distance, for observations of seven times of natural rupture of the thin film.

Table 5.2 Sliding time, contact spreading time and sliding distance of a single observation at inclination of 1°.

List of symbols

\( k \) spring constant
\( q \) shape parameter
\( F_{\text{vdW}} \) van der Waals forces
\( F_{\text{EDL}} \) electrical double layer forces
\( A \) Hamaker constant
\( D \) distance
\( R/r \) Radius
\( W_{\text{vdW}} \) van der Waals interaction free energy
\( \rho \) Density
\( \kappa \) Debye-Huckel parameter
\( \psi \) surface potential of two surfaces
ψ_M \quad \text{surface potential of the metal}

ψ_S \quad \text{potential of the solution}

h \quad \text{thickness}

a \quad \text{acceleration}

m \quad \text{mass}

u \quad \text{velocity}

t \quad \text{time}

ρB \quad \text{total long-range force acting per unit volume}

B \quad \text{body force}

∇p \quad \text{local gradient of the pressure}

η \quad \text{viscosity of the fluid}

\eta \nabla^2 \quad \text{the viscous forces acting on the element of volume of the fluid}

V \quad \text{velocity of the upper body with respect to the lower body}

γ \quad \text{surface tension}

Δp \quad \text{pressure difference}

g \quad \text{acceleration due to gravity}

σ \quad \text{interfacial(surface) tension}

Ca \quad \text{Capillary number}

λ \quad \text{wavelength}

n \quad \text{refractive index}

U_t \quad \text{terminal speed}

K \quad \text{constant depending on the properties of the fluid}

θ \quad \text{inclination value}
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFA</td>
<td>Surface force apparatus</td>
</tr>
<tr>
<td>IEP</td>
<td>Isoelectric point</td>
</tr>
<tr>
<td>DLVO:</td>
<td>Derjaguin, Landau, Verwey and Overbeek</td>
</tr>
<tr>
<td>vdW</td>
<td>Van der Waals</td>
</tr>
<tr>
<td>EDL:</td>
<td>Electrical double layer</td>
</tr>
<tr>
<td>HHF</td>
<td>Hogg-Healy-Fuerstenau approximation</td>
</tr>
<tr>
<td>MASIF</td>
<td>Measurement and analysis of surface interaction and force</td>
</tr>
<tr>
<td>AFM:</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>EHD</td>
<td>Elasto-hydrodynamic</td>
</tr>
<tr>
<td>PHD</td>
<td>Plasto-hydrodynamic</td>
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Abstract

A sound understanding of drops or bubbles interacting with another solid surface can be very helpful in many areas such as agricultural spraying, inkjet printing, spray coating, fuel injection in internal combustion engines, drug formulation, aerosol drug delivery, multiphase flow and others. For example, agricultural spraying wants the pesticide drops to stay with plants as long as possible, inkjet printing requires ink drops to absorb to paper quickly and uniformly, multiphase flows frequently want phases to remain dispersed by avoiding drop or bubble coalescence. All these phenomena require basic study of drop (bubble) and surface collisions. However, currently the vast majority of investigations into drop and bubble collisions have considered only head-on collisions between drops (bubbles) or perpendicular approach of drops (bubbles) to surfaces. These investigations are only the first step toward helping industry to develop a better system because drops (bubbles) in our real world are overwhelmingly more likely to collide with each other or with surfaces at random angles, and there are very few detailed investigations into the effects that non-perpendicular approach angles will have. This project has developed a new experiment with single bubbles rising vertically to non-horizontal solid surface so the collision occurs at oblique angles, observed by looking directly at the bubble’s top surface. The true thin film deformation details were obtained by analyzing the Newton’s rings shown in the images recording from the top. The effects of parameters including liquid viscosity, salt concentration, inclination value, bubble size and solid surface hydrophobicity on the thin film drainage process have been studied.
Acknowledgement

This could be my easiest section to write all through this thesis. To be honest, I have suffered a really tough time when I was writing up this thesis, anxiety and disgust filled up my mind especially after my grandpa (mum’s dad), grandma (dad’s mum) and a friend of mine (Mr. Stan Shaochuan Chen) have passed away continuously in early 2015. I have got a lot of people to appreciate here because without their help and encouragement I would not be able to hold this on, thanks again everyone.

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Chapter 1 Introduction

1.1 Background

Drops and bubbles are everywhere in the world and play a major role in the exchange of mass and heat between the oceans and the atmosphere. Surfaces are obviously everywhere in the world as well. Therefore, the coalescence between drops (bubbles) and other surfaces is happening everywhere and every minute in our world: we can observe those collisions when rain droplets fall and hit your vehicle’s front window, when dishwashing liquid creates bubbles; we can even feel those collisions when we forget our umbrella during a sudden rain, when we use shampoo or body wash during showering time, or when we open a shaken Coke by accident.

It is a platitude but we have to say here, the behavior of drop (bubble) interactions and how they are influenced by other factors are still not fully understood. The vast majority of previous investigations have considered only head-on collisions between drops (bubbles) or perpendicular approach of drops (bubbles) to surfaces. However, when it comes to drops or bubbles approaching other surfaces at an angle, or approaching each other off-centre, there are very few detailed investigations into the effects that non-perpendicular approach angles will have. Considering that drops (bubbles) in our real world are overwhelmingly more likely to collide with surface at different angles, the study of drops or bubbles approaching other surfaces at angle is important in many practical applications including agricultural spraying, inkjet printing, spray coating, fuel injection in internal combustion engines, drug formulation, aerosol drug delivery, and many others.
1.1.1 Drop collision

Tryggvason\(^1\) in his book described the drop collision as ‘a spectacular impact that symbolizes the beauty and fascination of fluid mechanics’. The studies and simulations of drop collisions in two-dimensional and axisymmetric systems dates back to very early times of two-phase flow simulation, however, those of fully three-dimensional simulations of drop collisions only became possible to perform experimentally and analyze theoretically in recent years and it remains difficult to perform realistic simulations of real world situations or even of laboratory experiments.

Drop collisions are significantly critical in fluid flow, emulsions and a number of other research fields, which leads to major industrial interest in impacts of drop collision. In one important application, fuel drops collide with the walls of pipes and combustion chambers, there they may either spread and form thin films or break into a spray of smaller drops. Metallurgy could be another application of drop collisions in industrial processes\(^1\). In the agriculture area, the erosion of rain on soil, the spraying of pesticides on plants and the irrigation system all involve the collision of drops.

Given the vital roles of drop collision in research and industry applications, the behavior of drops when they are colliding with another solid surface is an important topic for investigation and understanding.

1.1.2 Bubble collision

The interactions of drops with surfaces and bubbles with surfaces are quite similar in principle, and the same experimental techniques can be applied to investigate interactions of both drops with surface and bubbles with surfaces, so reference to ‘drops’ in this thesis should generally be taken to include ‘bubbles’.
'There are few physical objects as beautiful or as fascinating as a bubble', said George Porter of The Royal Institution London. Generally speaking the significance of bubble collision with other materials is also considerable, for example in natural system, such as oceans and rivers, industrial products such as foams in fire-fighting, foods, separation processes for recycled plastics and mineral flotation, multiphase (bubbly) flows, carbonated beverages, etc.

To understand their behavior in order to control and optimize the processes involving bubbles, the study of their interactions with each other and with other surfaces is interesting and as important as studying drops.

1.2 Research significance

To date, the vast majority of investigations into collisions involving drops or bubbles, whether they are theoretical models or experimental measurements, have investigated collisions at normal incidence (these will be presented in detail in Chapter 2). That is, drops colliding with a surface are assumed to do so in the direction perpendicular to the surface, or two drops colliding with each other are assumed to approach along the line joining their centres. These simplifications are made by physicists or mathematicians to make their investigations tractable. But drops in the real world are overwhelmingly more likely to collide with surfaces at angles other than the perpendicular, or to approach each other obliquely and experience glancing collisions. There is clearly a need to study drop collisions under these more realistic conditions, and there are very few detailed investigations into the effects that non-perpendicular approach angles will have.

Although those perpendicular investigations of drop and bubble coalescence are obviously too ideal for the realistic world, the methods that have been employed or developed to study drop or bubble colliding with another solid surface have provided...
A new angle on the coalescence of drops

enough basis for further studies of collision in non-perpendicular directions or coalescence in sheared directions.

1.3 Research aims

Based on the current understanding of perpendicular collision investigations and for the purpose of addressing the lack of knowledge by conducting experiments at the level of thin film drainage between a drop and a wall when they collide at an oblique angle, this proposed project has got the following three main aims:

1. Devise an experiment to investigate thin film drainage between a drop or bubble approaching a flat solid surface at an oblique angle.
2. Compare the film drainage rate and the drop (or bubble) deformation with literature results for perpendicular approach.
3. Study the influence of different parameters (viscosity, salt concentration, inclination, bubble size and surface hydrophobicity) to the film drainage process in oblique system.
Chapter 2 Literature review

2.1 Experimental measurements

Previous investigations have used a variety of methods to study bubbles and drops, I am going to review some of the methods that either provide the basic idea to this project or contain qualitatively similar results with ours in this section.

2.1.1 Surface force apparatus

The surface force apparatus (SFA) is an instrument that can measure surface-surface interactions. The first SFA was designed by Tabor, Winterton and Israelachvili\(^3,4\) in the early 1970s at Cambridge University, and this development has had great impact on studies of surface interactions in the decades since then. The original version of SFA helped Tabor\(^3\) to investigate van der Waals forces in air between two cylindrical sheets of mica with their axes mutually at right angles. This method was extended from air environment into vacuum environment and the van der Waals dispersion forces between curved mica surfaces in the range 1.5 to 130 nm were successfully measured\(^4\). Further studies with SFA were carried out by Israelachvili\(^5\) to describe the shear properties of stearate monolayers and multilayers trapped between curved mica surfaces. Later, Israelachvili and Adams\(^6\) developed a modified version of SFA called ‘SFA Mark I’, which allowed the measurement of forces between surfaces immersed in a liquid environment, and from this original version many modern variants of the surface force apparatus have emerged.
A new angle on the coalescence of drops

Figure 2.1 Conventional SFA for solid-solid interactions. (a) Two cylindrically-curved solid surfaces are positioned in a crossed-cylinder geometry; the lower solid is attached to a spring. (b) As the upper solid is driven towards the other surface, the spring (with a spring constant, $k$) gets deflected. The SFA gives the actual surface separation, $h$.

Figure 2.1 shows the very early version of SFA of Tabor and Israelachvili. As described above, the interacting surfaces were two thin molecularly smooth mica sheets with cylindrical shape. These two cylindrical mica sheets were aligned orthogonally to produce the crossed cylinder geometry. One main advantage of this shape designing was that, if the contact point between mica sheets became contaminated, a new contact point could be easily found by shifting one of the surfaces relative to the other. The Derjaguin approximation was employed and proved to be very suitable for their SFA experiments.

Knowing the distance between surfaces is critical for understanding surface-surface interactions. The SFA was designed to give a direct measurement of the minimum distance between the surfaces (the surface separation) using interferometry or fringes of equal chromatic order (FECO), which is considered to be one of the most

Ninghui Han  Sep 2016
significant features of the SFA. For this purpose, 95% reflecting thin silver layer forming partial mirrors were deposited onto the outer surfaces of each mica sheet before experiments. With this arrangement, white light underwent multiple reflections and was then directed into a spectrometer which splits up the wavelengths and allows the FECO fringes to be observed. The surface separation can be simply calculated as long as the wavelengths of the light source are measured.

Since then, the SFA has successfully been extended to perform dynamic measurements, thereby determining viscous and viscoelastic properties of fluids, frictional and tribological properties of surfaces\textsuperscript{13, 14} and even the time-dependent interactions between biological structures.

Mica sheets were used for just the initial studies of the surface-surface interaction carried out by SFA. More recently, solid surfaces other than mica have been studied, either by of modifying the surface of the mica\textsuperscript{5, 6}, or by replacing mica with other surfaces\textsuperscript{15-18}. Silica was considered to be a good study target, at the beginning only of sheet of solid in the SFA was replaced by silica and once the mica and silica had a non-sliding contact in dry nitrogen environment, the strong attraction force due to the spontaneous transfer of electrical charge was tested\textsuperscript{16}. Then the other sheet of mica was replaced into silica logically\textsuperscript{15, 17}. Sapphire was also employed to replace mica in the SFA\textsuperscript{18}.

The SFA has also been adapted to study fluid interfaces. Horn\textsuperscript{19-24} and his group have extended the SFA method to the study of collisions between drops or bubbles and surfaces for several years. A unique experimental facility was developed by Connor and Horn\textsuperscript{20, 21} based on SFA techniques. In Connor’s\textsuperscript{20, 21} studies, mica was still chosen as the solid surface for its good physical and chemical stability, however, different from Israelachvili’s\textsuperscript{4-6} studies, the second solid mica surface was replaced by a liquid mercury drop surface. This allowed investigation of the surface deformation by surface
interactions. In addition, the mica surface was not curved any more but smoothly flat. Figure 2.2 shows how the version of the SFA extended by Connor and Horn works\textsuperscript{20, 21}. The bottom surface is a spherical deformable mercury drop, and the upper surface is the flat mica sheet with a partially reflective silver layer on the backside. In this SFA set-up there is no spring, however, the drop deforms in response to an applied force, so in a sense it provides its own spring. The analysis of this experiment relied on FECO to measure the water film thickness and the mercury drop deformation against approach time was obtained.

![Schematic diagram of the SFA of Connor and Horn\textsuperscript{20, 21}.](image)

Connor and Horn’s\textsuperscript{20, 21} experiments were first conducted in pure water environment and then extended to an aqueous electrolyte solution of 0.1mM KCl in which mica’s surface potential is -100mV. An interesting “dimple” surface deformation (Figure 2.3 a) of the mercury drop was observed as the mercury drop (with an applied potential of -483 mV) was approached by mica: as a result of the combination of repulsive hydrodynamic disjoining interaction and electrical double layer, firstly the mercury
drop was flattened and a concave region began to form from the center top of the drop, then the drop flattened out again with the thin film drainage process going on until a stable film was formed preventing further approach of the two surfaces.

Figure 2.3 Special names of surface deformation of a deformable body: (a) ‘dimple’ shape, (b) ‘wimple’ shape.

By applying an opposite potential to the mercury drop, the case of repulsive interaction between the mica and the mercury drop could be turned into attractive interaction, and both the repulsive and attractive disjoining pressure can be controlled either strongly or weakly. Details of these developments were reported by Manica et al.\textsuperscript{23}. The dimple shape of the mercury drop was deformed for both repulsive and attractive cases, but the size and deformation time were different for different surface charge conditions, and finally the evolution of dimple to a flat stable film or the collapse of an unstable film depended on whether the interaction was repulsive or attractive between mica and mercury surfaces. A mathematical model developed by Manica et al.\textsuperscript{23} to explain those observed profile changes of mercury drop showed they are in good agreement with the profile changes predicted by a model having three ingredients: hydrodynamics (Reynolds Lubrication Theory), interface curvature (Young-Laplace Equation), and double layer disjoining pressure (Poisson-Boltzmann Equation) to account for surface forces.
‘Dimple’ is not the only surface curvature that caused by hydrodynamic pressures in a thin draining liquid film. Clasohm et al.\textsuperscript{22} reported a different shape, dubbed a ‘wimple’ (Figure 2.3 b), formed between a mercury drop and a mica surface with the modified SFA. This case of curvature happens, when a fluid drop, which is already in the field of repulsive surface forces, is abruptly pushed toward the solid surface. The wimple curvature includes a central region in which the film remains thin, surrounded by a ring of greater film thickness that is bounded at the outer edge by a barrier rim where the film is thin. This shape later evolves into a conventional dimple bounded by the barrier rim, which then drains to a stable thin film (repulsive disjoining pressure). Tsekov and Vinogradova\textsuperscript{25, 26} obtained analytical estimates about wimpling for characteristic times of different stages of film drainage and were shown to be in good agreement with Clasohm and Horn’s\textsuperscript{22} experimental data. Therefore they demonstrated that wimpling is a general phenomenon that can be encountered in many different systems.

The extended version of the SFA by Connor and Horn\textsuperscript{20, 21} made it possible to explore interactions between a solid and deformable bodies in liquid media systems, and the mercury drop could be replaced by other deformable bodies for alternative investigations. Those deformable bodies were bubbles\textsuperscript{27, 28} and oil drops\textsuperscript{23}. However, the quality of the fringes depends on the reflectivity of the surfaces, therefore, the surface separation resolution is not as good for air-water and oil-water systems as it is for highly reflective mercury.

Pushkarova and Horn\textsuperscript{27, 28} investigated an air bubble approaching mica surface using the same version of the SFA instrument and similar experimental methods. It was observed that if the mica is driven very slowly (in a series of 200 nm steps, one step every 10 s) to the bubble, the bubble starts to flatten at around 70 nm separation but continues to approach the mica with an intriguing profile change: changing from curved to flattened and then, unlike the mercury drop where the end result is a
flattened drop, the bubble surface changed back to curved again until it reaches its final separation. This study was extended by Del Castillo and Horn\textsuperscript{7,29}, with the profile of a fixed bubble as the mica approaches the bubble in liquid at varying speeds being recorded, and the effect of salt concentration in the medium was also studied.

Although the SFA has been invented and optimized for many years, the main limitation of it is still the materials required. Traditional optical interferometry method (FECO) for SFA requires transparent surfaces or at least one transparent surface and the other reflective surface. New methods have been applied in SFA like capacitance or piezoelectric bimorph sensors to allow the investigation of a wider range of surfaces\textsuperscript{30}.

2.1.2 Rising and sliding bubble experiments

The study of the motion of air bubble in liquids has received much attention for many years due to its fundamental and practical importance. One common method is to observe single rising bubble. These studies mainly include the effects of viscosity\textsuperscript{31}, velocity\textsuperscript{32,33}, and viscoelasticity\textsuperscript{34} in different liquids from water to polymer solution\textsuperscript{35}. During the rising process of an air bubble, the dynamics of rising bubbles depends primarily on surface tension and the Reynolds number\textsuperscript{34}. However, when that rising bubble collides with another surface at the end, different factors enter the balance between the driving force pushing them together and the opposing forces keeping them apart. Since the study of the hydrodynamic process of interaction between a rising bubble and another surface is important in many industrial processes such as flotation, food processing etc., it is obviously important to measure experimentally the performance of single rising bubble colliding with another solid surface in liquid system.

When a single rising bubble approaches a flat solid surface in liquid, the system consists of the rising bubble, the solid surface, and the thin film between them. How the thin film drains and whether or not the thin film rupture have a direct influence on
the bubble/surface collision. About 100 years ago, scientists began to realize the importance of thin films and the earliest experiment on thin film stability was carried out by Derjaguin and Kussakov\textsuperscript{8} in 1939. Derjaguin\textsuperscript{8} observed that there was an equilibrium thickness of the thin film between a rising air bubble and a flat hydrophilic glass surface, and once the critical thickness of the thin film was reached there would be no rupture, hence no coalescence of the bubble with the surface. That film thickness was of very small range so that the film was described by Derjaguin as ‘thin polymolecular film’.

Although the rising bubble was always the simplest air bubble, the solid surface and the liquid type could be easily changed for different experimental measurements. The first quantitative measurements of the thin film thickness in rising bubble experiments were done by Platikanov\textsuperscript{36} using a silica surface. Read and Kitchener\textsuperscript{37, 38} continued the study of rising bubble and silica surfaces in solutions of several electrolytes including potassium chloride, barium chloride, lithium chloride etc.. These authors\textsuperscript{37, 38} indicated that electrostatic interactions are responsible for thin film stability at separations greater than 20 nm.

Hydrophobic surfaces have also been investigated in rising bubble experiment. Schulze\textsuperscript{39} reported that the stability of the thin film can be affected by the degree of surface hydrophobicity, the higher the contact angle was, the larger the critical thickness and the shorter lifetime of the film were. Another study was by Krasowska and Malysa\textsuperscript{40} who observed the collision of an air bubble rising in clean water with hydrophobic Teflon plates. By keeping every other parameter constant, Krasowska and Malysa\textsuperscript{40} indicated that the only varying parameter, the surface roughness of the Teflon plates, was of crucial importance for the attachment time of the colliding bubble. They also found that the high hydrophobicity of the solid surface is a necessary but not sufficient condition for immediate bubble attachment. Niecikowska et al.\textsuperscript{41} got a similar result that in the case of highly hydrophobic solid surfaces, the effect of surface
hydrophobicity was negligible and surface roughness was the key factor determining the kinetics of the thin film rupture between a rising bubble and a solid surface.

When an air bubble is rising in aqueous system, the buoyancy, combined with Laplace pressure and the Reynolds number have an influence on the final collision with solid surfaces. However, if the size of the rising bubble goes down to a very small value, the small buoyancy and the very small Reynolds number will minimize bubble deformation. Parkinson\textsuperscript{42} developed a novel experiment device (shown in Figure 2.4) which allowed a very small air bubble (15 to 120 μm) to approach a hydrophilic titania surface. This development made the rising bubble ideal for making measurements of both the thin film drainage process and the disjoining force between the bubble and solid surface. Nieckowska’s\textsuperscript{41} recent study confirmed that the time of thin film drainage decreased with the bubble diameter.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Schematic diagram of Parkinson’s rising bubble experiment\textsuperscript{42}.}
\end{figure}

Electrolyte selection is significant in a rising bubble experiment, and the effect of electrolyte type, concentration, ionic strength and pH have been studied for many years. Parkinson’s\textsuperscript{42} experiments were conducted in 0 to 10\textsuperscript{-1} mol/L aqueous KCl or (CH\textsubscript{3})\textsubscript{4}NBr at pH 3.5 or pH 6.3, and he indicated that the bubble boundary condition transition from full-slip to no-slip in the absence of surfactant contamination was

\textit{Ninghui Han} \hspace{1em} \textit{Sep 2016}
depend on electrolyte pH, ionic strength and thin film thickness. The isoelectric point (IEP) of the surface is also very important because Niecikowska recently found out that for pH values below the IEP the time of thin film drainage was significantly shorter than for pH values above the IEP.

