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# Experimental Investigation of Dynamic and Metastable Contact Angles

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UNIVERSITY OF CALGARY

EXPERIMENTAL INVESTIGATION OF DYNAMIC  
AND METASTABLE CONTACT ANGLES

by

KE ZHANG

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
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# Abstract

Contact angle phenomena are complicated. There exist many experimental contact angles and many researchers employed them widely in Young's equation for the determination of solid surface tensions. This thesis examined the thermodynamics status of contact angles and experimentally determined the various metastable contact angles. Experimental setup for metastable contact angles was designed by carefully controlling the vibration amplitude via loudspeakers. It has been demonstrated that only the advancing contact angle on smooth surfaces are compatible with Young's equation. Attempts in the literature to determine the true equilibrium contact angle are meaningless in terms of Young's equation. Only the advancing angle on smooth and heterogeneous surfaces is a good approximation of the contact angle in Young's equation.

A new model to determine the maximum and minimum spreading ratio of droplets impacting onto smooth surfaces was also established. Good agreement was found between the predicted and experimental values. Impacting droplet experiments were also employed to examine carbon/polymer surfaces as a new way of characterizing such surfaces.

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# List of Symbols, Abbreviations and Nomenclature

| Nomenclature  | Definition                              |
|---------------|-----------------------------------------|
| $\theta$      | Contact angle                           |
| $\theta_Y$    | Young's contact angle                   |
| $\theta_a$    | Advancing contact angle                 |
| $\theta_r$    | Receding contact angle                  |
| $\theta_e$    | Equilibrium contact angle               |
| $\theta_m$    | metastable contact angle                |
| $\gamma_{lv}$ | liquid-vapor interfacial tension        |
| $\gamma_{sv}$ | solid-vapor interfacial tension         |
| $\gamma_{sl}$ | solid-liquid interfacial tension        |
| G             | Gibbs free energy                       |
| $\rho$        | density                                 |
| $\beta$       | spreading ratio                         |
| $\beta_{max}$ | maximum spreading ratio                 |
| $\beta_{min}$ | minimum spreading ratio                 |
| Re            | $\rho u d / \mu$ Reynolds number        |
| We            | $\rho u^2 D / \gamma_{lv}$ Weber number |
| u             | impacting velocity                      |
| $\mu$         | viscosity                               |
| $D_0$         | drop diameter                           |
| $D$           | spreading diameter                      |

| Abbreviation | Definition                       |
|--------------|----------------------------------|
| PMMA         | poly(methyl methacrylate)        |
| PnBMA        | poly(n-butyl methacrylate)       |
| PS           | polystyrene                      |
| PDMS         | polydimethylsiloxane             |
| PET          | polyethylene terephthalate       |
| ADSA         | Axisymmetric Drop Shape Analysis |
| APF          | automated polynomial fitting     |
| VC           | Vulcan carbon                    |
| CNTs         | carbon nanotubes                 |
| SWNTs        | single-walled carbon nanotubes   |
| MWNTs        | multi-walled carbon nanotubes    |
| MEMs         | micro-electro-mechanical         |

# Chapter 1

## Background and Introduction

### 1.1 Introduction

When a sessile drop sits on a solid surface or liquid climbs up along the wall in a capillary tube, three interfaces exist: They are the liquid-vapor, solid-vapor and solid-liquid interfaces. These interfaces co-exist to form a three-phase contact line. When symmetry is taken into consideration, the three interfaces form a three-phase contact point and the tangent drawn between the liquid-vapor and solid-liquid interfaces results in the so-called contact angle  $\theta$ , as illustrated in Figure 1.1. The importance of such a contact angle lies in the fact that this macroscopic measurable quantity manifests itself due to the relative strength between the three interfacial tensions (see Figure 1.1): liquid-vapor surface tension  $\gamma_{lv}$ , solid-vapor surface tension  $\gamma_{sv}$  and solid-liquid surface tension  $\gamma_{sl}$ . For example, the larger the  $\gamma_{lv}$ , the higher it is for the contact angle  $\theta$  with fixed  $\gamma_{sv}$  and  $\gamma_{sl}$ . Since interfacial tensions are well-defined thermodynamic properties [1], their strengths, of course, depend on how strong the various intermolecular interactions that are presented at a specific interface. Therefore, the macroscopic measurable contact angle is understood to be related to the specific interactions between the liquid and solid. It is also a qualitative indicator to wetting phenomena: Near zero contact angle means complete wetting and a contact angle value of larger than  $90^\circ$  implies non-wetting.

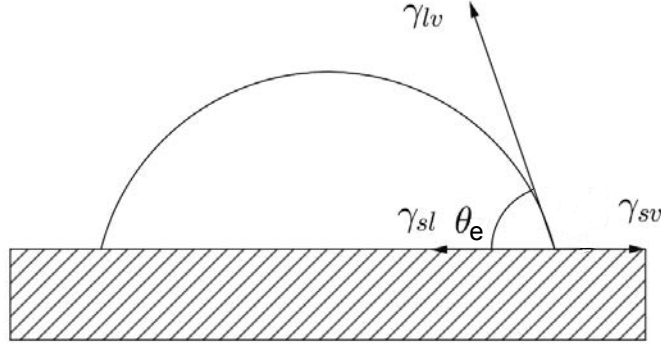


Figure 1.1: Schematic of a sessile-drop contact angle system.

Thermodynamically, contact angle relates to the three interfacial tensions via the so-called Young's equation [2]:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl}$$

Since interfacial tensions are thermodynamic properties [1], contact angle should also be a unique thermodynamic property because of Young's equation. When a given liquid and solid surface combination is fixed, the experimental contact angle should also be well-defined and fixed due to Young's equation. Here, Young's equation relates the experimentally measurable contact angles to  $\gamma_{lv}$ ,  $\gamma_{sv}$  and  $\gamma_{sl}$ . However, the interfacial tensions that are associated with the solid surfaces,  $\gamma_{sv}$  and  $\gamma_{sl}$ , are not experimentally measurable even though they are thermodynamic properties. The experimental difficulties in measuring interfacial tensions with the solid properties are due to the absence of surface mobility [1]. The fact is that generating a unit interfacial area without affecting stress and strain of the bulk phases is not possible experimentally. Hence, another attractiveness of contact angle is that it relates to the three thermodynamics interfacial tensions via Young's equation, from which the two

solid surface tensions are non-measurable. Therefore, an additional independent equation can be sought for in order to determine the two non-measurable solid properties  $\gamma_{sv}$  and  $\gamma_{sl}$ . Determination of solid surface tensions from contact angle has been an active research for over 50 years since Zismans work [1, 3, 4, 5].