The previous literature on rising bubble collision experiments has provided us plenty of acceptable methods for this proposed project, and the design of our experiment device is an extension of Parkinson’s rising bubble experimental set-up. However, the most significant difference between that our experimental device and Parkinson’s is that we tilt the upper surface at a fixed angle. This means that the bubble collides at an oblique rather than perpendicular angle, and in general it causes bubbles to slide along our target solid surface under liquid environment after rising and colliding. Therefore, the behavior of bubble sliding along surface is critical to our project as well. More details for the proposed project’s experimental set-up can be found in Chapter 3.

As mentioned previously, the study of the motion of air bubbles in liquids has been studied a lot, and measurements of a single or multiple sliding bubbles along inclined surfaces in liquid have been reported under various experiment conditions. The effects of bubble size, bubble shape and value of angle have been investigated.

An very early experiment on sliding bubbles dates from 1966, when Zukoski performed air bubble sliding experiments in closed tubes with water, but his bubbles were large and elongated which made the propagation complex so that he actually found that the bubble’s sliding velocity decreased for angles beyond 45°. Zukoski also reported the significance of surface tension in the system of bubble sliding. Weber & Alarie did experiments on air bubbles in different liquids with different sizes of inclined circular tubes, they also agreed that when surface tension dominated, bubbles did not move. Maxworthy tried bubble sliding experiments in a high Reynolds
number (Re) system with water. He indicated that larger bubbles rose faster, and those bubbles’ sliding velocity increased with the angle value getting larger until a maximum sliding velocity happened near a critical angle of 50°, which was consistent with Zukuski’s study. Chen also reported that with increasing bubble size, the terminal sliding velocity increased as well.

All the above sliding bubble experiments were employing large bubbles. Millimeter size bubbles sliding were first studied by Masliyah et al. In their experiments water-glycerol solutions were employed to provide Re from low to intermediate value, and their bubbles’ radius was no more than 1.5 mm. Results came out differently from what had been studied before, with no critical angle value found in the experiments, and the bubbles’ sliding velocity kept increasing as the angle increased. Tsao & Koch continued the experiments on sliding bubbles with mm size and they found an angle value that separated sliding and repeated bouncing of those air bubbles.

Solutions other than just water were tested with air bubbles too. Cavanagh & Eckmann mixed water with the surfactant SDS (sodium dodecyl sulphate) and they observed that bubbles made direct contact with the tube wall. They also indicated that the effects of surfactants on the motion and detachment of bubbles are critical, the addition of surfactant can lead to a stuck bubble being detached from the tube wall and returning to a flattened shape. Aussilous & Quere did sliding bubble experiments without water, they employed silicone oil to take the place of water and the angle value they investigated was also very small (0.7° to 5.7°) compared to the experiments above. They found out that in the air bubble/silicone oil system, the presence of a lubricating film implied non-trivial laws for the viscous dissipation.

Castillo studied the terminal velocities of single air bubbles sliding along the underside of an inclined glass surface with water and KCl solutions. The effects of bubble size, angle of inclination, and salt concentration on the bubble’s terminal
velocity were recorded. She indicated that under a very small angle range (1° to 5°), the bubble’s terminal velocity is not only influenced by the bubble size and angle of inclination, but also by the salt concentration of the media, this means that the disjoining pressure due to double-layer interaction can influence the terminal velocity of a sliding bubble due to salt concentrations has negligible effects on solution density and the surface tension.

### 2.1.3 Coalescence experiments

Coalescence between a pair of drops or bubbles is a common phenomenon in natural systems such as rain-drop formation in clouds. Over a hundred years the coalescence of drops and bubbles has been studied for a wide variety of applications including transportation processes in industry, environment engineering, and energy systems.

A detailed review of the experimental studies aiming at dynamic of drop coalescence was provided by Ashgriz and Poo\textsuperscript{59}. In this review Ashgriz\textsuperscript{59} classified the outcome of drop collision into four different types: bouncing, coalescence, separation and shattering collisions\textsuperscript{59} Bouncing happens when the surrounding fluid prevents the two drops from touching. Coalescence occurs in the case where two drops combine and become one drop. Separation and shattering collision are the consequences of higher impact energy collisions\textsuperscript{60}.

Water drops could be a good starting point for coalescence experiments\textsuperscript{61, 62}. Very early experiments by Foote\textsuperscript{61} provided a marker-and-cell method to measure equal-size water drops in the head-on direction. Another method was developed by Poo and Ashgriz\textsuperscript{62} called volume-of-fluid based method to study the coalescence dynamics of two drops in two-dimensional Cartesian coordinate system. Pine and Leal\textsuperscript{63} studied the breakup and coalescence of polybutadiene drops in polydimethylsiloxane, in their studies both head-on collisions and collisions with a finite offset from the inflow axis.
A new angle on the coalescence of drops

for several different flow types produced in the four-roll mill\textsuperscript{64}. Leal's experimental results\textsuperscript{63-66} have been compared with theoretical investigations such as Baldessari’s\textsuperscript{67} study of simulations of the hydrodynamic collision and coalescence of two drops in linear flows. Leal has also reported boundary integral simulations of the flow-induced head-on coalescence of a pair of equal size drops in an axisymmetric extensional flow\textsuperscript{68}.

Many studies have been undertaken in recent years with different kind of drops in different liquid systems\textsuperscript{69-74}. Nobari et al.\textsuperscript{69} used a front tracking method to measure the head-on approach of two drops, this study mainly focused on the boundary between coalescence and bouncing. Cărjan et al.\textsuperscript{70} developed a nuclear-reacting dynamic model and Menchaca-Rocha et al.\textsuperscript{71} used it to simulate the coalescence of mercury drops. Ban et al.\textsuperscript{75} observed a time evolution of coalescence for toluene drops formed in water environment. Liao et al.\textsuperscript{72, 73} experimentally studied coalescence of drops on a horizontal homogeneous surface and reported the effects of drop size and hydrophobicity. These studies all chose or developed suitable theoretical models to support their experimental results, however, there were also several investigations that were less successful in fitting theory to data, such as Riebner and Frohn\textsuperscript{74} who reported that in their study of drop collision and coalescence process, those numerical models were not able to describe the observed collision behavior.

As presented in the introduction chapter, the interactions of drops and bubbles are quite similar in principle. Therefore besides drop coalescence studies, there have also been many investigations into bubble coalescence in different situations that have been reported recently\textsuperscript{76, 77}. Wang\textsuperscript{76} reported that in the inviscid and incompressible fluid flow regime, surface tension played a significant role when two spherical and equal-size rising bubbles coalesce with each other. Sanada et al.\textsuperscript{77} studied a pair of slightly deformed bubbles rising side by side in silicone oil and water, and the shape change of coalescence bubbles is shown in Figure 2.5. In this study\textsuperscript{77}, a decrease of the rise velocity was observed after coalescence happened.
The above studies include drop coalescence and bubble coalescence, and they all have one thing in common: the size of the coalescing pair of drops or bubble is equal or essentially equal. However, we all know that these kinds of coalescence are not always happening in nature, and the approach and coalescence of drops or bubbles with different size also needs to be studied. Mashayek and Ashgriz studied drop coalescence with two different size liquid drops approaching to each other and the difference of that compared to same size liquid drops can be seen in Figure 2.6.
Figure 2.6 Time resolved shape evolution of the head-on collision of (a) two sheared equal-size drops and (b) two drops with size ratio 0.5\(^6\).

In fact, most of the studies including experimental measurements and theoretical models have investigated drops or bubbles coalescence and collision in the simplest direction, that is, drops or bubbles approaching each other along a line joining their centres (also called ‘head-on’ direction) or a drop or bubble colliding with a solid.
A new angle on the coalescence of drops

surface perpendicularly. Based on techniques and mathematic models of the current perpendicular direction’s studies, several oblique experiments have been reported.

In the case of coalescence, the oblique or off-centre direction is normally called ‘shear-induced’ coalescence. Its direction is shown in Figure 2.7.

![Figure 2.7 Depiction of the two types of droplet–droplet encounter: (a) head-on-head and (b) shear-induced.](image)

Yeung et al.\textsuperscript{78} mentioned in their study of shear-induced coalescence of emulsified oil drops that oblique approach of oil drops could result in faster and more efficient coalescence compared to head-on approach. Other shear-induced coalescing studies were not only about two drops but a number of drops coalescing obliquely\textsuperscript{79–81}, such as shear-induced coalescence in polymer blends\textsuperscript{79}, in aqueous biopolymer mixtures\textsuperscript{80} and in oil-in-water Pickering emulsions\textsuperscript{81}.

For oblique collisions with surfaces, there are very few detailed studies reported until now. The only investigation of a similar situation was a 45° oblique collision of a water drop with a smooth solid surface in air\textsuperscript{82}. However, Fujimoto and Takuda\textsuperscript{82} in this study mainly focused on the physics of phenomena occurring on the solid surface just after collision. They pointed out that entrapment of air between the drop and the solid
surface occurs for all cases and the approaching velocity determined whether or not the satellite bubbles formed.

The lack of investigation of oblique conditions of drop or bubble collision provides the research significance of the proposed project, and this proposed project will be the first study of thin film drainage and drop coalescence processes occurring at the sub-microscopic scale in oblique collisions.

### 2.1.4 Rolling and sliding arguments

When it rains, we see water droplets moving down windows and other solid surfaces. The motion of such a droplet is quite different from that of a solid object with the same shape and size. For solid objects moves down an oblique solid surface, the way a spherical object like a tennis ball moves is defined as ‘rolling’, while the way a cuboid object like a book moving is known as ‘sliding’. But that issue turns into a complex way when the moving object is not solid but liquid droplet or liquid/gas bubble. Thampi et al.\(^8\) pointed out that the way a liquid droplet moves along a solid surface could be either sliding or rolling, or a combination of the two. The question is, is there a key determinant that decides the way a liquid droplet moves along solid surface?

Surface hydrophobicity was considered as one of the key issues that determine the way a liquid droplet moves. A completely rolling motion of liquid droplets was observed on superhydrophobic surfaces\(^8\). At the same time, experimental investigations on hydrophilic surfaces showed a sliding motion of liquid droplets\(^8\). However, there was another idea that the size of the droplet was also very significant based on an anomalous increase in the speed of very small drops observed. Mahadevan and Pomeau\(^8\) showed a size independent velocity of large pancake drops sliding on non-wetting surfaces, so that they indicated that the stronger dependency of size on viscous losses compared to the driving body forces resulted in smaller
droplets moving with very high velocities, and when it came to very large droplets, the velocity would be independent of droplet size.

A lot of studies have been reported for liquid drop motion on both hydrophilic\textsuperscript{86-88} and superhydrophobic\textsuperscript{84, 85} surfaces due to simplifications possible in those situations, and complete sliding/rolling were observed for these two conditions respectively. For contact angles between superhydrophobic and hydrophilic, mostly around 60 to 150 degrees, the liquid droplets’ motion was a combination of rolling and sliding. Thampi et al.\textsuperscript{83} indicated that in this case, for given viscosities and slip length, the only parameter that determined the proportion of rolling to sliding was a shape parameter, which told us how far away from circular the drop cross section was. For any given viscosity and slip length, this shape parameter was decided by the combination of contact angle and oblique angle value that the solid surface was tilted. Thampi et al.\textsuperscript{83} gave the equation for calculating this shape parameter $q$:

$$q = \frac{4\pi \times \text{Area}}{\text{Perimeter}^2}$$  \hspace{1cm} (2.1)

The name of this shape parameter $q$ is isoperimetric quotient. Thampi found out that droplets with different shape but the same $q$ value displayed the same amount of roll.

Theoretical studies on drops and bubbles motion on solid surfaces have continued in the past years. When the contact angle was small, the lubrication approximation of the Navier-Stokes equation was the model mostly employed to describe the dynamics. For contact angles in between hydrophilic and superhydrophobic, Boltzmann simulations\textsuperscript{89, 90} as well as molecular dynamics have been both employed to describe the motion. More details of these theoretical models can be found in Chapter 2.2.
2.1.5 Interference pattern observation for drops or bubble.

As mentioned above, the collision between drops or bubbles with another solid surface have only been studied for those perpendicular approaching situations. Therefore, there would not be any motion for the drop or bubble along the solid surface after the collision. However, when the solid surface is not horizontal, the motion of drops or bubbles is significant and there are many studies reporting about the motion of a single drop or bubble on an inclined surface\textsuperscript{7, 57, 58, 91-96}. But many of them have a limitation, which is that the motion studies of both drops and bubbles was only observed in a simple way, from the side of the drop or bubble (like the red arrow direction of Figure 2.8).

![Figure 2.8 3D picture of a gravity driven moving droplet on a solid surface, black arrow: moving direction; red arrow: side view direction; blue arrow: vertical (top) view direction.](image)

The side observation of the drop or bubble’s motion can easily measure the moving velocity\textsuperscript{7, 57, 58}, which is one of the most important parameters of the dynamic system. However, the drop or bubble’s surface deformation due to its the interaction with the solid surface cannot easily be observed especially when the drop or bubble size is on
the mm scale or less. What’s more, the thin film between drop or bubble and the solid surface cannot be measured accurately from the side view, even when the resolution of the camera is very high. Therefore, observation from the vertical direction was required (blue arrow direction of Figure 2.8). Only a few studies have reported results using the vertical observation (also called ‘top’ view) of a deformable drop or bubble interacting with another solid surface.

The main objective of top observation was to collect data of the optical interference fringes (Newton’s rings) of a drop or bubble during its motion along the solid surface. This required the solid surface to be transparent. The information from interference fringes can tell us the deformation details of the drop or bubble and the maximum/minimum film thickness between drop/bubble and the solid surface (more details for the fringe analysis can be found in Chapter 3).

Past studies employing optical interferometry for investigating drop/bubble surface interactions were mostly in perpendicular approach\textsuperscript{42, 97, 98}, like Figure 2.9 A shows in Parkinson’s study\textsuperscript{42}. These works were generally 2-dimensional and they is a 3-dimensional colored contour map reported by Poliščuk\textsuperscript{99} (Figure 2.9 B). This map was obtained from a Fizeau interferometer based tribometer\textsuperscript{100} between a highly polished steel ball rolling on glass disc coated with a CrO\textsubscript{2} semi reflective layer. However, this steel ball cannot be treated as a deformable body like drop or bubble.

In this project we have developed an experimentally vertical direction observation of a 3-dimensional bubble/solid surface collision at an angle in liquid medium in order to detect the thin film drainage during the sliding process and the true thin film profile between a sliding bubble and solid surface was obtained (see Chapter 4).
2.2 Theoretical models

In general, when a deformable body, for example a drop or bubble, approaches another solid surface in liquid environment, three main phenomena need to be discussed in order to understand the whole system and the collision process: surface forces, hydrodynamic forces and the equilibrium shape of the deformable body.

2.2.1 Surface forces

The forces which act between two very close surfaces are called surface forces, and these forces mainly reflect the interactions between those two surfaces. Surface forces play important roles in many research areas including colloid science, material science and medical science.

The first quantitative theory which explained the stability of colloidal systems is well known as the DLVO theory (named after the four theoreticians who formulated the theory: Derjaguin, Landau, Verwey, and Overbeek). This theory shows that the stability of colloids in polar liquids depends on the balance between two surface forces – the electrostatic repulsion and the van der Waals attraction (Equation 1). Therefore, according to the DLVO theory, the total force acting between macroscopic bodies \( F \)
is the algebraic sum of the electrical double layer ($F_{\text{EDL}}$) and van der Waals forces ($F_{\text{vdW}}$).

$$F = F_{\text{EDL}} + F_{\text{vdW}}$$  \hspace{1cm} (2.2)

With the development of several new instruments for measuring surface forces, such as SFA (surface force apparatus\(^4\)-\(^6\), \(^{19}\)-\(^{22}\), \(^{27}\), \(^{28}\), \(^{102}\)), MASIF (measurement and analysis of surface interaction and forces\(^{103}\)-\(^{105}\)), and AFM (atomic force microscope\(^{106}\), \(^{107}\)), scientists found that the DLVO theory is not suitable for every situation and there are some new types of forces not considered in the development of the DLVO theory. These forces include structural\(^{102}\), \(^{108}\), hydration\(^{109}\), solvation\(^{110}\), steric\(^{109}\), and hydrophobic forces\(^{19}\). As a result, the general equation for the total force acting in a system consisting of two surfaces immersed in an aqueous solution can be described with the following expression:

$$\sum F = F_{\text{DLVO}}(F_{\text{EDL}} + F_{\text{vdW}}) + F_{\text{non-DLVO}}(F_{\text{steric}} + F_{\text{structural}} + F_{\text{hydration}} + F_{\text{solvation}} + F_{\text{hydrophobic}})$$  \hspace{1cm} (2.3)

As this proposed project is mainly going to study the collision of a deformable body and another flat solid surface in simple electrolyte solutions, those non-DLVO forces are considered to be negligible but the van der Waals force and the electrical double layer force are the main factors in the study.

**Van der Waals forces**

In physical chemistry, the van der Waals force (or van der Waals interaction), named after Dutch scientist Johannes Diderik van der Waals, is the sum of intermolecular dipole-dipole interactions across macromolecular bodies, it can be long or short range, attractive or repulsive, although in most cases it is found to be attractive\(^{111}\)-\(^{114}\). Van der Waals forces include attractions between atoms, molecules, and surfaces. They differ from covalent and ionic bonding in that they are caused by correlations in the
fluctuating polarizations of nearby particles.

To calculate the distance dependence of the van der Waals force between two macroscopic bodies, Hamaker \textsuperscript{112} made a pair-wise summation over all the atoms in the bodies, and he showed that for large bodies the force depends on the surface separation $D$ between the bodies (Figure 2.10).

![Figure 2.10](image)

**Figure 2.10.** Non-retarded van der Waals interaction free energies between bodies of different geometries calculated on the basis of pair-wise additivity (Hamaker summation method\textsuperscript{112}).

According to this calculation, for two spheres 1 and 2 (Figure 2.10 a), separated by a distance $D$, the van der Waals interaction free energy could be calculated from a compound of pairwise Hamaker constants $A$:

\[
W_{vdW} = -\frac{A}{6D} \cdot \frac{R_1R_2}{R_1 + R_2}
\]

where, $A$ is the Hamaker constant, which is defined as:

\[
A = \pi^2 C \rho_1 \rho_2
\]
For two infinite half spaces (bodies 1 and 2), separated by a distance $D$, the energy of interaction is:

$$W_{vdW} = \frac{-A}{12\pi D^2} \quad (2.6)$$

and the force per unit area, also known as the van der Waals free energy is:

$$W_{vdW} = \frac{-AR}{6D} \quad (2.7)$$

More geometries such as cylinders, atoms, etc. can be found in texts such as Israelachvili\textsuperscript{115}.

It can be seen from the equations above that the van der Waals force is distance dependent and becomes increasingly significant with decreasing separation, particularly at distances below 100 nm. Equation 2.4 is valid only when $D$ is much less than the radius of the approaching interfaces.

The limitation in Hamaker’s model was in the calculation of the Hamaker constant based on pairwise interactions. The model for van der Waals forces was thus further developed by Lifshitz\textsuperscript{116-118} who took the macroscopic approach of considering interacting bodies as continuous media with fluctuating electromagnetic fields. The model developed by Lifshitz allowed a more comprehensive calculation of the Hamaker constant for macroscopic bodies interacting across a third medium.

For most of the experiments presented in this thesis, the separation between surfaces is over several hundred nanometers so that the van der Waals force can be neglected.

\textit{Ninghui Han} \quad \textit{Sep 2016}
Electrical double layer force
When a surface is placed in an aqueous solution, a phase boundary is brought into the bulk solution and breaks the equilibrium; hence a new force is generated which causes the ions and water molecules to re-distribute according to a balance between electrostatic attraction to the surface and the entropic tendency of the ions to disperse in the solution. At the same time, any charges carried in the region will also be re-distributed in such a way as to generate an electric field near the interface. This varies the charge distribution of the adjoining phase and hence it will also have a different charge distribution near the boundary compared to the bulk. The electrical double layer (EDL) is a term used to describe the distribution of charges at the interphase between two materials. In polar liquid system, a redistribution of charges occurs at materials’ interfaces when a dielectric material approaches another, and electrical double layer is made of the surface charge plus the diffuse layer of opposite charge. The thickness of the double layer depends on the concentration of ions in the polar liquid system: the more ions available in the liquid, the thinner double layer will form. There are various theoretical models of the electrical double layer structure formed on different materials and forces that result from overlapping double layers\textsuperscript{89}. Detailed discussions on these models are readily available in texts such as\textsuperscript{7}. Among these models, the most famous three are the Helmholtz model\textsuperscript{119}, the Gouy-Chapman model\textsuperscript{120,121} and the Stern model\textsuperscript{122}.

Helmholtz model
The earliest models of the double layer was proposed by Helmholtz who suggested that the charge at the solid surface is compensated by a parallel layer of equal and opposite charge on the solution side. This model disregards the disrupting effect of thermal motion, which tends to break up and disperse the layer of charge on the solution side. The term double layer originally referred to such a picture (Figure 2.11).
Figure 2.11 (a) A schematic representation of the electrical double layer based on the Helmholtz model. (b) Corresponding potential distribution across the interface. $\psi_M$ is the surface potential of the metal and $\psi_S$ is the potential of the solution.

**Gouy-Chapman model**

As presented above, Helmholtz’s model is too simplistic and ignores the effects of thermal motion of ions and solvent molecules in the solution. Gouy\textsuperscript{120} and Chapman\textsuperscript{121} independently developed a new model of the double layer, now called the Gouy-Chapman model. According to the Gouy-Chapman model, two competing forces cause the formation of diffuse layer of ions near the surface: the electric field near the surface which attracts counter ions as near as possible to the surface and the Brownian motion which causes uniform distribution of ions in the bulk solution. This results in the majority of the counter ions residing near the interface with the concentration levelling off with the distance from the interface until it becomes the same charge distribution as that within the bulk solution, as shown in Figure 2.12 a.
Figure 2.12 (a) A schematic representation of the electrical double layer based on the Gouy-Chapman model. (b) Corresponding potential distribution across the interface.

Stern model

The Gouy-Chapman model fails for highly charged distribute liquids. In 1924 Otto Stern suggested combining the Helmholtz model with the Gouy-Chapman model, this is now called Stern's model. Since the double layer is assumed to be a continuum in the Gouy-Chapman model, it only works well at low electrolyte concentration when the finite size of the ions adsorbed on the surface is negligible when compared to the effective thickness of the double layer. At higher electrolyte concentration, the effective thickness of the double layer is reduced significantly and the finite-sized ions on the surface need to be taken into consideration. Stern\textsuperscript{122} proposed a model which combined the Helmholtz model and the Gouy-Chapman model (Figure 2.13 (a)) to describe the electrical double layer.
Figure 2.13 (a) A schematic representation of the electrical double layer based on the Stern model. (b) Corresponding potential distribution across the interface.

The calculation of the electrical double layer force is difficult without any assumptions to make it easier. For the one-dimensional and asymmetric interaction between a drop or bubble and a surface, one famous solution of the electrical double layer force is known as the Hogg-Healy-Fuerstenau (HHF) approximation (see Hunter\textsuperscript{30} for derivation). For example, in Del Castillo’s\textsuperscript{123} studies of air bubble and mica surface interaction in electrolytes, the equation used for the double layer force’s is:

\[
W_{\text{EDL}} = -\frac{\varepsilon k^2}{2 \sinh(\kappa h)} \cdot [\left(\psi_{01}^2 + \psi_{02}^2\right) \csc(\kappa h) - 2\psi_{01} \psi_{02} \coth(\kappa h)]
\] (2.8)

where \( \kappa \) is the Debye-Huckel parameter, \( \Psi \) is the surface potential of two surfaces, \( h \) is the double layer thickness.

Another method for electrical double layer force calculation is the numerical algorithm developed by Chan et al.\textsuperscript{124}. This method also provides a way of calculating the interaction potential for surfaces with different geometries and conditions.
2.2.2 Hydrodynamic force

The hydrodynamic force between drop or bubble and surface in liquid plays a significant role in the collision process through and the way it affects the change of shape of the deformable body (drop or bubble).

A significant number of both experimental and theoretical studies have been attempting to describe the thin film drainage process by hydrodynamic force. The most difficulty in modeling the thin film drainage process is the complexity of the mathematics involved in the hydrodynamic force calculation. Here we present several theoretical foundations on the hydrodynamics of thin film drainage which has been used to model drop (bubble) and surface interaction in the perpendicular direction.

A good starting point of hydrodynamic study for collision purpose could be the Navier-Stokes equation (named after Claude-Louis Navier and George Gabriel Stokes). Generally speaking, the Navier-Stokes equation can apply in many areas including physics, chemistry, mathematics and even economic.

To describe collision process, according to the Newton’s law, the sum of all forces $F$ applied to an object is equal to the product of its mass $m$ and its acceleration $a$.

$$\bar{F} = ma$$

(2.9)

When dealing with liquids, it is necessary to think of the liquid in a small element rather than considering it as a rigid body moving as whole. Therefore, the equation above is transferred in to:

$$\bar{F} = \rho \frac{du}{dt}$$

(2.10)
where $\rho$ is the volumetric mass (or density) of the liquid, $u$ is the velocity of an element of volume. The $F$ is generally the sum of a driving term and viscous term that opposes any movement.

A more complex equation comes out if we consider a three-dimensional space:

$$\rho \bar{B} - \nabla p + \eta \nabla^2 \bar{u} = \rho \left( \frac{d\bar{u}}{dt} + \bar{u} \cdot \nabla \bar{u} \right)$$  \hspace{1cm} (2.11)

where: $\rho B$ is the total long-range force acting per unit volume, $B$ is a body force (like gravity), $\nabla p$ is the gradient of the pressure, $\eta$ is the fluid viscosity, and $\eta \nabla^2$ are the viscous forces acting on the element of volume of the fluid. The symbol $\nabla$ (called ‘del’) in equation 2.11 stands for the operator:

$$\left( \frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \frac{\partial}{\partial x_3} \right)$$  \hspace{1cm} (2.12)

More details for this equation can be found in the textbook of Hunter\textsuperscript{90}.

To simplify the mathematics, several assumptions can be brought in for the system studied here. (1) We indicate that we are dealing with Newtonian fluids. These fluids are defined as those that have constant viscosities $\eta$ and behave in a manner such that the shear stress is directly proportional to the velocity gradient in the fluid\textsuperscript{125}; (2) steady flow condition – meaning that at any point in space the velocity components and thermodynamic properties of the liquid do not change in time; (3) spatial variations in temperature in the region of interest are negligible; and (4) the liquid is incompressible – fluid parameters of viscosity and density are constants in both position and time, despite variations in pressure. These assumptions result in a quite simple form of the Stokes equation:
$\nabla \cdot \vec{u} = 0$  \hspace{1cm} (2.13)

Once the appropriate boundary conditions are fixed in a given region of viscous fluid flow, the Navier-Stokes equations can reveal the relation between the space-time distribution of $u$ and $p$.

The limitation of Navier-Stokes equations could be the complex nonlinear form of the equations. Nonlinearity always makes problems very difficult to solve, which mean, further simplification of the Navier-Stokes equations is required for specific experimental situations.

One of the most important applications of the Navier-Stokes equation goes back to Reynolds\textsuperscript{126} who reported his detailed analysis of hydrodynamic lubrication caused by a thin film of liquid confined between two solid surfaces approaching each other in a viscous medium. These experiments and his theory model then became the foundations of modern lubrication theory (for extensions and applications of the lubrication theory refer to text book\textsuperscript{127}).

![Figure 2.14. Geometry of thin film drainage problem where a bubble approaches a solid surface in liquid with a velocity $dD/dt$, where $D$ is the distance of closest approach between the two surfaces; $h(x,y)$ is the local distance between the surfaces\textsuperscript{7}.](image)

Based on a simplification of the Navier-Stokes equations, the key requirement for
lubrication theory is that the film thickness \((h)\) is significantly smaller than the length of substrate \((L)\), in another words, the ratio \(h/L \ll 1\) (the geometry can be seen in Figure 2.14). This ratio suggests that we can consider the liquid velocity in z-direction to be negligible, which leads to the simplification of the Navier-Stokes equations:

\[
\frac{\partial p}{\partial z} = 0
\]  
(2.14)

The liquid draining only along the x-y direction, the Navier-Stokes equations of x and y direction take the following forms:

\[
\begin{align*}
\frac{\partial p}{\partial x} &= \eta \frac{\partial^2 u_x}{\partial z^2} \\
\frac{\partial p}{\partial y} &= \eta \frac{\partial^2 u_y}{\partial z^2}
\end{align*}
\]  
(2.15)

Based on the previous assumptions, the Reynolds lubrication equation \(^{128}\) for the pressure that develops in a layer of fluid of thickness \(h\), which is confined between two solid bodies, is:

\[
12\eta \frac{d}{dt} \bullet (h \rho) + 6 \nabla \bullet (h \rho V) = \nabla \bullet (h^3 \rho \nabla p)
\]  
(2.16)

where \(\rho\) is the density, \(\eta\) is the viscosity of the fluid; \(V\) is the velocity of the upper body with respect to the lower body\(^{128}\). This equation is usually employed to model compressible films such as gas films, for example those gas films used to lubricate disk and tape magnetic recording system\(^{129, 130}\). However, if the lubricating film is incompressible (liquid films), another assumption is employed that the density of the liquid \(\rho\) remains constant. In this case, the classical Reynolds lubrication equation is
A new angle on the coalescence of drops

obtained\textsuperscript{128}:

\[
12\eta \frac{dD}{dt} + 6\nabla \eta \bullet (hV) = \nabla \bullet (h^3 \nabla p)
\]  
(2.17)

This equation can be to various types of lubrication such as hydrodynamic (HD)\textsuperscript{131}, elasto-hydrodynamic (EHD)\textsuperscript{132} and plasto-hydrodynamic (PHD)\textsuperscript{133}. Its application to engineering, fluid flow, emulsion and greases have been discovered and developed\textsuperscript{134-136}.

Apart from the previous applications, Reynolds theory also has the capacity to explain drop and surface interactions in liquid systems. When a drop or a bubble approaches a surface in liquid, the moving velocity $V$ is equal to $dD/dt$, the standard Reynolds lubrication equation (Equation 16) then becomes:

\[
\frac{dD}{dt} = \frac{1}{12\eta} \bullet \frac{d}{dr} \bullet (h^3 r \frac{dp}{dr})
\]  
(2.18)

where, $r$ is the drop or bubble radius. The derivation of this equation can be found in the study of Chan and Horn\textsuperscript{124}. This equation has been employed many times to explain the relationship between the velocities of the surfaces and the changes in hydrodynamic pressure in the radial direction of drops or bubbles, for example two mica surfaces\textsuperscript{124}, a mercury drop with mica surface\textsuperscript{20, 21, 23, 124}, an air bubble with mica surface\textsuperscript{27, 28, 123} and an air bubble with titania surface\textsuperscript{36}.

As the Reynolds theory has capability to explain the rate of drainage of thin films of liquid between solid, liquid, or vapor surfaces, it is very relevant to our proposed project. However, the mathematical difficulty becomes very high for deformable surfaces in an oblique system, so it is beyond the scope of this thesis.

\textit{Ninghui Han}  \hspace{1cm} Sep 2016
2.2.3 Surface deformation

 Compared to a rigid body, when a deformable body such as a drop or bubble approaches a surface, the measurement of forces on its surface is more complex. The reason which contributes most to this difficulty is that the surface of a deformable body will not remain a spherical shape all through the approach process. As a result, many interesting deformations of drops of bubbles are formed such as ‘dimple’\textsuperscript{20,21,23}, ‘wimple’\textsuperscript{22} and ‘pimple’\textsuperscript{137}. Understanding how and why the surface of a drop or bubble changes reveals important information about the interaction with another flat solid surface.

 For any irregular deformable curved surface, there will be two principal radii ($R_1$ and $R_2$) which are shown in Figure 2.15, the pressure difference $P$ between inner and outer sides of the surface can be calculated by the Young-Laplace equation:

$$\Delta P = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$  \hspace{1cm} (2.19)

where, $\gamma$ is the surface tension. The derivation of Equation 2.19 is based on Figure 2.15, detailed information can be seen in textbook of Shen\textsuperscript{138}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.15}
\caption{The analysis of any curved surface’s extending work\textsuperscript{138}.}
\end{figure}
When the surface is a sphere, $R_1$ equals $R_2$, and the Young-Laplace equation will simplify to:

$$\Delta P = \frac{2\gamma}{R}$$  \hspace{1cm} (2.20)

Making use of the Young-Laplace equation, Miklavcic et al.\cite{139} have modeled the shape of a deformable drop under the influence of equilibrium surface forces. Carnie and co-workers\cite{23,140} also employed the Young-Laplace equation for mathematical modeling of the SFA experimental results for thin film drainage between a mercury drop and a mica surface.

### 2.2.4 Theoretical modelling of a deformable body with an inclined surface

Griggs et al.\cite{94} have modelled a gravity-driven drop near an inclined surface at low Reynolds number. In their study, three main parameters were controlled, drop-to-medium viscosity ratio $\lambda$, wall inclination angle $\theta$ (from horizontal), and Bond number, $B = \Delta \rho gr^2/\sigma$, where $\Delta \rho$ is the density difference between the drop and suspending medium, $r$ is the non-deformed spherical radius of the drop, $g$ is the acceleration due to gravity, and $\sigma$ is the interfacial tension. Some of their results were presented in the form of a simulated interference figure showing how the Newton’s rings would appear. Figure 2.16 shows one of the results of Griggs’s study for a moving drop under the condition of $\theta = 15$ degree, $B = 3$ and $\lambda = 20$. The simulation shows groups of irregularly-shaped interference fringes corresponding to contours of constant the distance of the bottom of the drop interface from the solid surface.
Figure 2.16 Simulation results of Griggs’s study for Simulation results for oblique angle 15 degree and Bond number 3 as well as its contour map.

An angle range of 15° up to 75° was studied by Griggs with a detailed drop shape description and contour maps. However, even the smallest angle value that Griggs has tested was 15° which was still considered to be high. Until now there was no detailed experiment investigations using top observation for drop/bubble on an inclined surface at small angles under 5°. This thesis will present top view images and the contour maps after analysis for the angles went down to 0.5°. The interference fringes from our work look qualitatively similar to those of Griggs’s study. More details can be found in Chapter 4.
Chapter 3. Research Methodology

Our experimental set-up was an extension of the rising bubble experiment reported by Parkinson et al.\textsuperscript{42} (shown in Figure 3.1). In their experiment they studied the thin film drainage between a small rising bubble and a flat solid surface as the bubble rises to and collides with the horizontal surface. The film thickness is measured using the Newton’s rings method, which relies on optical interference between the two surfaces (solid and bubble) using monochromatic light.

![Figure 3.1 Experimental apparatus schematic diagram of Parkinson et al.\textsuperscript{42}.](image)

We have constructed a similar experimental set-up in which the surface is tilted at various angles, as can be seen in Figure 3.2. As the bubbles will still rise vertically, the collision will occur at an oblique angle when the solid surface is tilted. The optical system has to be tilted so that the optical path remains normal to the solid surface.
3.1 Experimental set-up development

Sliding bubble apparatus

Devising an experiment to investigate thin film drainage between a single bubble approaching a flat solid surface at an oblique angle is the starting point and also one of the main aims of this proposed project. The experimental set-up consisted of a tilting table, an optical system and a bubble releasing system.

Part 1, the tilting table.

The tilting table used in this project is designed by Dr. Wren Greene and manufactured by Russell Moore. Figure 3.3 shows the structure of this tilting table. The oblique angle value is controlled by a worm gear driven, a rotating handle, and a ±30 degree angle range can be reached easily and accurately to 0.1 degree. There are four ‘legs’ at the bottom of the table to adjust the system and keep it horizontal. An x-y positioning stage (39-930, Edmund Optics, Singapore) is fixed on the tilting table to provide lateral movements over a short range, and a motorized stage (59-747, Edmund Optics, Singapore) is placed on the top of the positioning stage to allow a further forward-backward movement of the system. Finally, there is a connection arm placed on the
table in order to keep the optical system at a fixed angle with respect to target surface. Up-down movement is allowed for the optical system only to focus the microscope objective on the surface.

![Figure 3.3 The tilting table.](image)

**Part 2, the optical system.**

The optical system is made of a light source, a research high speed camera, a beam splitter and a microscope objective, with the camera controlled by a work station PC (Figure 3.4). A LED fiber optic illuminator (Edmund optics, Singapore) has been chosen to play the role of light source in our experiments, three different wave lengths of blue (465 nm), green (521 nm) and red (630 nm) can be provided by the illuminator. A research high speed camera of type FASTCAM SA3 is employed for providing an ultra-high speed frame rate of 500 to 2000 frames per second with a resolution of 1024×1024, which is very suitable for observing dynamic bodies such as drop or bubble collisions. Between the camera and the light source is where we place the beam splitter. Three types of plate beam splitters (30T(through)/70R(right), 50T/50R, 70T/30R, Edmund optics, Singapore) were tested in the experiments and the type 30T/70R plate beam splitter provided the best observation condition for the bubbles.

*Ninghui Han  Sep 2016*
The beam splitter is placed in to a standard holder (Edmund optics, Singapore) which is then connected to the camera, light source and the microscope objective lens (shown in Figure 3.4). Different microscope lenses with 4X (Edmund optics, Singapore), 5X (Newport, Australia) and 10X (Newport Australia) magnification are employed for the experiment. And finally the images are collected by specific software (PFV Ver.331) from the high speed camera company (Photron) on the PC.

![Figure 3.4 The optical system.](image)

**Part 3, the bubble releasing system**

The bubble releasing system requires a sealed container filled with liquid medium, a specific syringe connection and a syringe pump for releasing air bubbles into the system.

In the flat surface system, the container is also designed by Dr. Wren Greene and manufactured by Russell Moore. This container, which we call the ‘bubble chamber’, is a sealed Teflon box with a length of 180 mm, width 50 mm and height 55 mm (structure is shown in Figure 3.5). There is an opening on the top side of the bubble chamber (77 mm length and 22 mm width) which allows us to change solid surfaces, with standard glass microscope slides being the most commonly used. All the solid surfaces that were tested in this project need to be cut into the same size as the
chamber’s opening. After sliding the solid surface into the opening, a custom-designed cover was placed onto the solid surface to seal the whole chamber. On one side of the bubble chamber, there is a glass window which allows us to observe the experiment by eye or with a video camera. On one end of the bubble chamber, there is a small hole to fit the capillary that releases bubbles or drops.

Single air bubbles were formed by a 5 mL plastic syringe connecting to a syringe pump (NE-1000, New Era Pump Systems, USA) and pumped into the bubble chamber through a long capillary. The air bubbles are allowed to rise up vertically and collide with the target glass microscope slide surface at a specific angle controlled by the tilting table mechanism.

![Figure 3.5 Structure of custom-designed bubble chamber.](image)

**Cleaning procedures**

All the preparation of the experiments were carried out in a dust-free flow bio-cabinet (Air science, Australia), with gloves, cap and sleeves worn to avoid any dust or skin flakes dropping from clothing or the body. All the purified water using in this project was treated in a high-purity system (MilliQ, Element) for at least 12 hours (referred to as ‘clean’ water). Viscosity of clean water and sucrose solution were measured by viscometer (DV-E, Can-am, USA).
The microscope glass slide was rinsed with clean water and ethanol (96%, chem-supply) and dried before it was put in to a UN-Ozone pro-cleaner (Bioforce, USA) for of 30 minutes each side. The glass slide was then either put into use immediately for hydrophilic experiments, or received further treatment as described below for hydrophobic experiments.

The Teflon container was treated with hot methanol for 1 hour before initial use in order to remove all the organic layers on the surface. Each time before use, the container was carefully rinsed with ethanol and clean water.

### 3.2 Hydrophobic treatment.

As mentioned above, both sides of the microscope glass slide need to be treated in the UV-Ozone pro-cleaner before receiving hydrophobic modifications. Chlorotrimethylsilane (TCI) and hexyltrimethoxysilane (TCI) were selected as the hydrophobic treatment chemicals\textsuperscript{141,142}. In order to avoid dust, hydrophobic treatment was carried out in a ground glass desiccator under vacuum. A volume of 250 μmol of chlorotrimethylsilane or hexyltrimethoxysilane was used by the method of vapor phase reaction. Vacuum cannot only prevent contamination from air but also accelerate the vaporization of the silane. After a number of hours’ reaction (normally two to three hours), the hydrophobic glass slide would be ready to use. Figure 3.6 shows the contact angle value of the glass slide after hydrophobic treatment (the contact angle on the hydrophilic surface was measured to be zero). We did not test the surface roughness of our glass slides (both before and after treated), however, due to the vapour deposition treated method, there should not be a big difference between our hydrophobic and hydrophilic surfaces.
A new angle on the coalescence of drops

Ninghui Han  Sep 2016

Figure 3.6 Image of contact angle of glass slide after hydrophobic treatment.

A group of microscope glass slides can be treated at the same time with this vapor phase method, and in order to avoid further dust absorbing on the hydrophobic surfaces after treatment, those slides were stored in another dust free desiccator under vacuum. When opening the desiccator, it was placed in the bio-cabinet with a filter connected to the desiccator to prevent contamination. Also, every time when we need to break a vacuum, the procedure has to be taken in the bio-cabinet with a filter connected to the desiccator to avoid dust entering the desiccator when it was opened.

3.3 Newton’s rings and their analysis method

The phenomenon of Newton's rings, named after Isaac Newton who first analyzed them in the year of 1717, is an interference pattern caused by the reflection of light between two surfaces, a spherical surface and an adjacent flat surface (Figure 3.7 a).
When viewed with monochromatic light the pattern appears as a series of concentric, alternating bright and dark rings centered at the point of contact between the two surfaces (Figure 3.7 b). When viewed with white light, the concentric ring pattern has rainbow colours because the different wavelengths of light interfere at different thicknesses of the air layer between the surfaces (Figure 3.7 c).