Two major schools of thought exist in the literature [1, 6, 7, 8, 9, 10]: the surface tension component [6, 7, 8, 9] and the equation of states approaches [10, 11, 12, 13, 14]. The former postulates that surface tensions can be divided into the various surface tension components due to the specific intermolecular interactions. The latter was based on thermodynamics [15] that an equation of state relationship indeed exists between the solid and liquid when certain assumptions are met. This has been the longest debate ever relating to contact angles for over 50 years. Even today, researchers working in the area are still extremely confused when contact angles are used in conjunction with Young's equation. Literature citing the correctness of the different approaches are scattered [16, 17, 18, 19]. Majority of researchers in the area favored the concept of surface tension components as the approach appears to have provided some favor into intermolecular interactions [20, 21]. Detailed discussion of these approaches are beyond the scope of this thesis.

Based on Young's equation, when a solid and a liquid surface are fixed, Young's equation implies a unique experimentally determined contact angles. Since the equation of state approach implies that it is the thermodynamic property surface tension that matters, while the component approach insists that the surface tension component matters and not the thermodynamic surface tensions. The two approaches are indeed mutually exclusive and should be easily disproved based on Young's equation and experimental contact angles. Experimentally, if the solid surface is fixed, a systematic variation of liquid with its surface tension (regardless of the surface tension components) would yield scatter in experimental



contact angles if the surface tension component approach is correct. On the contrary, if a systematic variation of experimental contact angles exists when  $\gamma_{lv}$  is changed, this would validate the equation of state approach [13, 14].

Young’s equation implies a unique experimental contact angle  $\theta$ . In reality, experimentally determined contact angles are scattered even for the same liquid and solid pair [22, 23, 24, 25]. For example, variation of experimental contact angles can be as high as  $50^\circ$ , depending on the laboratories and researchers. Question arises as to which contact angles should be used in conjunction with Young’s equation. If interfacial tensions are thermodynamic properties, contact angle should also be a unique thermodynamic property. Therefore, validation of any approaches to determine solid surface tensions would not be possible if the thermodynamic status of contact angles are not understood.

It is a well known fact in the literature that there exists the so-called contact angles hysteresis [1]. A maximum contact angle can be obtained while advancing the liquid front for contact angle. This is known as the advancing contact angle. A minimum contact angle can also be obtained while receding the three-phase contact line for contact angle. This is known as the receding contact angle. The difference between these two values results in the so-called contact angle hysteresis. Contact angle hysteresis can be due to surface roughness and chemical heterogeneity of the surface [1, 26]. Depending on how the researchers measure the contact angle, different contact angles between the advancing and receding contact angles exist widely in the literature [27, 28, 29, 30, 31]. The “straight-forward” measurement of contact angle has now become the most confusing aspect in the center of contact angle research. Various models have been developed [32, 33] in attempt to understand the thermodynamic status of contact angles as they relate to Young’s equation. Various approaches suggest that there exists something known as the metastable contact angles. Experimentally, the determi-

nation of metastable contact angles are not well understood in the literature [27, 28, 34, 35]. Some researchers employed acoustic vibrations to determine metastable contact angles and used the minimum of these metastable contact angles in Young's equation for solid surface tensions [36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46]. Literature use of such metastable angles are misleading and it is the purpose of this thesis to examine the thermodynamic status of contact angles carefully.

## 1.2 Motivation

It is the motivation of this thesis to examine experimentally the thermodynamic status of contact angles in terms of its metastable states. The various complexity of contact angle measurements will be examined and discussed.

## 1.3 Organization of this thesis

Chapter 2 provides an overview and background knowledge for the thermodynamic status of contact angles. Experimental study and its analysis of the metastable contact angles in this thesis will be discussed in Chapter 3. Chapter 4 employs the understanding of contact angles for use in droplet impacting experiment as they relate to solid surface tensions. A new model to determine the minimum spreading ratio and droplet recoil during impacting onto a surface will be discussed. Good agreement was found between experimental results and those predicted from the model proposed in this thesis. Chapter 5 provides additional experimental data for droplet impacting experiments onto the surfaces of carbon/polymer composites, in attempt to characterize these surfaces qualitatively. Chapters 6 and 7 summarize conclusions in this thesis and provide suggestions for possible future work.

## Chapter 2

### Literature review

#### 2.1 Contact angles

##### 2.1.1 Basic equations of contact angles

There are two important equations relating to contact angles: Laplace equation of capillarity and Young's equation.

Laplace equation of capillarity as shown in Equation 2.1 is the basic equation of the capillarity given by Laplace.

$$\gamma_{lv}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \Delta P \quad (2.1)$$

where,  $\gamma_{lv}$  is the liquid-vapor surface tension,  $R_1$  and  $R_2$  are the radii of surface curvature, which are equal for a sphere, and  $\Delta P$  is the pressure difference across the interface.

Laplace equation of capillarity can be derived as follows: Consider a random curved surface shown in Figure 2.1 with the radii of surface curvature  $R_1$  and  $R_2$ . If the surface moves in a very small displacement  $\delta z$  along the  $z$  direction, the change in the surface area will be

$$\delta A = (x + \delta x)(y + \delta y) - xy = x\delta y + y\delta x \quad (2.2)$$

The work done comes from the change in the interfacial area will be

$$\delta W = \gamma_{lv}\delta A = \gamma_{lv}(x\delta y + y\delta x) \quad (2.3)$$

The corresponding work done by the pressure difference  $\delta P$  applied on the surface and along the direction  $z$  will be

$$\delta W = (\delta P)xy\delta z \quad (2.4)$$

It can be found out from geometrical relations that

$$\delta x = \frac{x\delta z}{R_1} \quad (2.5)$$

and

$$\delta y = \frac{y\delta z}{R_2} \quad (2.6)$$

From energy conservation, work done caused by the change in area and done by the pressure difference should have the same value. After the substitution of  $\delta x$  and  $\delta y$  into Equation 2.4, the Laplace equation of capillarity can be obtained.

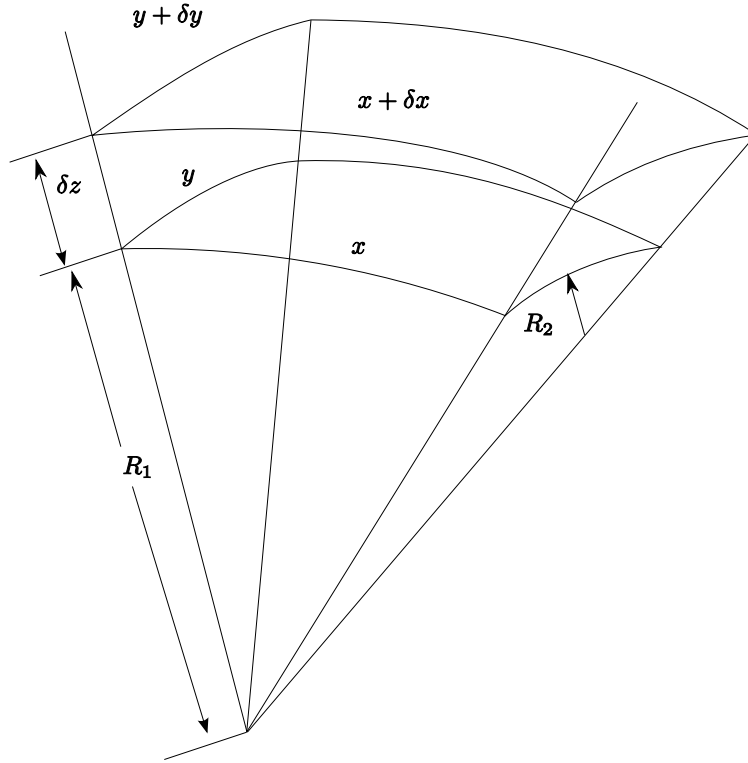


Figure 2.1: A curved surface with a small displacement  $\delta z$  through the  $z$  direction.

The Laplace equation is one of the governing equations of capillarity. When applied to sessile drops, the Laplace equation determines the shape of drop by relating it to the capillary pressure, which is a function of the elevation when there is no external force other than gravity [47].

Another important equation relating the interfacial tensions to contact angle is Young's equation (Equation 2.7), which was stated by Young in 1805 [2].

$$\gamma_{lv} \cos \theta_e = \gamma_{sv} - \gamma_{sl} \quad (2.7)$$

where  $\gamma_{sv}$  is the solid-vapor interfacial tension,  $\gamma_{sl}$  is the solid-liquid interfacial tension,  $\gamma_{lv}$  is the liquid-vapor interfacial tension and  $\theta_e$  is the equilibrium contact angle.

As illustrated in Figure 1.1, Young's equation can be derived simply from the mechanical equilibrium of three interfacial tensions.

The derivation of Young's equation is based on the assumption that the solid surface is an ideal surface, which means the solid surface should be perfectly smooth, chemically homogeneous, inert and isotropic. Because real solid surfaces do not meet the above restrictions, in order to use Young's equation to solve solid-vapor interfacial tension ( $\gamma_{sv}$ ) and solid-liquid interfacial tension ( $\gamma_{sl}$ ), it is important to find a good approximation of the equilibrium contact angle ( $\theta_e$ ).

### 2.1.2 Experimental contact angles

In order to use Young's equation for the solid-vapor interfacial tension,  $\gamma_{sv}$  and solid-liquid interfacial tension,  $\gamma_{lv}$ , the equilibrium contact angle,  $\theta_e$  is considered to be measurable and having a unique value because  $\gamma_{sv}$ ,  $\gamma_{lv}$  and  $\gamma_{sl}$  are supposed to be thermodynamic properties. However, there exists a range for the experimentally measured contact angles [48, 49]. The experimentally observed contact angles could be any value that lies within the range between the largest contact angle made by advancing the liquid drop (advancing angle,  $\theta_a$ ) and the smallest contact angle made by receding the liquid drop (receding angle  $\theta_r$ ). The difference between  $\theta_a$  and  $\theta_r$  is defined as the contact angle hysteresis, which exists in any real solid surface.

$$H_r = \theta_a - \theta_r \quad (2.8)$$

Contact angle hysteresis is due to the imperfection of solid surfaces, more specifically, roughness and chemical heterogeneous of solid surfaces [32, 33]. In order to explain contact angle hysteresis, and to justify which experiment contact angle can be used in Young's equation,

different theoretical models have been proposed by researchers.

### 2.1.3 Early theoretical studies on surface hysteresis

Contact angle hysteresis has been recognized by Wenzel as early as 1936 [50]. Because of the complexity to combine surface roughness and chemical heterogeneity, it is instructive to separate roughness and heterogeneity by focusing into (1) smooth surface with chemical heterogeneity and (2) rough surface that are chemically homogeneous.

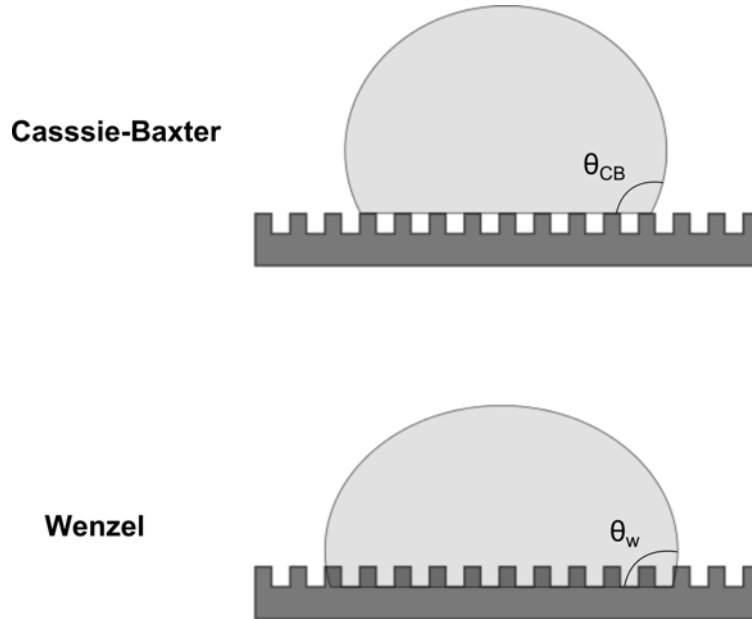


Figure 2.2: A schematic of the Wenzel model and Cassie-Baxter model for contact angles on rough surfaces.

By taking into account the solid surface roughness and assuming that all the solid surface is covered by the liquid in contact with as shown in Figure 2.2, Wenzel proposed that the actual solid-liquid interfacial area is greater than the geometric interfacial area and defined

the average surface roughness ratio  $r$  as

$$r = \frac{\text{actual surface area}}{\text{geometric surface area}} \quad (2.9)$$

After introducing  $r$  into Young's equation, the Wenzel equation was obtained:

$$\gamma_{lv} \cos \theta_w = r(\gamma_{sv} - \gamma_{sl}) \quad (2.10)$$

where  $\theta_w$  is called Wenzel contact angle. A more rigorous derivation was given by Good [51] later in 1952. It is interesting to note that, when the apparent contact angle  $\theta$  is less than  $90^\circ$ ,  $\theta$  increases with the solid surface roughness; on the other hand, when  $\theta$  is larger than  $90^\circ$ , it will decrease with the increase in roughness.

Another model for rough solid surfaces, especially for porous solid surfaces, is the Cassie-Baxter model [52]. They assumed that there is air trapped under the liquid and the drop is suspending on the rough surface as shown in Figure 2.2. The Cassie Baxter angle  $\theta_{CB}$  is expressed as:

$$\cos \theta_{CB} = f_s(\cos \theta_e + 1) - 1 \quad (2.11)$$

where  $f_s$  is the fractional area where the solid and liquid are in contact with,  $\theta_e$  is the equilibrium contact angle on the equivalent smooth solid surface.