For monochromatic light illumination, the bright rings are caused by constructive interference between the light rays reflected from both surfaces, while the dark rings are caused by destructive interference. Each ring represents a contour of constant separation between the surfaces. The outer rings are spaced more closely than the inner ones because the slope of the convex lens surface increases outwards, the separation of the rings gets smaller for the outer rings. Each fringe represents a line of constant separation between the surfaces. For surfaces which are not convex and cylindrically symmetric, the fringes will not be rings but will have other shapes.

For optical observation of Newton’s rings through a hemispherical lens on a flat surface, the positions of the rings are readily calculated by determining the height, \( h \), of the gap between the hemisphere surface and the specimen as depicted in Figure 3.7.
Assuming a rigid sphere model (no deformation) is used, the height is related to the position, $x$, of the rings by:

$$h = R - \sqrt{R^2 - x^2}$$  \hspace{1cm} (3.1)

where $R$ is the radius of the hemisphere and $x$ is the distance from the centre axis of the hemisphere to the spot on the surface. The height difference between neighboring dark fringes is $\lambda/2$, where $\lambda$ is the wavelength of the light going through the lens. Since there is no gap at the contact point, the radius $r_N$ of the $N^{th}$ Newton's bright ring is given by

$$r_N = \left[\left(N - \frac{1}{2}\right)\lambda R\right]^{1/2}$$  \hspace{1cm} (3.2)

and the heights at the rings are:

$$h_1 = R - \sqrt{R^2 - r_1^2}$$
$$h_2 = R - \sqrt{R^2 - r_2^2}$$
......
$$h_n = R - \sqrt{R^2 - r_n^2}$$  \hspace{1cm} (3.3)

Currently the Newton’s rings experiment is one of the basic optical experiments in physics education due to its understandable basis, simple set-up and visual experimental results. In the research area, the Newton’s rings method has been widely used for various purposes. For example, in characterizing a light-emitting device, it is reported by Tsai\textsuperscript{143} that based on a Newton’s rings apparatus the coherence lengths of different organic light-emitting devices could be characterized, including the light-emitting device being non-doped/doped and being bottom-emitting or top-emitting.
For monitoring and quantifying the thickness of a solid lubricant transfer film, Wahl\textsuperscript{144} investigated a method based on Newton’s rings analysis during in situ tribological studies.

Since optical interference is a powerful method for measuring the distance between two surfaces, it is highly suitable for coalescence experiments between bubbles and flat surfaces in an aqueous system. If the critical film thickness between the bubble and solid surface against approach time is monitored, the interaction between a bubble and a flat surface can be found, as Parkinson et al.\textsuperscript{42} have reported for the interaction between a very small rising bubble and a hydrophilic titania surface.

However, those experiments presented above were mostly carried out with bubbles approaching the surface in a perpendicular direction, which means that the surface of the bubble maintains cylindrical symmetry when approaching. In that case the Newton’s rings remain circular, although if the bubble deforms their radius would no longer be given by the above equations. However, the Newton’s rings also can be used to observe when the deformation occurs. When the bubble approaches at an angle to the surface (no longer perpendicular), the symmetry of the rings will be broken and the fringes will not be circular but will have other shapes depending on what kind of surface deformation occurs. Figure 3.8 A is an example of original image of asymmetric rings we observed with an air bubble in water sliding along a hydrophilic glass slide. With proper image analysis treatment (Matlab), the background of Figure 3.8 A can be removed and a clearer image of the Newton’s rings can be obtained like Figure 3.8 B. However, due to the optical system’s limitation, there are two defects in those images. The first one is a central reflection spot which showed up every single image, this spot is possibly caused by the reflection of the beam splitter and we do not have a way to remove it even after the image treatment. However, the central spot position is fixed and it would not affect the analysis of the Newton’s rings much. The second defect is shown in Figure 3.8 C. Due to our high speed camera having an intermittent fault.
during a short period, the images we obtained during that time were all with vertical stripes (Figure 3.8 C). Although those stripes cannot be simply removed by image treatment and they partly blocked the fringes in the image, they did not have a significant influence on the results because the contour map could still be drawn from the image even when the stripes are present. More details of the analysis for those irregular fringes will presented in Chapter 4.

Figure 3.8 Image of asymmetric Newton’s ring obtained in our experiment. A, original image we obtained, B, image after treatment and C, original image with stripes on it.

**Statics measurements with watch glass**

A first test of the previously discussed experimental set-up was made with a single bubble under a watch glass in distilled water. The schematic diagram of the single bubble that has collided with a watch glass is shown in Figure 3.9 a. All the glasses in this experiment were well-cleaned by pure ethanol and acetone to remove dust from the surface, followed by a 20 minutes (for each side) in a UV/Ozone pro-cleaner to remove organic impurities.
A single air bubble of 1.5 mm in diameter was released and collided with the top surface of the watch glass under distilled water environment. Using the optical system shown in the figure, video images showing interference fringes (Newton's rings) were obtained after proper alignment of the components.

The light source is an LED fiber optic illuminator that includes three LEDs: blue, green and red. Figure 3.10 is the image of Newton's rings observed with green light in the bubble/watch glass collision system. Interference area, the area inside where fringes can been seen is very circular and the fringes inside the interference area are regular and easy to count. We notice that the fringes disappear quickly outside the edge of the interference area, and one reasonable explanation is the bubble was deformed as a ‘dimple’ shape in this photo so that the water thickness increases rapidly outside the dimple region (more details about what is a dimple and how it formed can be found in section 1), a picture of the presumed bubble deformation is shown in Figure 3.9 b.
Calculation from the Newton’s rings: the absolute film thickness $h$:

Once the clear and countable fringes are observed, the absolute film thickness of each fringe can be calculated by the wavelength of the light and the refractive index of the medium. For the $N^{th}$ bright fringe, the film thickness $h$ can be calculated by the following equation

$$2nh = N\lambda$$

(3.4)

where $\lambda$ is the wavelength of the light, $n$ is the refractive index which is determined by the type of the medium and the light wavelength $\lambda$ (dispersion).

In our experiments, wavelength and refractive index are known from the LED supplier.
and reference data, but the fringe number \( N \) cannot be read directly from the photo. That is because we can only count the total number of the fringes observed, but we do not know which number should be the start number of \( N \) for the calculation. Using the green light photo of Figure 3.10 as an example, the wavelength of the green light of our LED light source is known to be 521nm and the refractive index of water at this wavelength is 1.335. We also can count eleven fringes from the photo. However, we cannot calculate the absolute thickness because we do not know the starting number of the observed fringes. Those eleven fringes can be the 1\(^{st}\) to 11\(^{th}\) fringe, 2\(^{nd}\) to 12\(^{th}\) fringe or even the 10\(^{th}\) to 20\(^{th}\). Therefore, if we want to calculate the thickness of fringe observed in the photo with green light, we need to add an unknown number of fringes \( N_0 \), and use \((N_0 + N_r)\) as the \( N \)th value of equation 3.5.

\[
2nh = (N_0 + N_r)\lambda \\
h = \frac{(N_0 + N_r)\lambda}{2n}
\tag{3.5}
\]

Although the unknown number of fringes \( N_0 \) cannot be read from the photo, we are able to calculate it by changing the wavelength of the light while keeping film thickness at the same value. The number of fringes that can be observed in the photo of the same collision system is influenced by the wavelength of the light. Interferograms for different types of light with their wave length and refractive index value are presented in Figure 3.11. Using blue light (\(\lambda=465\text{nm}, n=1.339\)), the highest number of rings, 13 was derived. Using green light (\(\lambda=521\text{nm}, n=1.335\)) and red light (\(\lambda=630\text{nm}, n=1.331\)), a lower number of visible rings, 11 and 9 respectively, are derived.

The reason why smaller wavelength provides larger number of fringes can be explained from equation 3.3. The change of the wavelength has no effect on the position of the bubble surface, therefore the radius of curvature and the size of
interference area would not show any change. However, a larger wavelength produces interference fringes at a further distance from the center, which means a smaller number of rings would be observable in the interference area. Blue light has the smallest wavelength compared to green and red light, therefore, the number of rings observed with blue light was the highest.

Figure 3.11 Top images of single bubble of 1.5mm in diameter collided with watch glass in distilled water with (a) blue light $\lambda=465\text{nm}$, $n=1.339$, (b) green light $\lambda=521\text{nm}$, $n=1.335$ and (c) red light $\lambda=630\text{nm}$, $n=1.331$.

In order to obtain the absolute thickness of the film between the bubble and the glass
surface, trial values of $N_0$ from 1 to 8 were presumed for each wavelength. When the correct values are guessed, the film thicknesses calculated from each wavelength must match each other. For each value of $N_0$, absolute thickness of the thin film was calculated by equation 3.4 and a Figure of thickness against fringe radius was drawn (Figure 3.12).

![Figure 3.12](image)

**Figure 3.12** Absolute film thickness against fringe radius. Bubble radius = 0.75 mm, red symbols for red light ($N_0$ value from 1 to 5), green symbols for green light ($N_0$ value from 1 to 5) and black/white symbols for blue light ($N_0$ value from 1 to 8).

In Figure 3.12 there are 5 groups of red symbols for invisible fringe number $N_0$ from 1 to 5, each group of symbols represents one possible film thickness and the bubble shape condition. However, there is only one correct bubble shape trend among them. In order to identify which group is the correct answer, at least one other group of data with different light wavelength is required. In our case, images using green light with 11 fringes (green symbols in Figure 3.12) were analysed the same way as images obtained with the red light. When another 5 groups of symbols were put into the same
A new angle on the coalescence of drops

figure, we are able to determine that if there are two groups of data points match very closely to each other. This group of data represents the real absolute film thickness and the bubble shape. In Figure 3.12 there are two possible groups of data after comparing red symbols with green ones, $N_0=1$ (for both) and $N_0=4$ (red light)/5 (green light). This means a third group of data is required to distinguish the correct and choice. Blue light of a large group number of 8 (black/white symbols in Figure 3.12) were added into the figure by the same method, and we can conclude that the trend line passes $N_0=4$ (red light)/5 (green light)/$N_0=7$(blue light) is the correct bubble shape line.

<table>
<thead>
<tr>
<th>Fringe order</th>
<th>1st</th>
<th>2nd</th>
<th>3th</th>
<th>4th</th>
<th>5th</th>
<th>6th</th>
<th>7th</th>
<th>8th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (nm)</td>
<td>237</td>
<td>473</td>
<td>710</td>
<td>947</td>
<td>1183</td>
<td>1420</td>
<td>1657</td>
<td>1953</td>
</tr>
<tr>
<td>Fringe order</td>
<td>9th</td>
<td>10th</td>
<td>11th</td>
<td>12th</td>
<td>13th</td>
<td>14th</td>
<td>15th</td>
<td>16th</td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>2130</td>
<td>2367</td>
<td>2603</td>
<td>2840</td>
<td>3077</td>
<td>3313</td>
<td>3550</td>
<td>3787</td>
</tr>
</tbody>
</table>

Table 3.1 Fringe order number and the film thickness it represents (red light, wavelength 630 nm, refractive index 1.331).

The film shape as well as the ‘dimple’ formation of the bubble is drawn in Figure 3.13. Black lines are the absolute thickness calculated from the fringes and they are axially symmetric. The dashed line in the middle is the central shape of the bubble surmised from the trend of the black lines, the maximum absolute thickness of that ‘dimple’ shape is presumed to appear there, but the central dark ring of the Newton’s rings in our images prohibited us to apply the calculation of the absolute thickness in the very central area. The maximum absolute film thickness of a single air bubble of 1.5 mm in diameter with the watch glass in distilled water was about 3 μm. As the fringes
disappear quickly when the radius reached the edge of the interference area, we surmise that the absolute thickness of the film had a sharp increase, shown by the dashed lines at the sides of Figure 3.13.

Figure 3.13 Whole profile of the dimple formation of the bubble.
Chapter 4 Results and discussion for a hydrophilic surface

The collision of a single rising air bubble with a tilted hydrophilic solid surface in liquid environment can be divided into three main steps: approaching, bouncing and sliding (shown in Figure 4.1).

![Figure 4.1 Single air bubble approaching tilted hydrophilic solid surface.]

During the approach step, important parameters of the system in our experiments are bubble rise speed, bubble size, liquid viscosity, solid surface hydrophobicity, and the angle that the surface has been tilted (shown in Figure 4.2). In our experiments, side view images were taken during the approach step so that we would be able to calculate the rising speed of the bubble by using the distance from the releasing point to the solid surface divided by the time bubble travelled from releasing to the first touch point. At the same time, bubble size can also be measured. The viscosity of the liquid and the water contact angle of the solid surface were tested before the experiment started. And finally the tilt angle of the system was set within a reasonable range for different purposes.
Figure 4.2 Important parameters in rising bubble/solid surface system.

As reported by previous scientists such as Niecikowska et al.\textsuperscript{41}, after the first collision of the bubble with the surface, mm-size bubbles at their terminal speed in water will bounce several times before coming to rest. The number of times that the bubble bounces before it stops bouncing is considered as an important parameter of the collision system. Therefore, we combine the top view video with the side view video to count the exact number of times a single bubble bounced in different tilt angle conditions for qualitative comparison with that of a perpendicular collision.

The main difference of an oblique collision compared to a perpendicular collision between a single air bubble and a solid surface is that, with the surface inclined at a small angle to the horizontal, the bubble starts to slide along the solid surface even before it finishes bouncing instead of remaining at the same place on the surface (perpendicular condition). During this sliding step, new parameters of the system need to be taken into consideration such as sliding speed of the bubble, thin film thickness between the bubble and the solid surface, and the bubble top surface deformation.
A new angle on the coalescence of drops

condition (Shown in Figure 4.3).

![Figure 4.3 Important parameters in sliding bubble/solid surface system.](image)

Once the bubble has a sliding velocity, it usually combines with viscosity and surface tension ($\sigma$) to be the capillary number $Ca$:

$$Ca = \frac{U \eta}{\sigma}$$

(4.1)

Surface hydrophobicity is critical during the sliding situation because hydrophilic and hydrophobic surfaces will reach completely different final outcomes for the bubble. In the case of hydrophilic solid surfaces, the vertical speed of each subsequent bounce during the collision was reduced as a result of the energy dissipation until it started to slide steadily along the surface as far as could. In hydrophobic cases, the bubble will slide just a small distance before sticking on the surface without any further movement. Therefore the sliding speed of the bubble has different meanings for those two situations: the stable speed of the sliding bubble for hydrophilic conditions and the
average speed from first touch to its adhesion in the hydrophobic case. Side view images can help us to measure the sliding speed all the time. Meantime, Newton’s rings were observable when the bubble was sliding, therefore the thin film thickness and the bubble top surface deformation can be found by analysis of those Newton’s rings. This chapter presents results for the hydrophilic case, and the hydrophobic data are presented in the following chapter.

4.1 Baseline experiment

Here we discuss an experiment under the following parameter values as the standard experiment data with which other experiments will later be compared to explore the effects of varying the parameters one by one (Table 4.1):

<table>
<thead>
<tr>
<th></th>
<th>Rising speed (average) mm/s</th>
<th>Bubble size (diameter) mm</th>
<th>Solid surface contact angle value degree</th>
<th>Tilt angle degree</th>
<th>Liquid viscosity Pa(\times)s (water at room temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard experiment</td>
<td>237.5</td>
<td>3.3</td>
<td>0</td>
<td>0.5°</td>
<td>0.89 x 10^{-3}</td>
</tr>
</tbody>
</table>

Table 4.1 Standard experiment parameters (light source: red light, 630 nm wavelength).

4.1.1 Description of baseline experiment

Figure 4.4 shows an overview of a sliding bubble interacting with a flat hydrophilic microscope glass slide from the time it initially touched the surface until the limit distance we could reach at an oblique angle of 0.5° in water environment. The maximum observable distance results from the cell design being limited by the size of the glass slide.

Ninghui Han Sep 2016
Figure 4.4 Brief procedure of a sliding bubble interacting with a flat hydrophilic microscope glass slide at 0.5° (view from left to right, top to bottom). The central bright spot is caused from the reflection of our microscope (or beam splitter), as presented in Chapter 3, it can be removed by image processing as shown in Figure 4.10 and Figure 4.14 later in this chapter. The image brightness and bubble orientation is not the same for every picture because each of them comes from an independent experiment.

Figure 4.4 shows an overview of a sliding bubble interacting with the hydrophilic surface at 0.5°. This procedure can be generally divided into three stages, big bouncing, small bouncing and sliding. At the big bouncing stage, like images 1 and 2 in Figure 4.4, the bubble bounced several times and we were not able to observe any interference.
fringes in the image, because in this stage the bubble was too far away from the surface. Naturally, the maximum distance that the bubble could reach after each bounce was decreasing with every bounce and after a couple of bounces the bubble was close enough to the surface so that interference fringes could be seen, as in images 3 to 5 in Figure 4.4. Many papers\textsuperscript{145-147} have reported that a single air bubble will only bounce a couple of times before it starts to slide stably, but this is not what we observed. The Newton’s rings show that, even if there was not a clear separating distance for the whole bubble, the central area of the bubble still bounced five or more times (image 3 to 5 in Figure 4.4). In these images each closed ring group in the fringes near the middle line is the remnant of one bounce. The rings are separated along the sliding direction because the bubble has already started to slide up the inclined surface. More details can be found in Figures 4.6 to 4.8. We call this stage the small bouncing stage. Then after the bubble completely finished bouncing, it finally began to slide stably, as can be proved by the stable interference patterns we observed from images 7 and 8 in Figure 4.4. During this stage, the thin film between bubble and the surface is gradually getting thinner, the height of the dimple is decreasing (the numbers of fringes in the central area is decreasing). Unfortunately, due to the limited length of our experiment equipment we do not have longer time images with the bubble at 0.5º. However, we do have those thin film evolution details at a lower angle of 0.2º, which will be shown in section 4.4 of this chapter, and the qualitative features of the shape do not change at longer times.

The whole shape of the bubble’s top surface is described as ‘toboggan shape’ by us due to it having two ‘rails’ at the left and right edges and a central channel in the middle, parallel to the direction of motion. More details of the toboggan shape will be described in the next section of this chapter.

Although the general shape of the bubble’s top surface does not change qualitatively after the small bouncing stage, it does evolve as the bubble gradually approaches the
solid surface over time. The interference patterns in images 5 to 8 in Figure 4.4 show the film flattening and the approach of the bubble to the solid by a decrease in the number of fringes. Figure 4.5 a shows the number of both bright and dark fringes between the thinnest and thickest parts of the film changing as time increases, and Figure 4.5 b shows the same fringe changes plotted against distance that the bubble has travelled.

![Graph a) Number of bright fringes vs. time](image)

![Graph b) Number of bright fringes vs. distance](image)

**Figure 4.5** Number of visible bright fringes we observed as a function of (a) sliding time and (b) distance, both referenced to the bubble's first approach to the surface.

From Figure 4.4 we can see that Newton’s rings appeared immediately after the
bubble finished the big bouncing stage, and fringes became clear enough to analyze about 0.2 seconds after first (microscopic) contact between bubble and solid surface. In the small bouncing stage, we can observe Newton’s rings with a complicated pattern, with more than one dimple on the top surface of the bubble, each dimple being the remnant of a small bounce, and there were more than 16 bright and 16 dark fringes between the minimum and maximum film thickness in the image during the small bouncing stage (image 3 in Figure 4.4). With time, the bubble got closer to the solid surface, and the central dimple’s fringe number decreased as can be seen in Figure 4.5. The numbers of both bright and dark fringes kept decreasing until only 9 bright and 9 dark fringes were visible in the image after 2.5 seconds of sliding (image 8 in Figure 4.4). Figure 4.5 shows the number of bright fringes visible between the maximum and minimum thickness decreasing against time and sliding distance of the bubble. Due to the limited size of the microscope glass slide, there is only a certain sliding distance that we could monitor in our experiment. At 0.5°, the number of bright fringes decreased from 16 to 9 in 2.5 seconds, and the bubble travelled 35 mm from the first touch point. We assume that the fringe number would keep decreasing as time and distance increase, and this is shown by the lower angle experiment that will be presented in section 4.4.

4.1.2 Fringe shape profile and 3D map

In the previous part we have shown the interference patterns associated with the complicated shape of the bubble’s top surface shape, which will now be discussed in more detail. By analyzing the fringes we can draw a 3D surface map of the thin film thickness, which also represents the deformation of the bubble’s top surface when it is close to the flat solid surface.

As presented in the last part, the bubble would bounce a couple of times after its initial collision with the hydrophilic surface and during this stage no clear fringes could be
observed. After the big bouncing stage, the bubble continued into the small bouncing stage and this is when we started to observe clear enough fringes to be analyzed. Figure 4.6 shows an image of a single air bubble in the stage of small bouncing. It is different from a symmetric Newton’s rings pattern of concentric fringes expected on perpendicular approach. The irregular fringes can be divided into three general areas, front and back edges, middle area, and left and right edges. After tracing all the bright fringes in Figure 4.6 we obtained the contour map shown in Figure 4.7 (details about analysis can be found in the section 3.3). The 3D surface map of the thin film of the bubble in the image of 4.6 is shown in Figure 4.8.

Figure 4.6 Image of bubble’s top surface in the small bouncing stage (sliding distance: 7.5 mm).
Figure 4.7 Contour map of the bubble’s top surface from Figure 4.6 (for all the contour maps the fringe orders are linked to a particular color of data points in the figure, the correspondence between fringe order number and film thickness can be found in Table 3.1. Sliding distance 7.5 mm).
A new angle on the coalescence of drops

Ninghui Han    Sep 2016

Figure 4.8 3D map of the thin film plotted from Figure 4.7 (the solid surface is at the bottom in this map and the blue arrow is the bubble’s sliding direction, red symbols in picture A are the original data points in Figure 4.7. Sliding distance 7.5 mm).

From Figure 4.8 we see that in the stage of small bounces, the minimum film thickness appeared at the left and right edges of the bubble, with the film being thicker in the front, back and central regions. The left and right edge regions were also where the fringes were closest together, indicating the steepest gradient in film thickness. Therefore, the film thickness increased more from the left/right edges to the middle area rather than to the front or back area. It is also worth noticing that the thinnest parts were not exactly at the 3 o’clock and 9 o’clock positions (with respect to the sliding direction) of the roughly circular area where we can observe Newton’s rings, they were actually slightly towards the rear of the circle. The maximum film thickness appeared along the central axis parallel to the direction of travel, as we can see in Figure 4.8. The maximum film thickness part looks roughly like an asymmetric dimple
but it happened to be more than one dimple in this stage because of bouncing. Two dimples can be observed in Figure 4.8, with the front dimple thinner than the back dimple because the fringe order number of back dimple is two more than that of front dimple, indicating that with each bounce, the dimple height is reduced. There was a thinner film thickness forming a saddle point between these two dimples, which was still not as thin as the thinnest part at the left/right edges. Starting from the thinnest film regions at the left and right edges again, and tracing toward the front and back areas this time, it can be seen from Figure 4.8 that the film thickness increases more to the back area than to the front. There was a circular barrier rim at the edge of where we could observe fringes, with the fringes not observable outside this rim. This indicates there was a steep increase in the film thickness outside the area within the barrier rim, as seen in the whole bubble 3D picture shown in Figure 4.9.

Figure 4.9 Inverted 3D picture with faint blue lines indicating the curvature of the bubble outside the dimpled region. The vertical scale exaggerates the apparent curvature of the bubble and its deformation (sliding distance 7.5 mm).
Once the bubble completely stopped bouncing, the thin film would evolve into the ‘toboggan shape’ as mentioned before. Figure 4.10 is an image taken just after the bubble finished bouncing, as indicated by only one dimple appearing. Again, the bright fringes in Figure 4.10 were tracked and the contour map shown in Figure 4.11 was obtained. From this 3D surface map of the thin film as well as the bubble’s top surface was constructed (Figure 4.12).

![Figure 4.10 Image of bubble’s top surface after it finished bouncing (sliding distance 14 mm).](image-url)
Figure 4.11 Contour map of the bubble’s top surface from Figure 4.10 (sliding distance 14 mm).
Figure 4.12 3D map of the thin film plotted from Figure 4.11 (the solid surface is at the bottom in this map and the blue arrow is the bubble’s sliding direction, sliding distance 14 mm).

The 3D map of the bubble (Figure 4.12) shows the thin film shape as well as the bubble’s top surface after the bouncing had stopped. As already seen in the small bouncing stage, the thinnest part of the thin film thickness was observed at the left and right edges of the barrier rim, still slightly toward the rear from the 3 o’clock position on the barrier rim. From the thinnest part, the film thickness increased toward the front, back and middle areas. The maximum film thickness also appeared in the dimple area, however, there was a significant difference from the small bouncing stage, which was that only a single dimple appeared, and the position of that dimple was not in the centre of the bubble but the middle-back area of the bubble. The fringes were crowded between the dimple and the back barrier rim of the bubble. On the other direction, from the dimple to the front barrier rim of the bubble, as well as from the...
left/right edge to the front barrier rim, the fringes were less crowded. This shows that the film thickness changed more gently to the sliding direction (front direction). The whole shape of the thin film as well as the bubble’s top surface can be likened to a ‘toboggan’, with two ‘rails’ (the thinnest film thickness parts at the left and right edges), a central channel (the central area from the front to the back of the barrier rim including the dimple area) and a higher gap at the front edge than at rear edge as it slides along the solid surface. This ‘toboggan shape’ is significant because we found that the bubble retained the ‘toboggan shape’ to the maximum distance and time we could trace (including longer times at lower inclination angles, described in Section 4.4 of this chapter). As before, the film thickness increases more rapidly outside the barrier rim area of the bubble and the whole bubble looked like Figure 4.13.

**Figure 4.13** Inverted 3D picture with faint blue lines indicating the curvature of the bubble outside the dimpled region. The vertical scale exaggerates the apparent curvature of the bubble and its deformation (sliding distance 14 mm).

Figure 4.14 shows a later stage from the image shown in Figure 4.10 (about 800 to
1400 ms later). The whole bubble has approached closer to the solid surface but retains the toboggan shape. Figure 4.15 was obtained by tracking the bright fringes from Figure 4.14 and 3D surface map of 4.16 was derived from Figure 4.15. The only difference between Figures 4.16 and 4.12 is that the number of fringes in the area has decreased from 16 to 10. This means the distance difference between the maximum film thickness and the minimum film thickness has decreased with time.

Figure 4.14 Images of a later stage of bubble’s top surface after Figure 4.10 (sliding distance 30 mm).
A new angle on the coalescence of drops

Figure 4.15 Contour map of the bubble’s top surface from Figure 4.14 (sliding distance 30 mm).

Figure 4.16 3D map of the thin film plotted from Figure 4.15 (the solid surface is at the bottom in this map and the blue arrow is the bubble’s sliding direction. Sliding distance 30 mm).

Ninghui Han  Sep 2016
4.1.3 Maximum and minimum film thickness against sliding time and distance

Another parameter of the bubble/solid surface system in our experiment is the absolute film thickness. With the complex deformation of the bubble described above, the film thickness is not uniform. We will present some data below for the maximum and minimum film thickness, with the difference between them giving some indication of the magnitude of the deformation.

The way we calculate the absolute thickness is by the method of wavelength swapping (more details of the wavelength swapping method to calculate absolute thickness can be found in Chapter 3). The absolute film thickness is not fixed during the stages of the bubble sliding and the whole bubble was gradually approaching the solid surface while sliding. Figure 4.17 shows the minimum and maximum film thicknesses against sliding time and distance. At the very early sliding stage we have called the big bouncing stage there were no fringes observed, therefore our data started from a couple of hundred ms after the initial touch between the bubble and the solid surface.
From Figure 4.17 we can see that the absolute thickness (minimum thickness) of the film decreased to about 200 nm after a sliding time of 2.5 seconds and a sliding distance of 35 mm at the inclined angle value of 0.5°. The maximum film thickness was also decreasing from more than 4500 nm to 2000 nm after 2.5 seconds’ sliding time. Because of the limitation of the length of the solid surface, we could not track the bubble further and longer. Although we cannot increase the length of the solid surface in our experiments, we can decrease the bubble’s sliding speed instead by lower the inclination of the system, and results for a lower angle of 0.25° are presented in section 4.4 below.

4.1.4 Sliding speed related to fringe shape and film 3D profile

The bubble’s sliding speed is another important parameter to describe the bubble/inclined solid surface system. We obtained the sliding speed of the bubble by calculating the position of the centre of the barrier rim as a function of the sliding time. Figure 4.18 shows the bubble’s sliding speed against sliding time.
The bubble’s initial sliding speed was above 30 mm/s but decreased to less than 20 mm/s. After 200 ms the sliding speed of the bubble reduced to 25 mm/s, and the bubble was still bouncing at this stage. Then the speed of the bubble kept decreasing and reached a final speed of about 15 mm/s after 1500 ms. This speed is very similar to the terminal speed value reported previously\(^7,58\) for similar size and similar values of the tilt angle in water. Therefore we can indicate that even if the bubble did not reach its terminal speed at the last stage we observed, it was not far from it.

The speed of the sliding bubble is considered to be very important because we want to know whether or not there is a relationship between the bubble’s sliding speed and the thin film profile. Therefore Figure 4.19 was made to link the bubble’s sliding speed with the thin film profile as well as the bubble’s 3D surface map at the same stage.
The relationship between the sliding speed and the thin film profile is not clear from the baseline experiment only, and further experiments were carried out by changing the liquid environment (salt concentration and viscosity), bubble size and the tilt angle compared to the baseline experiment to explore the relationship between the bubble’s sliding speed and the thin film profile.

4.2 Effect of salt concentration

Salt concentration can influence the sliding bubble’s terminal speed especially at a very low angle (lower than 4°) because the range of electric double-layer repulsion decreases as the salt concentration is increasing, and this has an influence on the disjoining pressure so that the bubble’s terminal speed will be influenced. Our experiments are all conducted between 0.2 to 2 degrees, which means that salt concentration is a significant feature in our bubble/solid surface system. In this part, one salt (potassium chloride KCl) with two different concentration values (0.1 mol/L and 0.01 mol/L) were investigated. The reason for choosing KCl is for easier comparison with literature. Every other parameter, including bubble size, inclined angle, viscosity of the liquid, surface type and condition were all kept the same as the baseline experiment.
Figure 4.20 shows the speed of the bubble as a function of sliding time for water, 0.1 mol/L KCl and 0.01 mol/L KCl. From the figure we can see that the higher the salt concentration was, the lower the sliding speed of the bubble was. This speed difference confirmed the report by Del Castillo who used the same salt and concentration as us.

![bubble sliding speed graph](image)

**Figure 4.20** Bubble’s sliding speed as a function of sliding time at different salt concentrations.

Since we want to discuss the relationship between the sliding speed of the bubble and the thin film profile, we selected one speed value (15 mm/s) and compared the interference pattern shape for different salt concentration values. Figure 4.21 shows the comparison result.
A new angle on the coalescence of drops

Image A of Figure 4.21 was taken at 500 ms sliding time and 8.65 mm sliding distance after first touch in 0.1 mol/L KCl solution, image B was at 1450 ms sliding time and 22.25 mm sliding distance after first touch in 0.01 mol/L KCl solution and image C was at 1550 ms sliding time and 23.42 mm sliding distance after first touch in water. All these three images shared a similar sliding speed of around 15 mm/s (±0.3), the reason why the speed is not exactly the same is because we calculate the sliding speed by the movement distance between two video frames of the bubble in the same group of data divided by the time, and this speed is considered to be the average speed over
the time between these two frames. Therefore, the instantaneous speed of the images in Figure 4.21 could have a slight difference of ±0.3 mm/s. Three images provided very similar fringe shape patterns and if we count the fringe numbers we found they are very similar as well: image A has 11 bright and 10 dark fringes, image B has 11 bright and 10 dark fringes as well and image C has 10 bright fringes and 10 dark fringes. The similar shape of fringe patterns indicates similar shapes of bubble’s top surface deformation. A possible reason why those fringe patterns were not exactly the same is because the instantaneous speed of the bubble in those images could have a slight difference. Based on equation 4.1, the capillary number is combined by the sliding velocity, viscosity and the surface tension, however, both the viscosity and the surface tension are not going to change significantly at such low salt concentrations. Therefore, this experiment gives a strong indication that the thin film shape is determined by the sliding speed of the bubble (or the other way around), and not by the sliding time or sliding distance.

4.3 Effect of viscosity

Liquid viscosity is an important parameter in the system of drop or bubble and solid surface in a liquid environment because it can influence the drop/bubble’s rising speed, sliding speed, film thickness and shape. In this chapter we are going to present the results in our bubble/solid surface system using a different viscosity compared to the baseline experiment.

In the baseline experiment the liquid we used is ‘cleaned’ water (the cleaning process is described in Chapter 3) which has a viscosity of 0.89 mPa•s at room temperature (25º C). In this part, 0.5 mol/L sucrose solution was employed instead of water in our bubble/solid system. This sucrose solution has a viscosity of 2.04 mPa•s at a temperature of 23.8 º C (the measured temperature of the liquid in this experiment). Every other parameter including bubble size, inclined angle, and surface condition
were all kept the same as the baseline experiment.

Figure 4.22 shows an overview of a sliding bubble interacting with a hydrophilic surface inclined at 0.5° in 0.5 mol/L sucrose solution. Compared to the process in water (Figure 4.4), there are three main differences caused by the difference in viscosity. Firstly, the bouncing stage cannot be divided into big and small bouncing stage at this time. In the baseline experiment results we defined the small bouncing stage as the time that there is not a clear separating distance for the whole bubble but multiple dimples appear in the central area of the bubble. With a higher viscosity in 0.5 mol/L sucrose solution, we did not observe such multiple dimples as Figure 4.6, and the fringes turn into toboggan shape directly as images two to four show in Figure 4.22. The total number of bounces is 10 in sucrose solution (after the 6th bounce the fringes can be observed clearly), this number is larger than the number of bounces of the bubble in the big bouncing stage (which is about 6) in water but smaller than the total number of bounces for the combined big and small bouncing stages in water (12 or more).

Figure 4.22 Overview of a sliding bubble/hydrophilic solid surface in 0.5 mol/L sucrose solution whose viscosity is just over twice that of water (view from left to right, top to bottom).
Secondly, the sliding speed decreased more quickly due to the higher viscosity. Figure 4.23 shows the sliding speed difference between sucrose solution and water at 0.5°.

![Figure 4.23 Sliding speed as a function of sliding distance with different viscosities.](image)

The third difference is the shape of the Newton’s rings shown in the images after bouncing. As Figure 4.24 shows, we can see that the shape of the fringes in sucrose solution still show the toboggan shape, the minimum film thickness still appeared at the left and right areas of the sliding direction, and there was still a central channel and a central back dimple which indicates where the maximum film thickness is located. However, in contrast to the baseline experiment, the thinnest parts of the thin film this time are located at the 3 o’clock and 9 o’clock positions, but there was a gap between the thinnest film thickness part and the left/right barrier rim edges. Also, although the dimple was still located at the middle-back area, the shape of the dimple was quite different and more complex from that of baseline experiment, it was larger, wider and less circular.
Figure 4.24 Image of bubble’s top surface in 0.5 mol/L sucrose solution after it finished bouncing (sliding distance: 12 mm).

Figure 4.25 Contour map of the bubble’s top surface from Figure 4.24 (sliding distance 12 mm).
Figure 4.26 3D map of the thin film plotted from Figure 4.25 (the solid surface is at the bottom in this map and the blue arrow is the bubble’s sliding direction. Sliding distance 12 mm).

An Image of the bubble’s top surface at a later stage (30 mm further from the position of Figure 4.24) is shown in Figure 4.27. From the contour map (Figure 4.28) we can see that the dimple at the middle-back area looks similar to its early stage (Figure 4.25), however, the thinnest film thickness position has changed. In the early stage (Figure 4.24) the thinnest film thickness was located at 3 o’clock and 9 o’clock but slightly away from the barrier rim, whereas at the later stage (Figure 4.27) the thinnest film thickness moved closer to the barrier rim and slightly towards the rear of the circle, which was quite similar to its location in the baseline experiment.
Figure 4.27 Image of bubble’s top surface in 0.5 mol/L sucrose solution at a later stage (sliding distance: 25 mm).

Figure 4.28 Contour map of the bubble’s top surface from Figure 4.27 (sliding distance 25 mm).

In addition to the position and shape difference, there is one more significant difference caused by the increased viscosity, which is the absolute film thickness. We
observed greater film thicknesses in 0.5 mol/L sucrose solution compared to water after comparable sliding distances and times. Figure 4.29 shows the maximum and minimum film thickness changing against sliding distance in 0.5 mol/L sucrose solution. Compared to baseline water experiments (Figure 4.17), the maximum film thickness was still over 3500 nm before 5 mm of sliding, however, the rate of decrease was very slow, and after 40 mm sliding distance the depth of the dimple (where the maximum film thickness was located) was still over 3000 nm, suggesting that liquid remains trapped in the dimple for longer in the higher viscosity solution. At the same time, the minimum film thickness shows a large difference between sucrose and water throughout the sliding process. The minimum film thickness was over 1300 nm when the bubble finished bouncing and gradually decreased to 950 nm after sliding 40 mm in sucrose solution.

Figure 4.29 Maximum and minimum film thickness against sliding distance in 0.5 mol/L sucrose solution.
4.4 Effect of inclined angle

The angle of inclination is significant in our experiments for two reasons. Firstly, the design structure of our ‘bubble chamber’ (see research methodology chapter) leads to a big limitation of our experiments, that is the observable sliding distance. Due to employing a standard microscope glass slide as our solid surface, the maximum sliding distance is 40 mm (the length of a standard microscope slide is 75 mm but our rising bubble approaches the middle region of the glass slide, so that only about 40 mm of the sliding distance can be traced). Therefore, in order to obtain a longer sliding time and reach a later sliding stage of the bubble, we can lower the inclination instead. Secondly, the inclined angle influences the bubble’s sliding speed, and because the speed of the bubble was shown in Section 4.2 to affect the thin film drainage process, there is a clear need to test the effect of inclined angle on the sliding bubble/solid surface system. The inclined angle of the baseline experiment is $0.5^\circ$, and a lower angle of $0.25^\circ$ was employed to compare with the baseline experiment. For the results presented here, the only parameter that has been changed is the inclination, while other parameters, including bubble size, viscosity of the liquid, electrolyte concentration, surface type and condition are all kept the same as the baseline experiment.

Figure 4.30 shows the sliding speed against time of the bubble at the angle of $0.25^\circ$, and Figure 4.31 shows the Newton’s rings shape of the times labelled a to f in Figure 4.30. At the lower angle of $0.25^\circ$ the sliding bubble appears to reach a steady stage, i.e. constant sliding speed, after about 7 s or a sliding distance of 25 mm, which is within the experimentally observable distance.
A new angle on the coalescence of drops

Figure 4.30 Sliding speed as a function of sliding time of bubble in 0.25°.

Figure 4.31 Brief overview of a sliding bubble/hydrophilic solid surface at 0.25° (view from left to right, top to bottom).

Compared to the Newton’s rings observed at 0.5° (Figure 4.4), Figure 4.31 shows a further drainage condition of the thin film. As can be seen in Figure 4.32 to 4.34, the
thinnest film thickness is still located at the edges at 3 o’clock and 9 o’clock, and maximum film thickness remained in the asymmetric dimple and still appeared at the middle-back area, but at this stage only 5 bright and dark fringes could be observed. The channel under the ‘toboggan’ is more uniform than that observed at an earlier stage of drainage in the baseline experiment, with only slight gradient between the opening at the front and the central part while the height difference between dimple and back barrier was also less pronounced since the fringes are not as crowded as before. The whole shape of the thin film was still a toboggan, but the depth of the central channel was decreasing gradually as the water drainage process went on. At the longest time we can reach (about 17s from Figure 4.30) the bubble’s sliding speed appeared to be stable. In section 4.2 of this chapter we have proved that the thin film profile is related to the bubble’s sliding speed. Therefore, Figure 4.32 to 4.34 is likely to be the final shape for steady-state sliding due to the bubble has appeared to reach a constant sliding speed.

Figure 4.32 Image of bubble’s top surface of the longest time we can reach (17 s). The inset shows the same image, rotated and with background intensity subtracted.
Figure 4.33 Contour map of the bubble’s top surface from Figure 4.32.

Figure 4.34 3D map of the thin film plotted from Figure 4.33 (the solid surface is at the bottom in this map and the blue arrow is the bubble’s sliding direction).
4.5 Effect of bubble size

Bubble size is another important parameter in the bubble/solid surface system, and bubbles of different size will have different initial and terminal velocities. This phenomenon has been experimentally observed as well as theoretically explained in a number of papers\textsuperscript{155, 156}. The bubble’s sliding speed has been shown earlier in this chapter to influence the thin film drainage process, which makes us interested in studying thin film drainage with different bubble size with the same viscosity, surface type and inclined angle value. Different bubble sizes will also make the size of the thin film as well as the deforming area of the bubble's top surface different, which could directly lead to a different depth of the dimple\textsuperscript{124}. Here we compare two sizes of the bubble, 1.67 mm (the baseline value) and 1.2 mm in radius respectively, interacting with a hydrophilic microscope glass slide in water inclined at an angle of 0.5°. The range of the bubble size was well controlled (maybe not perfectly controlled) in our experiments thanks to the inner diameter of our bubble releasing capillary always being the same.

![Figure 4.35 Sliding speed as a function of sliding time of different radii of bubble at 0.5° in water.](image)

Figure 4.35 shows the difference in sliding speed between bubbles of 1.67 mm in...
radius and 1.2 mm in radius against sliding time. Due to the limitation in sliding distance because of the length of the glass slide, the bubbles of different size had different observable sliding times. From the figure we can see that the larger (1.67 mm) bubble’s sliding speed at early stage (0-2 mm of sliding distance) was more than 30 mm/s and decreased quickly to 15 mm/s in 1.5 seconds, while the small bubble (1.2 mm) only has an sliding speed of 10 mm/s at first and reduced slowly to 7 mm/s after 2 seconds.

Figure 4.36 shows the sliding speed of both bubble sizes against sliding distance. Based on Figure 4.36, we show different stages of top view images of both sizes of the bubble in Figure 4.37.

Figure 4.36 Sliding speed as a function of sliding distance of different sizes of bubble at 0.5° in water.