For smooth but heterogeneous solid surfaces, Cassie and Baxter [53] considered a solid surface consisting of two different chemical compositions, with contact angle  $\theta_1$  and  $\theta_2$ , and occupying fraction  $f_1$  and  $f_2$ , respectively. They argued that the equilibrium contact angle will follow the so called Cassie equation,

$$\cos \theta_c = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (2.12)$$

or, in the context of Young's equation,

$$\gamma_{lv} \cos \theta_c = f_1(\gamma_{s_1v} - \gamma_{s_1l}) + f_2(\gamma_{s_2v} - \gamma_{s_2l}) \quad (2.13)$$



It should be noted that  $f_1$  and  $f_2$  has the relation that  $f_1 + f_2 = 1$ .

Both the Wenzel and Cassie equations are empirical or semi-empirical equations from simplified models. They lack rigorous analysis from thermodynamic principles. It was also found that Wenzel equation have conflicts with experimental results from other researchers. For example, if the apparent contact angle is larger than  $90^\circ$  on a solid surface, increasing the surface roughness will decrease the contact angle based on the prediction from Wenzel equation. However, the experimental results from Neumann [26] showed that by increasing the surface roughness, the advancing contact angles always increase and receding contact angles always decrease.

To explore the intrinsic relation between interfacial tensions and contact angle on experimental solid surfaces, and to get a better understanding to the contact angle hysteresis, there rises the needs of a more rigorous model and theoretical analysis. Dettre and Johnson [32, 54] examined a model of a sessile drop sitting on concentric rings with alternating equilibrium contact angles  $\theta_{e1}$  and  $\theta_{e2}$  in order to simulate the chemical heterogeneity of solid surface. By minimizing the total free energy, they calculated the global minimum contact angles and provided an explanation to the existence of several metastable contact angles within the range between advancing and receding contact angles. Inspired by Dettre and Johnson's work, Neumann and Good [33] developed a vertical plate model that I will discuss in the next section.

#### 2.1.4 Neumann and Good's vertical plate model for contact angle hysteresis

In the vertical plate model, when a vertical plate dipping into a pool of liquid, there exists the capillary rise of liquid on the solid surface. The contact angle at the three phase interface is the apparent contact angle and equals to the contact angle that can be measured by

using other methods, e.g., the sessile drop method. The advantage of using a vertical plate model rather than the sessile drop model is the simplicity of formulating the thermodynamic system. In addition, it is easier and more realistic to use parallel stripes instead of concentric rings.

To study the effect of chemical heterogeneity of solid surfaces, the vertical plate was considered to consist of two types of smooth and homogeneous strips with different equilibrium contact angles. Both horizontal and vertical stripes were studied in their work [33]. For the homogeneous but rough solid surface, They considered a plate consisting of homogeneous and smooth stripes with different inclinations so as to introduce a sawtooth like surface roughness [55].

By carefully analyzing the energy change from surface tension and work done by gravity with the change of  $\theta$ , the total free energy change  $\Delta G$  was then calculated as a function of the instantaneous contact angle  $\theta$ .

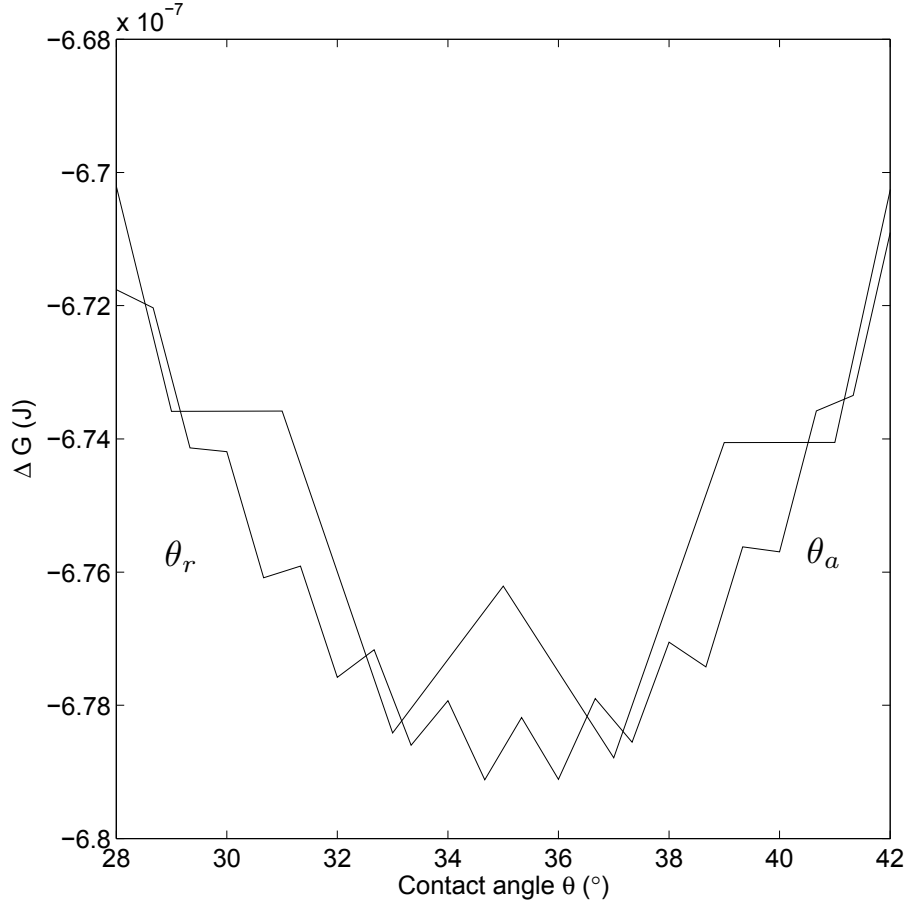


Figure 2.3: Free energy  $\Delta G$  as a function of contact angle  $\theta$  on surface consisting of two kinds of horizontal strips with alternating equilibrium contact angles.

Figure 2.3 shows the system free energy as a function of contact angle, on two surfaces consisting of two kind of horizontal strips with alternating equilibrium contact angles,  $\theta_{e1} = 40^\circ$  and  $\theta_{e1} = 30^\circ$ . The curve with a solid line is from the surface consisting of strips with equal width of  $2^\circ$ , while the strip width for the dash line curve is  $(2/3)^\circ$ . The free energy curves in Figure 2.3 contain information of the contact angle hysteresis as the following:

- From both curves, contact angle with a global minimum free energy can be found. This equilibrium angle of the surface lies between equilibrium angles of the two stripes, and can be predicted by the Cassie equation [53, 52].
- There are also some local minima of free energy in the range between  $30^\circ$  and  $40^\circ$ . These local minima are theoretical evidence for the existence of metastable contact angles  $\theta_m$ .
- As indicated in the figure, the smallest and largest metastable angles equals to the value of  $\theta_{e1}$  and  $\theta_{e2}$ . Therefore, the experimental advancing contact angle  $\theta_a$  equals to  $\theta_{e1}$ , and the experimental receding contact angle  $\theta_r$  equals to  $\theta_{e2}$ .

It could be concluded that for a given chemical heterogeneous surface, the experimental advancing contact angle  $\theta_a$  represents the surface region with low interfacial energy, and the experimental receding contact angle  $\theta_r$  represents the surface region with high interfacial energy.

Actual experimental results also support this finding. The value of the advancing contact angle  $\theta_a$  is usually reproducible on a smooth surface, while the value of the receding angle is sometimes reproducible. This may be caused by the liquid residue on the solid surfaces. Hence, the advancing contact angle  $\theta_a$  can be a good approximation of the equilibrium contact angle and can be used in Young's equation.

By using the vertical plate model for rough surfaces [55], as shown in Figure 2.4 [49], no such equality exists between  $\theta_a$  and  $\theta_e$ . Increasing surface roughness also increases the contact angles [56]. All contact angles measured on rough surfaces are meaningless in terms of Young's equation.

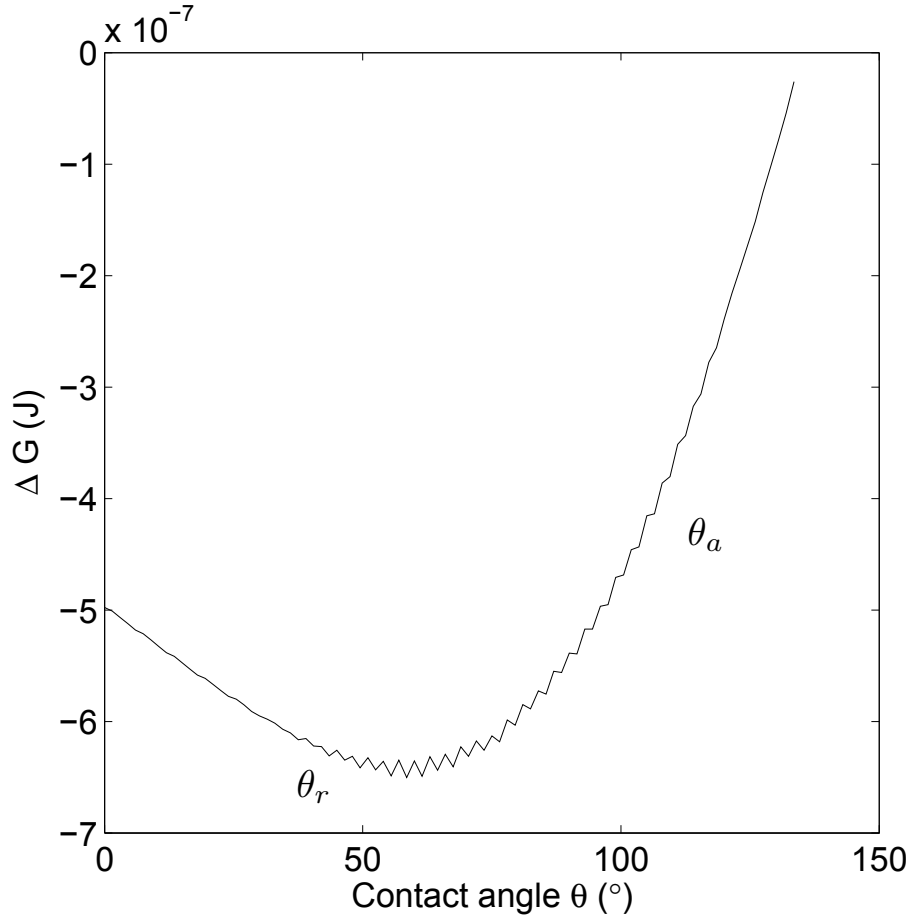


Figure 2.4: Free energy  $\Delta G$  as a function of contact angle  $\theta$  on rough but chemically homogeneous surface consisting of two kinds of inclination angles  $\beta_1$  and  $\beta_2$ .

#### 2.1.5 Summary of different types of contact angles

It becomes confusing after introducing the various contact angles, especially within the context using Young's equation for solid surface tensions. Here I clarify the concept of different contact angles as the following:

- $\theta$ : The general symbol for contact angles. It could be any phenomenological

contact angle.

- $\theta_{ES}$ : This is equilibrium contact angle for practical solid surface. As suggested by Neumann and Good' vertical plate model, this equilibrium contact corresponds to the global minimum of the system free energy. Wenzel angle  $\theta_w$  and Cassie angle  $\theta_c$  are specific type of equilibrium angles.  $\theta_E$  can not be used in Young's equation because it reflects both the material property and the imperfection of the solid surface.
- $\theta_e$  or  $\theta_Y$ : This is the contact angle coming from Young's equation, It refers to the equilibrium contact angle for an ideal solid surface. The term of  $\theta_e$  is a thermodynamic property which only relies on the material properties of chosen solid and liquid.
- $\theta_a$ :  $\theta_a$  is the contact angle when the sessile drop is advancing on the solid surface.  $\theta_a$  is also the largest contact angle of the solid surface. For a heterogeneous but smooth solid surface,  $\theta_a$  reflects the material property of the low energy solid surface region and can be used as a good substitution for  $\theta_e$  [49, 13].
- $\theta_r$ :  $\theta_r$  is the contact angle when the sessile drop is receding on the solid surface.  $\theta_r$  is also the smallest contact angle of the solid surface. For a heterogeneous but smooth solid surface,  $\theta_r$  reflects the property of the high energy solid surface region.
- $\theta_m$ :  $\theta_m$  is metastable contact angle within the range between  $\theta_r$  and  $\theta_a$ . As suggested by Neumann and Good' vertical plate model,  $\theta_m$  is the contact angle corresponding to the local minimum free energy.

## 2.2 Contact angle measurements and the determination of solid surface tensions

### 2.2.1 The ADSA and APF methods

In the long history of contact angle studies, various techniques have been developed for the measuring contact angles. Compared to other methods such as the captive bubble method developed by Adamson [57], or Wilhelmy slide technique developed by Neumann [58], the simplest way to determine the contact angle is to examine the drop profile of sessile drops. For the sessile drop profile measurements, the most frequently used method is the goniometer method and the Axisymmetric Drop Shape Analysis (ADSA) method [59].

In the goniometer method, contact angles are measured by simply drawing a tangent from where the solid, liquid and vapor phases meet. The accuracy of this method greatly depends on the experience of the operator and is normally no better than  $\pm 2^\circ$ .

By assuming that the drop profile is axisymmetric, the ADSA method uses the experimental profile to fit with the theoretical Laplacian curve given by the Laplace equation of capillary in Equation 2.1. Contact angle is then calculated from the theoretical curve. The ADSA method is widely used to provide reliable measurements of contact angles [60, 61, 62].

However, the ADSA method requires the drop profile to be Laplacian. The drop profiles of transient contact angles are not always Laplacian after applying the external force. Hence, another method, the automated polynomial fitting (APF) method, which provides the similar order of accuracy [63, 64] can also be a good substitution to determine the contact angles.