Figure 4.37 shows characteristic interference patterns for both large and small bubbles after various sliding distances. The difference between large and small bubbles began to show up from the first stage, as group A shows, when the small bubble had finished its large bouncing stage and began its small bouncing stage with clear fringes visible, the large bubble was still in its large bouncing step without any clear fringes. When

Ninghui Han   Sep 2016
the large bubble finished its large bouncing stage and started to show fringes during the small bouncing steps (group B in Figure 4.37) at 5 mm, the small bubble had finished its small bouncing steps already and the thin film had already deformed a toboggan shape. After 10 mm of sliding, the big bubble also finished its small bouncing stage, and formed a toboggan shape (group C of Figure 4.37). At a sliding distance of 20 mm (group D in Figure 4.37), the thin film between both large and small bubbles remained in the toboggan shape. However, due to the size difference, more fringes are observed in the deformed area of the larger bubble, which reflects the height difference between the maximum film thickness and the minimum film thickness. Although we cannot reach the distance when the thin film completely drained into a steady-state configuration and the large bubble reaches its terminal speed due to our equipment limitation, it is not hard to predict that large and small bubbles will have a different time for their thin film to drain because they have got different sliding speeds regardless to the time, different radius of the barrier rim, and different depth and size of dimples in the central-back area of the bubble’s top surface. All of these factors will affect the water draining progress from the dimple. We will discuss more about this feature in Chapter 4.6.
Figure 4.37 Interference patterns as a function of sliding distance of different sizes of bubble at 0.5° in water (the vertical stripes in the right-hand series of images are caused by an intermittent fault with our high-speed camera, see Chapter 3 for details).

Figure 4.38 shows the maximum and minimum (absolute) film thickness decreasing as a function of sliding distance for both large and small bubbles. As noted above, the small bubble’s fringes were visible at shorter distance and its dimple was less deep than that of the larger bubble. At the same time, the small bubble’s absolute thickness...
reduced to its minimum observation level (236 nm limited by the wavelength of red light) at an earlier distance than that of the large bubble.

Figure 4.38 Maximum and minimum film thicknesses against sliding distance for different bubble radii at 0.5° in water.

4.6 Discussion

4.6.1 The dynamics of thin film drainage at an inclined angle into the ‘toboggan shape’.

Our baseline experiment result (Section 4.1) has shown the irregular and complex shape (toboggan shape) of the bubble’s top surface deformation between a sliding bubble and a hydrophilic solid surface at an inclined angle of 0.5°. Figure 4.39 shows an example of the interference patterns of the toboggan shape we have discussed before. In their modelling work, scientists like Hodges et al.\textsuperscript{152} or Carnies et al.\textsuperscript{140} did not attempt to resolve the shape of the drop near the wall but instead the drop shape was prescribed as either spherical, or a flat top surface. Whether or not this toboggan shape is the final shape of the thin film, the 3-dimensional shape of the thin film
profiles is clearly complicated and is worth discussing at least for an understanding of the film drainage as it evolves toward a stable thin film configuration. As presented above, after the bubble finished bouncing the thin film would evolve into the toboggan shape and there would be no significant change for the shape apart from a progressive decrease of the central film thickness until the furthest sliding distance we could reach. During this process, the film’s general shape is still like the toboggan, but the number of fringes between the central maximum and the minima near the edges decreases. Therefore, we take Figure 4.39 for example to discuss the dynamics of the evolving deformable drop.

![Sliding direction](image)

Figure 4.39 Example of interference patterns and 3D surface map.
In order to have a better understanding of how the toboggan shape appears, we need to have an idea of which one or combination of these two factors dominate the deformation: hydrodynamic pressure and disjoining pressure (more details can be found in Chapter 2 of this thesis). Disjoining pressure (arising mainly from the electrical double layer and van der Waals forces) has an increasing effect when the bubble comes extremely close (less than 100 nm) to the solid surface. However, we observed the toboggan shape from a much larger film thickness (a few microns), which allows us to conclude that the hydrodynamic force is the main force that dominates the deformation of the bubble surface and the thickness profile of the thin film.

Chapter 2 has reviewed previous work on the perpendicular collision between a deformable body and a solid surface in liquid, including the symmetrical dimpling phenomenon illustrated in Figure 4.40. In this case of completely symmetry from any lines that cross the middle of the dimple (line a-b or c-d in Figure 4.40), lubrication theory produces the film drainage equation

$$\frac{\partial h}{\partial t} = \frac{1}{12\mu r} \frac{\partial}{\partial r} \left( rh^2 \frac{\partial p}{\partial r} \right)$$

(4.2)

where $h(r, t)$ is the film thickness as a function of radial coordinate $r$ and time $t$, $p(r, t)$ is the excess hydrodynamic pressure in the film relative to the bulk liquid, and $\mu$ is the assumed Newtonian film viscosity. This equation can explain how the dimple forms during the approach between a deformable body and a solid surface. Initially, the closer a point is to the central axis, the smaller $r$ is and the larger the hydrodynamic pressure will be. Therefore the central area has the largest hydrodynamic pressure which can invert the bubble’s local curvature and create a dimple centred on $r = 0$. The hydrodynamic pressure decreases from the central axis of the deformable body to the edge gradually and because of the axial symmetry the shape of the dimple is
completely symmetric, with the variation in film thickness from the centre of the
dimple to the edge being the same in all radial directions. In other words, no matter
how you view the cross section from direction a-b or c-d or any other direction that
crosses the centre of the dimple, you will always have the same dimple shape as
illustrated in Figure 4.40.

![Figure 4.40 Dimpling phenomenon of regular (symmetric) Newton's rings and its cross section shape in the perpendicular collision system.](image)

However, once there is an inclined angle, the axial symmetry system will be broken
into a mirror symmetry system, as Figure 4.41 shows, and in this case the dimple forms
in the shape we have called ‘toboggan’. The interference patterns clearly show that
the thin film is only symmetric about the y-axis (taking the bubble's sliding direction as
the y-axis) (line c-d in Figure 4.41) but never having x-axis symmetry.
Figure 4.41 Mirror-symmetric Newton’s rings from our experiment results, and different cross section cuts.

If we look at the cross sections parallel to the x-axis of the bubble in Figure 4.41, the inclined angle does not cause any asymmetry from the central line to the left or right direction. A group of pictures of selected cross sections parallel to the x-axis (a-b, e-f, g-h and i-j from Figure 4.42) is shown in Figure 4.42, from where we can see the general shape of them are all the same, but with differences in the maximum film thickness at the centre and the minimum film thickness at the edges. Compared to the perpendicular collision situation shown in Figure 4.40, there are two main differences caused by the oblique collision when the flat solid surface has even a small inclination. The first one is the location of the maximum film thickness of the bubble, which is not located on the line crossing the centre of the bubble but is moved to the rear of the bubble. The second difference is the minimum film thickness. In the perpendicular collision system, all the points on the barrier rim share the minimum film thickness,
thus any cross section (whether it passes through the center or not) would show two points of equal minimum thickness. In the oblique collision system, only one cross section, perpendicular to the y-axis and passing approximately (but not exactly) through the centre of the deformed area, would include the two points of minimal film thickness.

![Cross section shapes](image)

*Figure 4.42 Different cross section shapes of the thin film in Figure 4.41 (parallel to x-axis).*

Now, if we look at the cross section along the y-axis (line c-d in Figure 4.41), there is a clear difference from that of the perpendicular collision case because of the inclined
angle. Figure 4.43 shows a schematic of the cross section of line c-d in Figure 4.41. The dimple appears not in the centre but in the back area which suggests that that area is where the maximum hydrodynamic pressure appears. Also, the rate of film thickness decreasing from the dimple to the back edge and the front edge are completely different, the film thickness decreasing much more quickly from the dimple to the back edge compared to the front edge.

Figure 4.43 Cross section shape of the thin film parallel to y-axis in Figure 4.41. Insert picture is the image of cross section of drop shape from Griggs et al.94.

The toboggan shape we obtained differs from circular shape of regular Newton’s rings of perpendicular collision system in mainly two parts. Firstly, unlike a perpendicular collision resulting in a barrier rim that shares the minimum film thickness, the front and back part of barrier rim in our toboggan shape has been lifted up and the back barrier rim has a slight thicker film thickness than the front. This trend shows a disagreement with the result reported by Griggs et al.94 (insert picture from Figure 4.43), who found a higher lift in the front than at the back of the drop. However, our experimental data is more convincing because if you look at Figure 4.15 or 4.41, the bright fringe of order number 7 clearly crossed through the front area along cross section c-d (parallel to the y axis) but did not pass it at the back. This suggests that the
film thickness at the back barrier is thicker than the front. Although the liquid in the
dimple will drain in all directions from the middle, the fluid flow through the front and
back barrier rim is larger because of the sliding velocity, and this is why the front and
back barrier rim have been lifted up and the film thickness there is thicker than that of
the left/right barrier rim.

The second main issue of our toboggan shape thin film is the dimple’s position at the
middle-back area, with quasi-elliptical contours instead of circular ones in the
perpendicular collision system. The reason for this difference is also the sliding velocity
of the bubble, with the liquid trapped in the dimple having inertia and staying where
it was while the whole bubble was moving forward, while the bubble ‘carried’ the
liquid in the dimple to move together and the counterforce from the liquid deformed
the dimple to its elliptical shape and pulled the dimple position to the rear of the
bubble.

4.6.2 Evolution of toboggan thin film and its final shape

In the perpendicular collision system, unless there is attraction between the surfaces,
the dimple will gradually evolve toward a stable flat film whose thickness depends on
a balance between disjoining pressure in the film and Laplace pressure in the
deformable body. Once there is an inclination of the surface, gravity will drive the
deformable body to move along the surface, eventually reaching a terminal speed
where the gravitational force is balanced by hydrodynamic drag. It is not immediately
obvious whether the terminal shape of the sliding bubble is flat, or with a more
complicated deformation like a toboggan. The film has been considered to be flat and
smooth in some theoretical modelling papers. Our bubble/solid surface
experiments show that, at least in the initial time of sliding of the bubble, the shape
of the thin film is not flat and has reduced (mirror) symmetry with two rails at the
edges of the left and right side of the sliding direction and a central channel with a
dimple in the middle-back region. This complex toboggan shape of thin film will keep evolving as the water in the middle channel and dimple keeps draining, as Figure 4.44 shows, with the whole bubble approaching the solid surface gradually, the approach speed (the rate of decrease of film thickness) increasing from the minimum film thickness part (left/right edges) to the maximum film thickness part (middle-back dimple).

![Figure 4.44 Thin film deforming process for the toboggan profile.](image)

When a gravity-driven bubble in a liquid medium slides along an inclined wall, its terminal speed can be determined by the following equation:

\[ U_T = Kr^2 \sin \theta \]  

(4.3)
A new angle on the coalescence of drops

where $U_T$ is the bubble’s terminal speed, $K$ is a constant depending on the properties of the fluid, $r$ is the bubble’s radius and $\theta$ is the inclination value of the wall. This trend has been proved by many works, among which Castillo$^{57,58}$, Zukoski$^{46}$ and Aussillous$^{54}$ have employed similar bubble size and inclinations to our experiments. A comparison of our bubble’s latest speed and the terminal velocity presented by Castillo$^7$ is shown in Figure 4.45. The minimum inclination value that Castillo employed for her terminal velocity measurement was 0.6° which is a bit higher than our baseline experiment (0.5°), so we would expect the terminal speed of Castillo’s result to be slightly higher than ours because of the higher inclination. However, as Figure 4.45 shows, the sliding speeds we measured at the furthest sliding distance in both water and 0.1 mol/L KCl solution (15 and 11 mm/s respectively) are higher than Castillo’s results, suggesting that the bubble in our baseline experiment had not finished its drainage process yet because the sliding speed should decrease further.

In order to detect the thin film shape’s final stage, the bubble needs to be traced longer and further. Due to our experiment equipment’s limitation, we can only trace the bubble to a maximum sliding distance of 40 mm. We slowed the bubble down to achieve a longer tracing time by lower the inclination to a minimum of 0.25° (see Section 4.4), and Figure 4.32 to 4.34 are the pictures of the latest stage of the thin film

Figure 4.45 Bubble’s final sliding speed we measured compared to Castillo’s$^7$ results.
we reached. It is not certain whether this represents the thin film shape’s final equilibrium state, but the flowing argument suggests that it might be.

There is, another parameter that shows whether the drainage was on going, which is the sliding speed of the bubble. Our results with different salt concentrations (Section 4.2) prove that the sliding speed of the bubble can determine the thin film shape (or the other way around). Based on this we can assume that when the thin film shape is stable, either a flat film or other equilibrium shape, the sliding speed of the bubble is also stable, which means the bubble reaches its terminal speed. Conversely, if we can show in our experiment that the bubble’s sliding speed has not reached its terminal speed, we can conclude that the film would still be draining and the thin film shape still be evolving. In Section 4.4, with an inclination angle of 0.25° the sliding speed appears to have stabilized, i.e., to have reached its terminal speed (Figure 4.30), and so it is reasonable to conclude that the film shape (shown in Figure 4.32 to 4.34) has also reached its final form. This form is still that of a ‘toboggan’, not a uniform flat film. In order to obtain a stronger confirmation, we would need to trace the bubble a longer time or distance, as noted when discussing optimization of our experimental devices in Chapter 7.

4.6.3 The effect of viscosity on the thin film shape

Viscosity is a very important parameter in the drop or bubble and solid surface system because the hydrodynamic force and hence the deformable body’s shape is directly influenced by different viscosities. Griggs$^{94}$ reported that in both low (15° to 45°) and high (45° to 60°) inclination value, the drops become increasing deformed with the increasing value of viscosity (seen in Figure 4.46), similarly to earlier works of Stone$^{158, 159}$. 

$Ninghui Han  Sep 2016$
In our experiment, the importance of viscosity as a function of thin film drainage process has been proved even at a very small inclination value (0.5°). From the comparison of Figure 4.47 we can clearly see the interference patterns differ from higher sucrose solution (Figure 4.47 A) to water (Figure 4.47 B).

In the baseline experiment (Figure 4.39), the middle-back dimple was elliptical but not very far from circular, whereas in sucrose solution the dimple deformed wider and
appeared more like a crescent, and this made the cross section of the thin film from a line passing through the dimple (parallel to the x-axis, line c to d in Figure 4.48) an interesting shape (Figure 4.49).

Figure 4.48 Cross section parallel to x-axis of bubble in 0.5 mol/L sucrose solution.
Figure 4.49 Cross section shape of the thin film parallel to x-axis in Figure 4.48.

The thin film shape of Figure 4.48 can be described as a ‘wimple’ which means the film thickness decreased from the edge to the middle at the beginning, then the thickness increased in the middle and a rippled ‘wimple’ shape has formed. This wimple has been observed by Clasohm and Horn in their SFA experiments between mica and mercury drop, but in their experiment the wimple shape is just an intermediate form of the film drainage process and only lasts a short time before a real dimple formed. However, in our experiment this wimple cross section film shape stayed until the maximum sliding distance we could trace.

Apart from the shape difference of the dimple, the depth of the dimple between water and sucrose solution is also different. Figure 4.11 and 4.25 are the contour maps of water and 0.5 mol/L sucrose solution respectively, the central-back dimple’s fringe order is 18 of water compared to 14 of sucrose solution, this means the depth central-back dimple of bubble in sucrose solution is 1000 nanometers lower than water at the same stage. Moreover, as can be seen in Figure 4.29, not only the maximum film
thickness but also the minimum film thickness shows a difference between sucrose solution and water, the maximum film thickness (depth of the middle-back dimple), as presented, decreased as the viscosity increased, however, the minimum film thickness (left/right edges) increased in higher viscosity liquid.

4.6.4 Sliding vs rolling

The motion of a bubble along a solid surface could either be sliding, rolling or any combination of these two[83]. In our baseline experiment, the bubble’s motion was clearly recorded by the high speed camera from the top view and from the interference fringe patterns we can speculate on the mode of motion of the bubble.

To separate the motion of sliding and rolling, we need to compare the fringe patterns of the moving bubble at one stage and at a second stage a short time later. Figure 4.50 is one example.

![Figure 4.50 A bubble at different stages in the same experiment running (hydrophilic solid surface, 0.5º, water). Image B is taken 0.16 seconds later than image A.](image)

Figure 4.50 B is the stage 160 ms later than Figure 4.50 A. If the bubble were sliding, the fringes would move with the bubble during the motion, and if the bubble was
rolling, then the fringes should stay where they were in the screen during the motion. Figure 4.50 shows that neither the simple sliding nor simple rolling can explain the motion, so the motion of the bubble appears to be a combination of sliding and rolling because from closer inspection of Figure 4.50 we can see features of both sliding and rolling of the bubble.

Figure 4.51 shows the evidence of a rolling feature. If we point at one bright fringe in the middle channel of the bubble like Figure 4.51 A (red circle), then at the later stage of Figure 4.51 B we can see that the red circle, fixed with respect to the solid surface, is still pointing at the bright fringe which we marked before. This means the fringe did not move its position with the bubble but stayed where it was during the motion of the bubble. The same thing happened with all the fringes in the central channel to the back dimple position, suggesting that the central channel part of the bubble’s top surface was rolling like a ‘tank track’ (shown in Figure 4.52)

Figure 4.51 Comparison of middle bright fringes (position) in Figure 4.50.
However, the observation that the central channel part of the bubble was rolling does not mean the whole bubble was rolling. Figure 4.53 takes the same group of bubble images but looks at a different area of the bubble, the right edge area, Figure 4.53 shows that there is no difference between the edge fringes’ shape, they look very much the same, just displaced along the surface with the body of the bubble. This integral movement is what we expect for ‘sliding’, quite different from what we observe in the central channel of the bubble.
This phenomenon that a deformable body’s movement is a combination of both sliding and rolling has been reported in previous studies of rolling and sliding\textsuperscript{83, 152, 160}. Thampi et al.\textsuperscript{83} states that for given viscosities and slip length, the only parameter that determines the choice of rolling, sliding or a combination of the two is the shape parameter, which simply means how far away from circular the deformable body cross section is, the closer to circular, the higher the percentage of rolling. Thampi’s conclusion can easily be related to reality, a water drop slides down a window, but a small iron ball will roll. The iron ball is definitely more circular on the cross section than water drop because it would not deform easily. But our experiment result shows a more complicated situation.

If we look at the cross sections for lines c-d and k-l in Figure 4.41 we can easily figure out that the cross section along line k-l is much closer to a circle than along line c-d, but our images show that the part of bubble at the edge area (line k-l) is more sliding and the central channel part of bubble (line c-d) is more rolling. The fact that rolling and sliding are both seen, but in different areas of the bubble, implies that there must be shearing motion present within the bubble’s surface. Whether or not this shearing motion appears all through the bubble’s surface or just at certain areas require further detecting.
Chapter 5 Results and discussion for hydrophobic surfaces

In the previous chapter we presented and discussed the thin film profile between a single air bubble and a hydrophilic flat solid surface for the bubble sliding in a liquid environment at several inclined angles. In this chapter, we are going to discuss how the thin film deforming process occurs once we switch the hydrophilic solid surface to a hydrophobic one.

Method
The experimental method of this chapter is exactly the same as the previous chapter apart from changing the hydrophilic surface to a hydrophobic one. This was achieved by exposing the glass surface to chlorotrimethylsilane vapour, as described in Chapter 3. Two inclined angle values of 0.5 and 1° were studied with the hydrophobic surface, all the bubbles used were the same size (1.5 mm in radius) and the liquid was always water in this chapter.

5.1 Results at 0.5°

The most significant difference of the thin film drainage procedure between hydrophobic and hydrophilic surface conditions is that the thin film is expected to rupture completely sometime after the initial collision with hydrophobic surfaces. Here we present details of the thin film rupture process including sliding time and sliding distance for an inclination of 0.5°.

As noted before, the thin film between an air bubble and a hydrophobic solid surface will completely rupture during the collision process, whether the approach is perpendicular or oblique. However, once there is an inclined angle, even it is very small,
there will be a difference in the rupture process between the oblique and perpendicular cases. An example of the whole procedure for a single air bubble (1.5 mm in radius) colliding with a hydrophobic glass slide in water at inclined angle of 0.5° is shown in Figure 5.1. Figure 5.1 is a sequence of images starting after the air bubble just finished bouncing (when we started to observe fringes), first touched with the hydrophobic surface when the film ruptured, and finally fully attached to the surface with a large contact area.

Figure 5.1 shows us that at 0.5°, the air bubble would slide for a short distance before the film ruptured and the bubble stuck to the hydrophobic surface. After the initial collision the thin film profile of an air bubble against a hydrophobic surface is similar to that against a hydrophilic surface (described in Chapter 4), with a ‘toboggan’ shape forming. As seen in Figure 5.2, 5.3 and 5.4 below, there is no obvious difference between this shape and the ‘toboggan’ observed with a hydrophilic surface. However, before sliding very far, the thin film ruptured at a point near one of the toboggan’s rails (the fifth image of Figure 5.1). After this the bubble immediately stopped sliding and the contacting area between bubble and hydrophobic surface would spread very fast and finish with a large circular shape, which we refer to as ‘full contact’ when the large circular contacting area does not change any more. This spreading process takes less than 60 ms from the first touch until full contact.
Figure 5.1 Procedure of single air bubble colliding with hydrophobic glass slide in water at inclined angle of 0.5°.

In order to have a better idea of how the thin film completely ruptures, the interference image just 1 frame (about 5 ms) before the first touch between air bubble and hydrophobic surface is shown in Figure 5.2. We traced the bright fringes of Figure 5.2 as in the previous chapter for hydrophilic experiments and obtained a 2D map of
fringes in Figure 5.3. From with the wavelength of the red light we used, the 2D map can be converted into a 3D map as we did for hydrophilic results (more details can be found in Chapter 3). Figure 5.4 shows the 3D map of the thin film profile just before the first break through in oblique and side view directions.

![Image](image-url)

**Figure 5.2** Bubble’s top image 5 ms before the film rupture started (sliding distance 3 mm).
From Figure 5.1 and other comparable observations, we find that the thin film would lose its integrity from a single point each time, when some part of the bubble’s top surface broke through and touched the hydrophobic surface. Figure 5.5 shows an example of the first touch point. Collecting observations from 12 experiments on thin film rupture with a single air bubble against a hydrophobic surface at 0.5° in water, Figure 5.6 shows a map of where the first touch point happened with respect to the
sliding direction of the bubble. Blue crosses in Figure 5.6 indicate natural rupture of the thin film, which happened 7 times in our experiments. Those first touch points of natural rupture are located mostly at the left or right edge of the barrier rim, where as we saw in Chapter 4 the minimum film thicknesses are located. Green crosses in Figure 5.6 indicate four occasions when rupture of the thin film was caused by a visible particle on the hydrophobic surface. In these cases, the particles increased the height of the solid surface and made the local film thickness thinner than usual, which would increase the probability of thin film rupture at this location when the bubble passed by. Even with the random position of dirt particles, the rupture always occurred at a point around the barrier rim, though not always at the 3 o’clock and 9 o’clock positions of minimum thickness in the absence of particles. The black cross shows the only time thin film rupture did not start from the barrier rim but in the middle area. This only occurred once, and we are not able to offer a clear explanation. In general we conclude that film rupture is most likely to occur at or close to one of the two points where the film thickness is minimum, which are the 3 o’clock and 9 o’clock positions around the barrier rim. This predictability is in contrast to the situation for perpendicular approach\(^7\), where the barrier rim is a uniform circle, and initial rupture could occur at a random point anywhere around that circle. The interference fringe orders were unknown in these experiments because it was impossible to obtain images with different wavelengths of light source in one single running of the experiment. In contrast to the previous hydrophilic experiments, the previous bubble had stuck to the hydrophobic surface and blocked the following bubbles before we could switch the light source. As a result the absolute film thickness between bubble and hydrophobic surface was not known.
Figure 5.5 Example of the first touch point.

Figure 5.6 First touch points spreading map, blue symbols refer to naturally coalescence, green symbols refer to the cause of dirt and black symbol refers to unexpected coalescence.

Apart from the initial rupture position, there are another three parameters recorded.
in hydrophobic experiments. The first parameter is the time it takes from the initial bubble collision with the surface until the rupture occurred (at which time the bubble also stopped sliding), and the second is the time it takes from the rupture occurring until the contact area stopped extending (and a stable contact area formed). The third parameter is the sliding distance before a bubble stuck to the hydrophobic surface. Table 5.1 shows the information including sliding time, thin film rupture time and sliding distance for the coalescence events from Figure 5.6.

<table>
<thead>
<tr>
<th></th>
<th>Sliding time (ms)</th>
<th>Contact spreading time (ms)</th>
<th>Sliding distance (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st time</td>
<td>382.5</td>
<td>40</td>
<td>3.02</td>
</tr>
<tr>
<td>2nd time</td>
<td>349</td>
<td>38</td>
<td>3.20</td>
</tr>
<tr>
<td>3rd time</td>
<td>442.5</td>
<td>34</td>
<td>Not recorded</td>
</tr>
<tr>
<td>4th time</td>
<td>248</td>
<td>70</td>
<td>3.14</td>
</tr>
<tr>
<td>5th time</td>
<td>214</td>
<td>72</td>
<td>3.29</td>
</tr>
<tr>
<td>6th time</td>
<td>414</td>
<td>36</td>
<td>Not recorded</td>
</tr>
<tr>
<td>7th time</td>
<td>396.5</td>
<td>38</td>
<td>3.53</td>
</tr>
<tr>
<td>Average</td>
<td>349.5</td>
<td>46.8</td>
<td>3.24</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>80</td>
<td>15</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Table 5.1 Sliding time, contact spreading time (i.e., the time between initial film rupture and air-solid contact area reaching its maximum size) and sliding distance, for observations of seven times of natural rupture of the thin film.

According to Table 5.1 most of the times in our experiments the first touch of the air bubble and the hydrophobic surface happens after around 350 to 450 ms sliding time and the sliding distance varies from 3 to 4.5 mm.
5.2 Results at 1°

At the inclined angle of 1°, we did not obtain as many results as 0.5°, the reason being that the higher inclined angle made the bubble slide faster, so that the bubble would slide further before the thin film rupture happened. This made it difficult to get the images of rupture because we needed to predict the rupture position for the sliding bubble and place our camera there to record the rupture images (at 0.5°, the sliding distance before rupture remained within the camera’s field of view). We were also unable to observe a fringe pattern immediately before rupture occurred. For these reasons, we only got two groups of rupture data for the 1° situation and neither of them showed clear fringe patterns before the rupture occurred.

As shown in Figure 5.7, among the only two film rupture observed at 1° with hydrophobic surface, one of them (blue cross) happened naturally as shown in the left image of Figure 5.7, and the other one (green cross) film rupture was caused by a particle. Once again, rupture occurred at the barrier rim for both events. Because we did not observe clear fringes before thin film rupture, we were not able to do the detailed thin film profile analysis at 1° for hydrophobic experiments. However, we
recorded the sliding distance and time before the thin film rupture occurred for 1° situation (Table 5.2) to compare with the situation of 0.5°.

<table>
<thead>
<tr>
<th></th>
<th>Sliding time (ms)</th>
<th>Contact spreading time (ms)</th>
<th>Sliding distance (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st time</td>
<td>1212.6</td>
<td>45</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Table 5.2 Sliding time, contact spreading time and sliding distance of a single observation at inclination of 1°.

Comparing Table 5.2 to Table 5.1 we can see a longer lifetime of the thin film with the increase in inclination. The explanation could be the higher sliding speed of the bubble had a higher ‘lift’ force due to the lubricating effect, and that lift force prevented the bubble away from attaching the surface and increased the lifetime of the thin film. In order to confirm this, more groups of data on at 1° and higher angles need to be recorded and the absolute film thickness must be detected.

5.3 The critical parameter that triggers the thin film rupture

The life time of the thin film is an important question in the collisions of bubble with hydrophobic surfaces. The life time of the thin film refers to how long the film could remain intact after the first pseudo-contact of the bubble and surface, in other words, the time between bubble’s first bounce until the first film rupture appeared, after which film drainage is irreversible.

In two-dimensional experiments (perpendicular experiments) done previously, there is a critical film thickness considered to be the trigger of thin film rupture, and dating from the 1970s scientists started to detect the critical film thickness at which the film ruptures. These critical film thickness has been measured in different liquid environments, pH, hydrophobicity and deformable body types. Most of
those measurements find a critical thickness in the range from nm to tens of nm, and quite sensitive to those parameters listed above. In addition, Yoon\textsuperscript{163} has shown a reasonable correlation between the critical film thickness and the work of adhesion, which further shows the importance of critical thickness in the thin film rupture process.

In most of the perpendicular experiments the critical thickness turned out to be the only parameter that triggered the thin film rupture; the drop or bubble's approach speed and time were not the key factors in determining the rupture procedure. However, in our experiment the bubble/solid surface collision system does not have axial symmetry. The critical film thickness still considered by us to be the trigger of thin film rupture, but there is an inclined angle leading to a sliding speed due to the buoyancy force, and the film rupture happens naturally during the sliding procedure. Since rupture is thought to occur at the thinnest part of the film, and since there are now only two points at which the film is thinnest, the rupture time may become more predictable. Furthermore, there is an indication that the higher the sliding speed (due to increasing inclination) the stronger the 'lift' force from the lubricating film, and this delays the film rupture.

Table 5.1 shows that at 0.5\textdegree, natural film rupture always happened about 400 ms after first bouncing in our experiments, and the sliding distance varies from 3.00 mm to 4.50 mm. Both the time and distance did not seem to be perfectly stable. One possible reason is that our experiment could not guarantee that every single bubble is exactly the same, but we note that most previous observations of bubble coalescence\textsuperscript{166-168} in the literature also report a spread of coalescence times. In addition, even if we could perfectly control every condition, the sliding time and distance still cannot be considered as the trigger parameters for thin film rupture because our 1\textdegree (Table 5.2 in Chapter 5.2) results showed out that once we change the inclination angle value, the bubble’s sliding time and distance were both quite different from that of 0.5\textdegree.
In this study we failed to obtain a direct measurement of the critical thickness that triggered the thin film rupture because the absolute film thickness was unknown in the 0.5° experiments and there were no fringes observed in the 1° experiments, but a critical thickness remains the most likely explanation for film rupture.

5.4 Thin film rupture progression

The progression of thin film rupture between a bubble and a hydrophobic surface in following the non-perpendicular collision is also worth discussing. Let us take one series of thin film rupture images for a 1.5 mm bubble and a hydrophobic surface inclined at 0.5 ° as an example. Figure 5.8 shows the top image of the bubble before (a) and after (b) the thin film rupture process, and an overlay of the near-contact areas between these two stages (c). We notice that there is a slight movement of the centre of the contact (or near-contact) area between the first rupture point appearing until the contact area spread to the largest size. In other words, the bubble did not stay where it was after the initial rupture occurred. The centre of the bubble moved a little bit not along its original sliding direction but toward the first touching point, which as we have seen previously is usually at the 3 o’clock or 9 o’clock position. Figure 5.9 (c) shows that the sideways movement is 0.35 mm (bubble radius: 1.5 mm) from analysis of the profile before and after the thin film finished rupturing, and the direction of the sideways movement was not directly toward the point where the film rupture happened. More discussion about this sideways displacement can be found in Section 5.5.2.
Figure 5.8 Bubble’s top images of the stages a) 5 ms before thin film rupture happened, b) thin film completely ruptured and c) the two ‘contact’ areas before and after rupture has fully progressed, overlaid on the same scale (red dashed line: original interference area, red line: final contact area, blue dot: where thin film rupture started).

Another interesting issue we found here is the thin film rupture progression, shown in a brief sketch map in Figure 5.9. The thin film rupture started at the left edge (with respect to the sliding direction) of the toboggan where the thinnest part of the film is located. After the first rupture the contact area between bubble and hydrophobic surface started to spread out from the break through point to all directions (Figure 5.9 a). However, the spreading speed of the contact area toward the opposite side of the toboggan (right side with respect to the sliding direction) was much faster than other directions (Figure 5.9 b). This rapid spreading of the contact area from an initial rupture
point has also been observed by other scientists investigating drop or bubble collisions with hydrophobic surfaces. The fast spreading looked like the contact area immediately ‘pushed’ the water out of the thin film area after the first rupture point appeared. The spreading of the contact area continued (Figure 5.9 c) and once it reached the furthest position on the right side (Figure 5.9 d), the spreading to the right direction stopped, but on the other (left) side the area continued to spread, more slowly, outside the original toboggan area until it finally reached the maximum size of contact area (Figure 5.9 e). The maximum size of the contact area is related to the bubble’s radius and the contact angle between the bubble and the hydrophobic solid surface which is determined by the hydrophobicity of the solid surface.

Figure 5.9 Schematic pictures of bubble’s contact area spreading process during the thin film rupture (dashed red line: original interference area, dotted arrows: spreading direction, dark area: contact area in the stages, dashed dark line: contact area of the previous stage, red line: final contact area).
5.5 Discussion

5.5.1 New geometry for thin film rupture

The dynamics of rupture of thin films between a bubble (or drop) and solid substrates in liquid is a very interesting and challenging problem. Considering the dynamics of thin film rupture is a three-dimensional procedure (even for those axisymmetric or mirror symmetric situations), the geometry of thin film plays an important role. Ideally, if the solid surface is perfectly clean and smooth, and the bubble’s surface is also perfectly clean, the thin film rupture always starts from its thinnest part\textsuperscript{169}, the thinnest part could be a plane, a circular rim (Figure 5.10 a and b) or an irregular shape (Figure 5.11) like what we observed from bubble and hydrophobic surface experiments.

![Figure 5.10 thin film geometry of a) plane, and b) dimple\textsuperscript{169}.](image-url)

\textsuperscript{169}.
No matter what kind of geometry the thin film presents, it is very significant to know where the rupture will occur. Typical experiments\textsuperscript{170-172} have shown this and demonstrated that the film loses its integrity through a rupture at a point that is one of a random distribution of seemingly independent points on the thinnest part of the film. The theoretical explanation of why the thin film rupture starts from a point is discussed by Witelski and Bernoff\textsuperscript{169}, who have demonstrated that only the point rupture of the film is stable, any other film rupture dynamics such as line or ring rupture are unstable and will generically destabilize to produce rupture at isolated points. Many papers\textsuperscript{173-176} about thin film rupture further confirmed this theory and pointed out that the single point the film rupture starts from is most likely located in the film’s thinnest part. Once the thinnest film thickness appears at an area, no matter that area is a flat plane, a circular rim or even a line, the rupture point could distribute randomly at any place of the area (Figure 5.12). This makes it impossible to predict exactly where the initial thin film rupture will occur.
A new angle on the coalescence of drops

Figure 5.12 Possible rupture points for a) plane geometry and b) dimple geometry.

Our study of a single air bubble colliding with a hydrophobic solid surface at an inclined angle in liquid also supported the point rupture theory from the images taken from the top view camera. In our experiments the thin film started to lose its integrity from a single point distributed as shown in Figure 5.6. However, unlike previous studies, in which thin film geometry is always cylindrically symmetric like a flat plane or a dimple (with a circular rim at the edge), we observed a mirror-symmetric ‘toboggan’ thin film geometry, with the thinnest parts of film being two points located at the two side edges of the toboggan, at about 3 o’clock and 9 o’clock with respect to bubble’s sliding direction. Hence, our experiments suggest that for non-perpendicular approach of a bubble to a hydrophobic surface, the location of the film rupture point becomes more predictable, being at one of the two side edges. Because the thinnest part of the film appeared at the two side edges of the direction of bubble was sliding, it would be more likely for the rupture point locating over the left/right edge area rather than front/back (refer to the direction of motion) area.

5.5.2 Sideways displacement of the bubble

In Figure 5.8 we can see a sideways displacement of the bubble between when the thin film started to rupture and when the final contact area had formed. The distance of the displacement motion was 0.35 mm (23% of the bubble’s radius) and the
direction was not exactly toward the film rupture point but a bit toward the bubble’s sliding direction. This sideways displacement occurs because, as we discussed above, the thin film always loses its integrity from a single point on the thinnest part of it, and after that, the contact area will spread rapidly to all the surrounding directions from that point. Unless the rupture point shows up in the centre of the bubble, there will be a spreading speed difference from the rupture point to its surrounding directions, and that spreading speed difference will lead to a predictable sideways displacement of the bubble (deformable body). However, for both perpendicular and oblique approach situations, the sideways displacement can be only partly predicted.

In perpendicular approach situations, the barrier rim of the dimple shares the thinnest film thickness so that the film rupture point location is randomly spread on the barrier rim. In this case, logically the sideways motion of the deformable body would be toward the direction from the centre of the dimple to the rupture point location and the distance should be equal to the radius of the dimple, which means, the rupture point will become the new centre of both the bubble and its contact area with the hydrophobic solid surface. However, once there is an inclination, the position of the film rupture point can be narrowed down to the edges of the 3 and 9 o’clock position respected to the sliding direction. Combined with the initial sliding velocity of the bubble, the final direction of the sideways displacement should be toward the left or right front (with respect to the sliding direction). In Figure 5.8 we observed the distance (0.35 mm) of the sideways displacement was less than the radius of the toboggan (distance from the centre of the bubble to the thinnest film thickness parts, 0.58 mm), which is related to the uneven speeds at which the final contact area expands toward the thin film area (inside the barrier rim) and way from it (outside the barrier rim, Figure 5.9).
Chapter 6. Comparison between hydrophilic and hydrophobic collision experiments

Introduction

This chapter extends the previous two results chapters by putting hydrophilic and hydrophobic results together, comparing sliding speed of a single air bubble along inclined solid surfaces with different surface hydrophobicity. The sliding speed of the air bubble was recorded by our high speed camera which was always placed perpendicularly to the inclined solid surface. Three angle conditions were studied in this chapter, 0.5°, 1° and 2°. For each angle, the sliding speeds of single air bubble against sliding time and distance along both hydrophilic and hydrophobic solid surfaces were measured. The difference in sliding speeds along different surfaces at a same inclined angle and same sliding distance are discussed in this chapter, with all the experiments being done with the same size of bubble (1.5 mm in radius) and the same liquid environment (water).

6.1 Results

The speed of single air bubbles sliding along the underside of both inclined hydrophilic and hydrophobic solid surfaces at an angle of 0.5° against sliding distance are shown in Figure 6.1.
Figure 6.1 Bubble sliding speed versus sliding time along hydrophilic and hydrophobic solid surfaces at an inclined angle of 0.5° in water.

As can be seen in Figure 6.1, the initial sliding speed (just after bubble first touched the surface surface) of single air bubble with a hydrophobic surface was higher than that with hydrophilic surface. There was a deceleration in both cases, more rapid for the hydrophobic surface, so that the speeds became more similar with time. The same features were also seen with inclined angles of 1° and 2°. From the data in Figure 6.1. The speed difference is 9 mm/s at the initial stage of sliding after first pseudo-contact with the solid surface (19 mm/s for hydrophobic collision and 10 mm/s for hydrophilic collision respectively at t = 100 ms), that difference decreasing to 4 mm/s after 680 ms (11 mm/s for hydrophobic collision and 7 mm/s for hydrophilic collision respectively). There is no further speed data for hydrophobic sliding at 0.5° because the thin film between bubble and hydrophobic surface ruptured at t = 686 ms after its first touch with the surface. The time to rupture between the air bubble and hydrophobic surface is within the general rupture period discussed in Chapter 5 at 0.5° in water. On the other hand, air bubble’s sliding speed against the hydrophilic surface kept on decreasing to 6.5 mm/s, but we cannot say whether that speed is the bubble’s terminal speed because of the limited of the travel observable in the experiment. However,
according to the literature\textsuperscript{7}, a single air bubble with similar size of ours should have a terminal speed to 6 to 8 mm/s at the inclined angle of 0.5° in water, which suggests that the air bubble sliding along hydrophilic surface is close to its terminal speed at the end of our experiment.

![Figure 6.2 Bubble sliding speed versus sliding time along hydrophilic and hydrophobic solid surfaces at inclined angle of 1° in water.](image)

Figure 6.2 shows the data of the same hydrophilic and hydrophobic comparison experiment at an inclined angle of 1° in water. Similarly to what happened at 0.5°, the sliding speed of the air bubble decreased for both hydrophobic and hydrophilic situations. Again, there was a speed difference between sliding along hydrophobic and hydrophilic surfaces after the first touch to the surface. However, compared with Figure 6.1, there were several differences caused by the increased inclined angle. Firstly the thin film between air bubble and solid surface had a longer life-time in the hydrophobic situation (1200 ms at 1° compared to 680 ms at 0.5°), which means we could track an air bubble for longer times and distances than at 0.5°. This also gives
more time to allow the sliding speed of the air bubble to approach its terminal speed. Secondly, although for both hydrophobic and hydrophilic collisions the sliding speed of an air bubble increases with a larger inclined angle value, the speed difference between hydrophobic and hydrophilic actually decreased compared to 0.5°. The initial speed difference at 0.5° is 9 mm/s (Figure 6.1) while the initial speed difference at 1° was only 4 mm/s (Figure 6.2). Moreover, Figure 6.2 shows that the speed difference between hydrophobic and hydrophilic situations decreases against time, which is similar to the situation of 0.5°, but the at 1°, the speed difference went down to nearly zero after 1200 ms. The limitation was still the lack of sliding distance and time in order to ensure whether or not the bubble reached its terminal sliding speed, but according to the literature, a single air bubble with the same size at 1° in water is about 16 mm/s, which is close to the sliding speed of our final observation.

Figure 6.3 Bubble sliding speed versus sliding time along hydrophilic and hydrophobic solid surfaces at inclined angle of 2° in water.

Another inclined angle value of 2° was also tested and Figure 6.2 shows the information of sliding speed versus time of both hydrophobic collision and hydrophilic
collision. An air bubble still slid faster than along a hydrophobic surface than a hydrophilic surface at 2º but the initial speed difference was only 4 mm/s just after first pseudo-contact. However, unlike the with 0.5º and 1º situations, the sliding speed difference between hydrophobic collision and hydrophilic collision at 2º did not have a big decrease during the time we recorded (1000 ms). The reason may still be the lack of sliding distance and time, the air bubble slid very fast at an inclined angle of 2º and it only took about one second for it to slide to the end of the microscope glass slide. Because of that, the observation stopped before the speed difference had a chance to decrease measurably.

![Graph showing bubble sliding speed versus sliding time along hydrophilic and hydrophobic solid surfaces at inclined angle of 0.5, 1 and 2 degrees in water.]

All the data from Figures 6.1 to 6.3 are collected in Figure 6.4 to illustrate a comparison between bubble deformations under different conditions. Here we want to discuss the relationship between thin film drainage process and the bubble’s sliding speed. The first pair of data we compare are points A and B in Figure 6.4. Point A (hydrophilic) and
A new angle on the coalescence of drops

B (hydrophobic) have the same inclined angle of 1° and the same sliding speed of 20 mm/s but different sliding times. However, from Figure 6.5 a) and b) we see that the thin film shapes of the bubble at points A and B are very similar. By counting fringe numbers we found both picture a) and b) have 10 bright fringes and 9 dark fringes, showing they have the same shape of the bubble’s top surface deformation. However, as explained in Chapter 5.1 we were unable to identify the absolute fringe order in the hydrophobic case, so we cannot say with certainty that the absolute film thicknesses were the same between points A and B. For different surface type, even with the bubble size, inclined angle as well as the liquid medium all the same, there could still be a difference in absolute thickness of the thin film.