The APF method measures the contact angle by fitting polynomial curve to the sessile drop profile and then calculating the slope of the polynomial curve at the point where the three phase contact line meets the solid surface. The typical expression of the polynomial is

written as in Equation 2.14

$$y = \sum_{i=0}^M a_i x^i \quad (2.14)$$

and the value of contact angle can be calculated simply by using Equation 2.15

$$\theta = \tan^{-1}\left(\frac{dy}{dx}\right) \quad (2.15)$$

There are two parameters that largely affect the accuracy of APF method: the order of the polynomial  $M$  and the number of points used from the drop profile in the fitting.

### 2.2.2 Low-rate dynamic contact angle measurements

It is suggested by the vertical plate model from Good and Neumann, that the advancing contact angle reflect the low energy part for a smooth but chemical heterogeneous solid surfaces. It is obvious that the advancing contact angle  $\theta_a$  is a good substitution of Young's contact angle and thus applicable to Young's equation. By supplying water at a very slow speed into the sessile drop, to force the drop to advance at a very slow speed, the advancing contact angle can be measured. The validity of the method has been justified by comparing the contact angle value with the static advancing contact angles [65].

The typical low-rate dynamic contact angle measurements were carried out by supplying liquid from the bottom of the drop using a motorized syringe. Liquid coming from the bottom avoids the disturbance from the needle [66]. Images of the drop were then taken and the contact angle values were measured by the ADSA method.

A large number of liquids were studied extensively on various solid surfaces by Kwok et al. [67, 68, 69, 70, 71]. This approach provides accurate contact angle measurements and



the contact angles measured on these well-prepared solid surfaces can be used in Young’s equation.

### 2.2.3 Static contact angle measurements

This static contact angle measurements carried out by Li et al. [72, 73] is another approach of measuring the advancing contact angles. A syringe supplies water into the drop from the top and can be carefully removed by adjusting the height of the stage where the drop is sitting on.

### 2.2.4 Determination of solid surface tensions contact angles

Determination of solid surface tensions from contact angles requires accurate experimental contact angles. The measured contact angles should also reflect correct thermodynamics status of the solid surface as implied by the use of Young’s equation. The fact is that only Young’s equation can relate experimental contact angles to the two unknown solid surface tensions:  $\gamma_{sv}$  and  $\gamma_{sl}$ . Several indirect methods have been developed to estimate solid surface tensions. These methods include the capillary penetration [74, 75], heat of immersion [76, 77] and film flotation [78, 79]. It does appear that determination of solid surface tensions from contact angles via Young’s equation [80, 81, 82] could be the simplest approach.

A fundamental understanding of which contact angles should be used in conjunction with Young’s equation is urgently needed. We know from Neumann and Good’s model that only the advancing contact angles  $\theta_a$  on fairly smooth solid surfaces are good approximation of the contact angle that can be used in Young’s equation  $\theta_Y$ . Other researchers [36, 37, 41, 39, 40] have recently suggested the use of the so-called “equilibrium contact angles” using acoustic vibration during contact angle measurements, in search for the true metastable or equilibrium

contact angles. Such approach is confusing and the experimental contact angles obtained are also not compatible with Young's equation. We shall in the next sections to discuss these studies.

## 2.3 Research progress of using acoustic vibration in contact angle measurements

As predicted by Neumann and Good's model, there exist energy barriers on rough or heterogeneous solid surfaces that can prevent a liquid drop from spontaneously relaxing to its global minimum energy state. If a drop is randomly placed on a solid surface, it can be stuck in any metastable state corresponding to the local minimum free energy state. Similar theoretical analysis from Marmur and Brandon [83, 84] suggested that sufficient energy input can overcome the energy, and force the drop to reach the global equilibrium value. Thus, acoustic vibration was considered to be a good energy source to so as to overcome this energy barrier.

### 2.3.1 Brief description of the previous research

The first experiment using acoustic vibration was carried out by Smith and Lindberg [36] by supplying acoustic energy from a tiny loudspeaker to the water drops on rough nylon surfaces. The amplitude and the frequency of such vibration were controlled. The contact angle decreased with the increase of vibration amplitude and reached an equilibrium contact angle when the amplitude is within the range between 0.05 to 0.2 cm.

Andrieu and co-workers [37] used a acoustic vibration with 50  $Hz$  frequency and the amplitude up to 2.5  $mm$  to vibrate the drop for 1 minute. They created solid surfaces with different roughness and chemical heterogeneity by spraying Teflon, shoe protector, car paint

or spangled paint onto the substrates from various distances. They measured the advancing, receding contact angles and contact angles after the vibration for water and diiodomethane on these surfaces. It was suggested that the contact angles after the vibration is approximately equals to  $1/2(\theta_a + \theta_r)$ .

Meiron et al. [38] coated beeswax on different substrates to create solid surfaces with different roughness but same surface chemistry: plain glass slide as smooth surface and abrasive papers with different grit numbers as rough surfaces. The roughness of all surfaces were characterized by a optical profilometer. Continuous vibration was generated from a loudspeaker. The contact angles were then measured from the top-view. These results contradict with the work from Andrieu [37], as they suggested that the equilibrium contact angle at the global minimum free energy state should be approximately equals to the Wenzel angle instead of  $1/2(\theta_a + \theta_r)$ .

Bormashenko et al. [39, 40] examined the water contact angle on the honeycomb polystyrene patten using the vertical vibration. They suggested that transition from the Cassie-Baxter state to the Wenzel state can be observed after the vertical vibration. They also studied the contact angle of water drops on the same solid surfaces after applying the horizontal vibration.

Vibration was also used by Miguel et al. [41] to evaluate the most-stable contact angle for water drops on polydimethylsiloxane (PDMS) templates coated by paraffin wax for a wide range of roughness.

Garoff et al. [42, 43] investigated the effect of slow pulse vibration to the contact line in capillary rise. The experimental solid surfaces were Aquapel coated on glass slides. The roughness was measured to be tens of Å. Their results showed that large vibration amplitude was required to completely mitigate hysteresis while with smaller vibration amplitude, the

surface hysteresis was partially mitigated.

Noblin et al. [44, 45] investigated the oscillation behavior of the sessile drop on polymer surfaces by controlling the frequency and amplitude of the vertical vibration. They found that at low amplitude, the contact line remains pinned and the drop presents eigen modes at different resonance frequencies. At higher amplitude, the contact line moves, and the drop remains circular but the radius oscillates at the excitation frequency.

More recently, Mettu [46] et al. studied the effect of the white noise in the stochastic relaxation of water drops on Polydimethylsiloxane (PDMS). Instead of measuring the contact angle directly, they used the spreading ratios of testing drops to demonstrate the effect of acoustic vibration on contact angle hysteresis .

Other experiments relating to drop vibration were also carried out by researchers. Daniel et al. [85, 86] studied the motion of liquid drops on solid surfaces with a continuous gradient of wettability by using the vertical vibration under the substrates. Mettu and Chaudhury [87] used the asymmetric vibration to make liquid drops move on the solid surface. Brunet et al. [88] applied acoustic vibration along the vertical plate and cause the meniscus to climb up. Low frequency vibration ( $<500\text{ Hz}$ ) were used by Whitehill [89] to study the spreading of the water drop.

### 2.3.2 The effect of surface roughness

It is obvious from the literature that there has been growing interest recently on the use of acoustic vibration in search for an equilibrium contact angle for Young's equation. However, all studies appear to be confusing and misleading as the fundamental questions on the applicability of experimental contact angles in Young's equation was ignored (see later). Table 2.1 lists all testing liquids and solid surfaces used in these studies. It is apparent

that these researchers attempted to use acoustic vibration in studying equilibrium contact angles on rough solid surfaces. From the Neumann model on rough surfaces, it has been demonstrated clearly that there exists a contact angle at the global minimum free energy state. Experimentally, these studies attempted to relate such vibrated minimum angles to the advancing and receding angles and Young's equation. It should be realized that acoustic vibration can definitely be used to examine contact angle hysteresis. However, such studies should be qualitative and not quantitative so as to use such angles in conjunction with Young's equation. Neumann's model clearly demonstrates that, on rough surfaces, neither the advancing nor the receding angles bear any relation to the material properties of solid surfaces. All contact angles on rough surfaces are not applicable in Young's equation.

Table 2.1: Summary of liquids and solid surfaces used in the literature of contact angle measurements involving acoustic vibration.

| Author             | Year                  | Testing liquid         | Testing solid surface                                                               | Roughness     |
|--------------------|-----------------------|------------------------|-------------------------------------------------------------------------------------|---------------|
| Smith et al.       | 1974[36]              | water                  | rough nylon                                                                         | rough         |
| Andrieu et al.     | 1994 [37]             | water, diiodomethane   | PET, spraying Teflon, shoe protector, car paint and spangled paint onto PET surface | rough         |
| Garoff et al.      | 1994[42],<br>1996[43] | water                  | Aquapel coating on glass slides                                                     | smooth        |
| Meiron et al.      | 2004[38]              | water, ethylene glycol | beeswax coating on glass slides and abrasive papers with different grit sizes       | rough         |
| Noblin et al.      | 2004[44],<br>2009[45] | water                  | polystyrene                                                                         | N/A           |
| Bormashenko et al. | 2007 [39, 40, 90]     | water                  | honeycomb polystyrene patten                                                        | rough, porous |
| Mettu et al.       | 2010 [46]             | water                  | PDMS                                                                                | smooth        |
| Miguel et al.      | 2011[41]              | water                  | paraffin wax coating on PDMS templates                                              | rough         |

### 2.3.3 Methods of contact angle measurements

Different contact angle measurement techniques were used in these studies. The most common method is by means of the goniometer. Measuring the angle from a picture was used by some group of researchers [36, 37, 44]. This method has been suggested to be inaccurate and can not reflect the complexity of metastable contact angles. Axisymmetric drop shape analysis-profile (ADSA-P) technique was used by Miguel et al [41]. ADSA-P technique measures the contact angle by fitting the drop profile with the theoretical Laplacian drop profile and has a accuracy as good as  $\pm 0.3^\circ$ . However, vibration can easily cause the drop shape to be non-Laplacian. Meiron et al [38]. used top-view camera to capture the radius of the drops and measured the drop volume by a micro-balance. The contact angles were then calculated by fitting the drop shape with the theoretical shape using a computer program.

Some indirect methods without measuring the contact angle were also be used to examine the contact angle hysteresis. Garoff et al. [42] measured the contact line position of a vertical plate in water. Mettu et al. [46] compared the spreading ratio of the drop before and after vibration.

### 2.3.4 The effect of vibration types

Most of the experimental studies were using vibration which are continuous, sine functional and vertical. From the experiments of Garoff et al. [42], it appears that pulse vibration has the same effect of removing the energy barrier. This is not difficult to comprehend because the amount of vibrational energy inputting into the sessile drops reduces the effect of contact angle hysteresis. White noise is used by Mettu et al. [46] because they find that white noise is quite common in natural and moderate enough to keep the drop shape.

The only experimental study using horizontal vibration was carried out by Bormashenko

et al. [90]. Compared to their earlier work using vertical vibration [40], horizontal vibration has same effect in causing the transition between Cassie and Wenzel wetting regimes.

### 2.3.5 The effect of vibration amplitude and frequency

Vibration energy  $e_v$  can be affected by both the amplitude  $A$  and frequency  $f$ . For a continuous vibration in a unit time, it is apparent that  $e_v \sim A^2 f^3$ . Experimentally, however, amplitude is more influential in breaking the energy barrier and exciting the liquid to its state the with the global minimum free energy. The drop will reach that state only when the vibration amplitude is sufficiently large.

Noblin et al. [44] carefully examined drop oscillation by varying the vibration amplitude and frequency. Two types of oscillations were observed: At low amplitude, contact line of the drop does not move. The drop shape changes with the vibration frequency. At higher amplitude, the contact line moves and remains circular. The contact radius oscillates with the frequency.

### 2.3.6 Summary and objectives

To summarize the previous studies, the following details should be noted in my studies:

1. No rough solid surfaces should be used if the experimental results are to be related to previous theoretical works. The testing solid surface should be prepared as smooth as possible.
2. The testing solid surface should be well characterized.
3. A reliable contact angle measurement technique should be used.
4. The vibration amplitude should be carefully controlled.



5. An in-depth study of metastable contact angles on different solid surfaces is seriously lacking.

In this research work, two kinds of polymer: poly(methyl methacrylate) (PMMA) and poly(n-butyl methacrylate) (PnBMA) were selected to be experimental solid surfaces. These surfaces are sufficiently smooth and their surface properties have been systematically characterized by Kwok and coworkers [67, 68, 13]. Well controlled vibration will be used to examine the thermodynamic status of the metastable contact angle  $\theta_m$  and their relations to the amplitude and frequency of the vibration.

## Chapter 3

# Investigations to Metastable States of Water-Polymer Contact Angles using Acoustic Vibration

### 3.1 Introduction

It is a well known fact in the literature that there exists the so-called contact angles hysteresis [1]. A maximum contact angle can be obtained while advancing the liquid front for contact angle. This is known as the advancing contact angle. A minimum contact angle can also be obtained while receding the three-phase contact line for contact angle. This is known as the receding contact angle. The difference between these two values results in the so-called contact angle hysteresis. Contact angle hysteresis can be due to surface roughness and chemical heterogeneity of the surface [1, 49]. Depending on how the researchers measure the contact angle, different contact angles between the advancing and receding contact angles exist widely in the literature [27, 28, 29, 30, 31]. The “straight-forward” measurement of contact angle has now become the most confusing aspect in the center of contact angle research.