Figure 6.5 Newton’s rings observed at points a), b), c) and d) in Figure 6.4. Inclined angle value a), b) and d) are 1°, c) is 2°. The sliding speeds are the same between a) and b), and also between c) and d). (The vertical stripes are an artefact resulting from an intermittent fault in the high
Another pair of bubbles are also shown in Figure 6.5, parts c) and d), corresponding to point C (hydrophilic) and point D (hydrophobic) in Figure 6.4 respectively. Those two bubbles also had the same sliding speed and the same bubble size but different inclined angle values, 2° for picture c) and 1° for picture d). From Newton’s rings features we can see that those two bubbles did not have the same top surface deformation, and hence different thin film shapes. The bubble in picture d) was still bouncing and the other bubble had already finished bouncing. This comparison indicated that the bubble’s top surface deformation as well as the thin film shape also varies by the change of inclined angle values.

![Graph showing bubble sliding speed versus sliding distance](image)

**Figure 6.6** Bubble sliding speed versus sliding distance along hydrophilic and hydrophobic solid surfaces at inclined angle of 0.5, 1 and 2 degrees in water.

Figure 6.6 is an extension of Figure 6.4 but with the data plotted against sliding distance rather than time.

By putting together all four pictures we can conclude that if we keep every other parameter constant but only change the surface hydrophobicity, the air bubble’s top
surface deformation is determined by the sliding speed and not the sliding time nor distance. This is the same as the conclusion reached in Section 4.2 when conditions were kept constant apart from electrolyte concentration, which is expected to affect only the film thickness.

6.2 Discussion

6.2.1 The sliding speed difference of air bubble under inclined hydrophilic and hydrophobic surface.

Figures 6.1 to 6.3 show a clear difference in the air bubble’s sliding speed against hydrophilic and hydrophobic solid surfaces at very early sliding stage. Here we want to discuss possible reasons for this speed difference.

A sliding air bubble’s speed can be affected by a number of parameters such as the bubble size\textsuperscript{49, 54, 177-179}, liquid viscosity\textsuperscript{54}, inclined angle value of the surface\textsuperscript{46-49, 54, 94, 177, 179-182} and other liquid properties such as temperature, density and salt concentration\textsuperscript{179, 182}. In our experiment, the method is to just change the surface from hydrophilic situation into hydrophobic situation while keeping every other parameter constant. Therefore the speed difference should not come from the bubble size, liquid viscosity and the inclined angle value, but must be due to the surface condition changing from hydrophilic to hydrophobic.

Once the surface type has changed, the surface force would be different and this could be one of the reasons that led to the sliding speed difference between hydrophilic surface and hydrophobic surfaces. Surface forces (mainly talking about electrical double layer and van der Waals forces, as described in Chapter 2) play an increasingly important role as the bubble gets closer to the solid surface, particularly at distances below 100 nanometers. However, in our experiments even the thinnest part of the film...
thickness was over several hundred nanometers for both hydrophilic and hydrophobic situations, and the thickest part of the film thickness was always over a couple of micrometers during the bubble’s sliding period. Of course for hydrophobic situations, the film thickness could go below 100 nanometers at the time just before thin film ruptured, but we are actually discussing the sliding speed difference before that thin film ruptured for hydrophobic conditions and the same time of hydrophilic conditions, so the change in surface forces cannot explain the difference in speeds.

Another explanation could be the hydrodynamic force. As presented in Chapter 2, hydrodynamic force plays a significant role in bubble-inclined surface system, once the surface changes from hydrophilic to hydrophobic, the hydrodynamic force will be changed and lead to the sliding speed difference. The key factor that caused the difference in hydrodynamic forces between hydrophilic and hydrophobic surfaces is the boundary condition. If the solid surface is hydrophilic, a Newtonian liquid (as used in our experiments) and hydrophilic solid interface is assumed to have a no-slip boundary condition (also known as immobile or stick boundary condition). This no-slip boundary condition means we suppose that the speed of the fluid at the interface between the liquid and the solid surface is the same as the speed of the solid surface which in our case is zero because the solid surface is not moving at all. Then the speed of the fluid increases as the distance from the solid/liquid boundary is increasing (as can be seen in Figure 6.7 a). In our case, because our microscope glass slide is hydrophilic before treatment, water molecules are assumed to be stuck with the hydrophilic surface and the interface without moving. However, once the glass slide has been treated to be hydrophobic, water molecules do not ‘like’ it any more so that they are not stuck with it. Under shear they can move along the interface, therefore there is an initial fluid speed at the interface, which is called a slip boundary condition (Figure 6.7 b).

The difference of those two boundary conditions will allow a reduction in
hydrodynamic drag, however, scientists such as Voronov et al.\textsuperscript{183} pointed out that both experiments and molecular simulations showed that the slip lengths can reach from nanometers up to micrometers due to hydrophobic surfaces are not always the same. Factors of surface chemistry (affinity of walls toward the fluid) and surface morphology (roughness and patterns on the interface and its nanoscale structures) both can produce high hydrophobicity on surfaces and the slip lengths of those hydrophobic surfaces will be affected.

In our experiments the details of those factors of hydrophobic surface were not measured, therefore the slip length of our hydrophobic surfaces is uncertain to us. But a large slip length could be the explanation of the observed sliding speed difference between hydrophilic and hydrophobic conditions.
6.2.2 The relationship between the sliding speed and bubble’s surface deformation.

In Chapter 4.6 we pointed out that the bubble’s sliding speed could be linked to the thin film shape, since the experiments with different salt concentrations had shown that bubbles in different salt concentration sliding at the same speed had the same thin film shape, and we concluded that the bubble’s sliding speed was to a large extent determined by the thin film shape or the other way around. Unfortunately in the experiments on changing bubble size and inclination angle, we did not find a group of bubbles sharing the same sliding speed at different bubble sizes or tilt angles because the speed differences were too large. Although we failed to have further proof of the relationship between bubble’s sliding speed and the film shape in the experiments with different bubble size and inclined angle values over hydrophilic surfaces, we do find this association again with different surface hydrophobicity experiments.

Figures 6.4 and 6.5 have shown the two pairs of same sliding speed comparison, one pair showing similar fringe shapes and order numbers, indicating that the bubbles’ top surface deformations were similar too; while the other pair had different fringe shape
and order numbers, hence different top surface deformations. The difference between those two pairs is, the first pair (points A and B) share both the same inclined angle value and the sliding speed, but change only the surface hydrophobicity. However, the second pair (points C and D) share only the same sliding speed value, but differ in both the surface hydrophobicity and the inclined angle value.

It is not hard to explain why there is a difference in the thin film drainage process when the inclined angle value is changed even though the sliding speed is the same. Many papers have reported that the bubble (drop)’s terminal sliding speed depends largely on the inclined angle value, however, further details about the thin film drainage procedure before a bubble reaches its terminal speed have not been studied yet. Here and in Chapters 4 and 5 we have provided details of thin film drainage for both hydrophilic and hydrophobic situations with several inclined angle values, and based on what we have observed it can be said the thin film drainage procedure is significantly influenced by the inclined angle value as well. Therefore, it is not surprising to observe a difference of thin film drainage procedure between different inclined angle values, even when sliding speed is the same (points C and D).

However, once the sliding speed of the bubble is the same and there is no difference in inclined angle, as for points A and B in Figure 6.4, we do observe a similar shape of the Newton’s rings pattern, which shows that those two bubbles’ top surface deformations were similar.

This result reinforces the finding in Chapter 4.2, which also found that bubbles sliding at the same speed had very similar deformations. In that case all parameters except electrolyte concentration were held constant; here all parameters are constant apart from the surface condition. But the finding that bubbles sliding at the same speed along surfaces at different inclination angles have different shapes means we must qualify the previous conclusion – it only applies for the same angles.
Clearly there is difference in initial sliding speed when the surface is changed from hydrophilic (no-slip boundary condition) to hydrophobic (slip boundary condition). However when the speeds have become equal (after different sliding times for the two conditions) the bubble deformation is similar, which means the distribution of hydrodynamic pressure in the thin film must be quite similar between the two conditions. This leads to similar drag on bubbles in the two situations (hydrophilic and hydrophobic required to give the same sliding speed. But it is possible that the absolute film thickness is not the same due to the slip length at the hydrophobic surface (Figure 6.7 b). Unfortunately we could not measure the absolute film thickness in the hydrophobic experiments for the reason explained in Chapter 5.1.
Chapter 7. Summary and future work

7.1 Summary

In this project we have successfully confirmed that the thin film between a sliding bubble and a flat solid surface in liquid environment is not flat and uniform, but a complex ‘toboggan’ shape (research aim 1 achieved). A standard experiment (Table 4.1) with a single air bubble of 3.2 mm in diameter interacting with hydrophilic solid surface at an inclined angle of 0.5° in pure water environment has been discussed as a baseline experiment with which other experiments are compared to explore the effects of varying the parameters one by one. The optical interference fringes we observed in the baseline experiment show the thin film evolution from the time the bubble initially touched the surface until the limiting distance we could reach. The process can be divided into three stages, big bouncing stage (no interference fringes observed), small bouncing stage (multiple dimples observed) and sliding stage (‘toboggan’ shape). Past papers normally assume the bubble finishes its bouncing after there is no clear separating distance between it and the solid surface, but our results show that this is only the big bouncing step of the bubble. The central area of the bubble was still bouncing, creating multiple closed ring groups in the interference pattern, indicating multiple dimples that could be observed at the same time. Every closed ring group represents one bounce and we call this stage the small bouncing stage. Once there was only one closed ring group (dimple) left in the image, it suggested that the bubble had already moved to the sliding stage. The profile of thin film in the sliding stage is described as ‘toboggan’ because it has two ‘rails’ at the left and right edges and a central channel in the middle, parallel to the direction of motion. The thinnest parts of the film are located slightly toward the rear from the 3 and 9 o’clock positions on the barrier rim, and the maximum film thickness appeared at the central-back dimple. Film thickness decreased from the dimple to all the directions but the reduction is gentler to the sliding direction than the back. The interference fringes
disappeared outside the barrier rim of the bubble due to there being a rapid increase in the film thickness.

In the baseline experiment, the bubble’s top surface retained the ‘toboggan’ shape to the maximum sliding distance and time we could trace although both the maximum and minimum film thickness decreased as the increasing of the sliding distance and time. The effects of salt concentration, liquid viscosity, bubble size and inclination value on the thin film drainage were then studied in compare with the baseline experiment.

By changing the salt concentration rate of the liquid environment we have shown that the thin film shape is dependent not on the bubble’s sliding distance or time, but the sliding speed (Chapter 4.2). Based on this we also demonstrated that the equilibrium shape of the thin film is the ‘toboggan’ instead of flat, since the bubble’s sliding speed had appeared to reach its terminal value in the experiments at lower inclination angle.

Bubble size is another parameter that can influence the thin film drainage process because a different bubble’s diameter will directly lead to differences of sliding speed, size of the barrier rim and the film thickness. However, the parameter that had the strongest effect on thin film shape is the liquid viscosity. A higher viscosity reduced the bubble’s times of bounce and its sliding speed, increased the film thickness, and significantly changed the profile of the thin film by making its shape more complex and hard to analysis (research aim 3 achieved).

The profile of the thin film between a steady slide bubble and hydrophilic solid surface has been shown theoretically to be non-flat by the study by Griggs et al.\textsuperscript{94}. In this study we have experimentally obtained the true shape of thin film between a sliding bubble and a hydrophilic solid surface from its initially sliding. We have shown some qualitative similarity with Griggs’s\textsuperscript{94} work, like the general shape of the film (toboggan),
the location of maximum (middle-back dimple) and minimum film thickness (left/right edges), but also some disagreements like whether the front barrier rim is thicker than the back or the other way around. We also experimentally proved that the motion of a gravity-driven bubble along a hydrophilic solid surface in water is a combination of rolling and sliding because the interference fringes showed both the features of rolling and sliding. Unlike the study of Thampi et al. which only shows whether the whole bubble is more rolling or sliding, we found a mixed mode in which the closer to the central channel of the toboggan shape of the bubble, the higher percentage of rolling the bubble was.

The shape we have called ‘toboggan’ has also been observed very recently with a bubble in water being pushed through a square millimeter-size channel in a microfluidic device. This shows that the physics of flow in the microfluidic channel, which has many important applications, must be similar to flow in the liquid film that lubricates a sliding bubble driven by gravity near an inclined surface (research aim 2 achieved).

In this study we also obtained the information about a bubble colliding with a hydrophobic solid surface in water at an inclination of 0.5°, up to the point where the thin film completely ruptured. Repeating the baseline experiment but with a hydrophobic surface showed qualitative agreement with previous studies, the thin film rupture always happening at the thinnest part of the film, and starting from a single point. Due to the formation of the toboggan shape in the thin film, the thinnest parts were located on the left/right edges (with respect to the sliding direction) of the barrier rim. This suggests that, instead of randomly happened anywhere around the barrier rim of the bubble approaching a surface in the perpendicular direction, we have successfully narrowed down the region where the first rupture point is most likely to appear, because it will be on the thinnest part of the film. The thin film rupture progression after the first single point contact until a steady contact area had formed.
was also recorded in this study. One consequence that to our knowledge has not been noted before (although it should occur with a circular barrier rim too) is that a small sideways displacement of the bubble occurs during this progression.

By comparing the performance of the bubble interacting with hydrophilic and hydrophobic solid surfaces, we were not surprised that the bubble’s sliding speed is different between hydrophilic and hydrophobic situations when every other parameter was kept the same, because of the difference of the slip boundary conditions at the solid surface. The relationship between the bubble’s sliding speed and the thin film profile was proved one more time in this comparison of hydrophilic and hydrophobic.

In this project we have experimentally demonstrated the true shape (‘toboggan’) of the thin film profile of a sliding bubble and another solid surface in liquid environment. The sliding speed of the bubble has been shown to be the critical parameter that determines the drainage process of the thin film (or the other way around) when the inclination value, bubble size and viscosity were kept constant. A predictable film rupture point region has been obtained when the solid surface was hydrophobic, and since this region is at one side of the barrier rim, rupture is accompanied by a lateral displacement of the bubble. Rupture at a hydrophobic surface is postponed at increasing inclination angles due to the lubricating effect that accompanies bubble sliding. And the lubrication in this situation appears to be very similar to lubrication in two-phase flow in a rectangular microfluidic channel.

7.2 Unfinished and future work

7.2.1 Unfinished work

In our experiment we have proved that with an inclination, a sliding bubble’s top
A new angle on the coalescence of drops

surface shape is not flat or uniform but like a toboggan against a flat solid surface in liquid environment, but it is still significant to find out the thin film’s equilibrium shape for a sliding bubble. The equilibrium shape of the thin film means both the film shape and the sliding speed of the bubble are stable, i.e. the bubble has reached its terminal speed. In section 4.4 we have shown the result of an air bubble and hydrophilic solid surface at a lower angle of 0.25°, and from Figure 4.30 we can see the bubble’s sliding speed appeared to be stable at the furthest sliding distance we could reach. This suggests the toboggan shape of the thin film from Figure 4.32 to 4.34 is probably the equilibrium form, but in order to confirm that this is the equilibrium thin film shape, the bubble is required to be traced for a longer distance and time. Here we present some unfinished work of optimization of our experimental set-up for reaching longer tracing distances and times, and an explanation of why this work was not pursued within this thesis.

**Cylindrical surface container.**

Due to the length limitation of the microscope glass slide (76 mm in which a maximum 45 mm is accessible in our experiments), a sealed graduated glass cylinder (100 mL, Pyrex, England) was used as the target surface instead of the bubble chamber in our project. This idea was suggested by Del Castillo\(^7, 57, 58\) and the same cylinder tube (Figure 7.1) was used.

![Figure 7.1 Structure of the cylinder tube system.](image)
The first advantage of using a cylinder instead of a glass microscope slide was that the cylindrical geometry ensured the sliding bubble followed a straight path (Figure 7.2), which allowed the camera to catch and observe the sliding bubble more predictably. Secondly, the cylinder tube was much longer (150 mm) than a microscope slide (76 mm), which allowed us to track the bubble for a longer period during the thin film drainage process. In principle, even longer tubes could be used. Two Teflon caps were used to seal the cylinder with O-rings (shown in Figure 7.1). One of them had two holes: the first for a long stainless steel needle (Hamilton, 26s gauge, 38 mm long) inserted through a septum seal and the second (0.47 mm) for an air vent through a filter.

![Figure 7.2 The advantages of the cylinder tube compared with microscope glass slide.](image)

The glass cylinder tube was treated with a wash liquid of saturated KOH (Sigma Aldrich)/iso-propyl-alcohol (97%, Chem-supply) solution for 30 minutes, then rinsed with ethanol (96%, Chem-supply) and clean water before stored into a sealed container with clean water. This treatment was repeated weekly to prevent the cylinder from being contaminated after several experiments.

A single air bubble, formed by a 3 mL plastic syringe connecting to a syringe pump was pushed into the cylinder through the steel needle connecting the same plastic capillary as the baseline experiment at the end of the needle to generate the same size of bubble in the cylinder tube. Bubbles were allowed to bounce and could slide up to 100
mm before reaching the end of the cylinder tube.

A group of interference images of the bubble’s top surface as it slid along a hydrophilic cylinder tube inclined at an angle of 0.5° is shown in Figure 7.3. Figure 7.3 a) shows the period of small bouncing and b) shows the sliding step. We see a more complicated fringe pattern, which we have not been able to analyze. In Figure 7.3 we can observe multiple circle fringes in the big bouncing step (Figure 7.3 a) and multiple stripe fringes in the sliding step (Figure 7.3 b).

![Figure 7.3](image)

**Figure 7.3 Images of bubble’s top surface against cylinder tube surface (a, big bouncing step; b, sliding step).**

When we decided to employ the cylinder tube instead of the microscope glass slide we were expecting to obtain the same results with a longer tracing time and distance of the bubble, however, those irregular fringes in Figure 7.3 looked quite different to the fringes we got with the glass slide and they were not possible for us to analyze. The reason for the complicated fringe patterns could be that the ratio of the internal diameter of the cylinder (37 mm) was not large enough compared to the bubble’s diameter (3.2 mm) and the shape of the thin film between the bubble and curved glass defaces was more complicated than between a bubble and a flat surface. Alternatively, it could be an optical artefact due to the cylindrical lens created by the glass wall of the tube affecting the interference condition (Equation 3.4) that is calculated for light.
at normal incidence. Since we were unable to resolve this issue, we did not consider these results as valuable results to discuss in this thesis.

**Off-centre collisions of bubbles with each other**

Although the experimental device we designed was mainly used for the study of bubble and solid surface interactions, it can be partly employed for collisions of bubbles with each other. For example, we could increase the release rate of the bubbles and adjust the inclination to a suitable value (normally very low angle), and the second bubble we released would collide with the first bubble, as shown in Figure 7.4.

![Figure 7.4 Process of off-centre collisions air bubble with each other in water (viewing from left to right, top to bottom).](image)

The limitation of this collision in our study was obvious, the collision cannot be well controlled, especially the direction of collision of bubbles. The two bubbles in our experiments were not moving toward each other, but the second bubble caught up with the first bubble. Although the collision was always off-centre, significant parameters such as speed, collision direction and time cannot be well controlled, and
that is the reason why we did not take this result as one of the main finding in this project.

However, the brief process of off-centre collision between bubbles in Figure 7.4 shows some similar results with literatures of both ‘head-on’ collision\textsuperscript{60} and off-centre collision\textsuperscript{78}. Collisions between bubbles off-centre can also be a part of the future work of this study after we made some specific optimization of the experimental devices.

### 7.2.2 Future work

The first thing that should be done in future work is to try to find a way to trace the bubble a reasonably long time and distance in order to confirm that the final shape of the thin film retains its toboggan shape at the steady sliding stage. There are four possible ways of doing this: (i) we redesign our bubble chamber and the stage table to allow a longer glass slide to be our target solid surface; (ii) we move our solid surface (as well as the camera system) at a constant speed as well so that the bubble can slide longer without reaching the limited edge of the glass slide; (iii) we can try to turn down the inclination value as low as possible to increase the sliding time of the bubble; or (iv) we resolve the optical interference conditions for cylindrically-curved surfaces, and conduct further experiments with the elongated tube. Each of these ideas requires some re-arrangement of the experimental system.

Secondly, we want to give a small curvature to the target solid surface in order to guarantee the path way of the bubble which will be more helpful for hydrophobic experiments to catch the film rupture point and determine the sliding distance, especially for higher angles.

Thirdly, due to the change of viscosity leading to a dramatic change of the thin film profile, it is worth having more detailed investigations of a range of viscosities.
Fourthly, we want to detect the absolute film thickness in hydrophobic situations by automatically switching wavelengths in one single run, and reducing the inclination value to see whether the critical film thickness is the same for different inclinations when other parameters are held constant.

Fifthly, it is worth trying some other deformable body other than air bubble in the same experiment to compare with, like an oil droplet.

Finally and also most significantly, based on the experimental data we have obtained, we would like to cooperate with some theoretical analysis groups in the same area to model the thin film drainage process of a moving deformable body under the experimental conditions we are able to access.
A new angle on the coalescence of drops

References

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