Various models have been developed [32, 54, 33] in attempt to understand the thermodynamic status of contact angles as they relate to Young’s equation. Various approaches suggest that there exists something known as the metastable contact angles. Experimentally, the determination of metastable contact angles are not well understood and confusing in the literature [27, 28, 34, 35]. Some researchers employed acoustic vibrations to determine metastable contact angles and used the minimum of these metastable contact angles in

Young’s equation for solid surface tensions [36, 37, 38, 39, 40, 41, 42, 43, 44, 46]. Literature use of such metastable angles are misleading and it is the purpose of this chapter to examine the thermodynamic status of contact angles carefully.

## 3.2 Experiments and Data Analysis

### 3.2.1 Polymer surface preparation

Two polymer surfaces were selected to serve as the testing solid surface for both metastable and dynamic contact angle measurements: poly(methyl methacrylate) (PMMA) and poly(*n*-butyl methacrylate) (PnBMA). They are polymers with similar molecular structures but different side chains.

The reasons of selecting these two polymers are based on the following facts: (1) they are rigid and inert solid surfaces when the testing liquid is water, (2) The surface tension and the low-rate dynamic contact angles for these two polymer surfaces have been well characterized by Kwok et al. in the previous studies [67, 68]. (3) The water contact angle value of these two polymer surfaces are within the range between  $60^\circ$  to  $90^\circ$ , and sufficient for the measurements and comparison. For metastable contact angle experiments, the silicon wafers <100>(P/E, Wafer World) were selected as the substrates. Not only because they are extremely smooth with the roughness within the order several nanometers [91], they also provide better contrast for water drop imaging.

Silicon wafers were cut into 3 *cm* by 3 *cm* square pieces before cleaning in acetone ( $\geq 99.5\%$ , Sigma-Aldrich) and sonicating for 10 *min*. Square slides were then rinsed with deionized ultrafiltered (DIUF, from Fisher Scientific ) water and dried in the oven at  $200^\circ\text{C}$  for 2 *hr*. These slides were used as the substrates after they cooled off to room temperature.

Two different polymer solutions were prepared by dissolving PMMA ( $M_w = 350,000$ ,

purity  $\geq 95\%$ , Sigma-Aldrich) powder and PnBMA ( $\eta = 0.5$ , purity  $\geq 95\%$ ,  $M_w = 180,000$ , Polyscience) powder into chloroform ( $\geq 99.8\%$ , Sigma-Aldrich) respectively with the same weight percentage of 1%.

Solvent casting method was used to prepare the polymer films. A few drops of 1% polymer/chloroform solution were deposited on the clean solid substrates. After carefully turned the substrates with small angles of inclination to spread the solution over the solid substrates, the substrates were placed inside petri glass dishes overnight to ease solvent evaporation. Polymer films were also prepared by spin-coating the polymer solutions onto glass substrates using a spin-coater (Model WS-400B-6NPP-LITE, Laurell inc.) with a maximum spinning speed of 3000 *rpm*.

Both preparation methods produced polymer surfaces with good quality. Surface roughness cannot be observed by bare eyes. The solvent casting method produced polymer surfaces with light fringes, which come from the refraction of visible light at these surfaces, suggesting that roughness is in the order of nanometers. However, such phenomena can hardly be observed from slides prepared by the spin coating method. This is because the mechanical energy in the spin coating process forces the polymer solution to spread and also accelerates the evaporation of the solvent. The fast evaporation affects the crystallization process of the polymer. Nevertheless, the spin coating method has its advantage of shortening the preparing time of solid surfaces.

In my experiments, all the solid films for droplet impact experiments were prepared by the spin coating method because of the large number of tests as well the low accuracy requirement of contact angle measurements. On the other hand, for the metastable contact angle experiments, all polymers surface were prepared by solvent casting method because of the need of high accuracy.

### 3.2.2 Experiments of metastable contact angle measurements

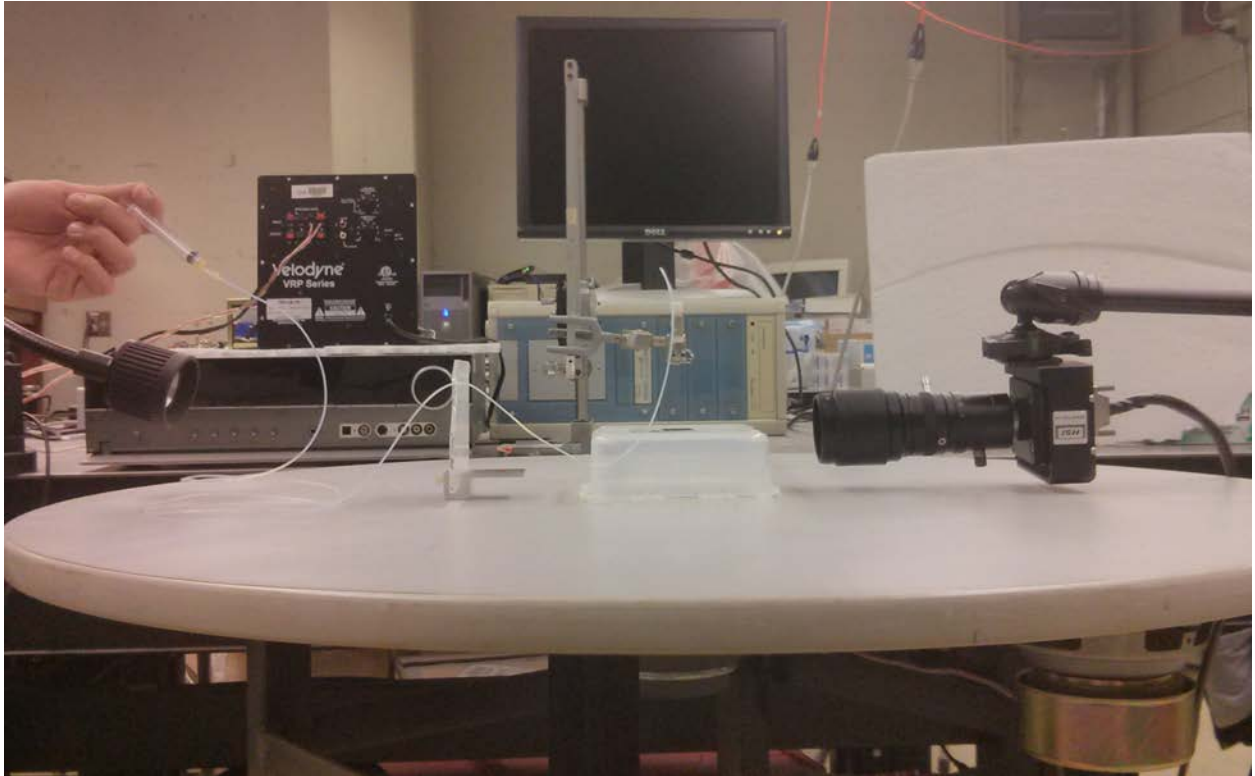


Figure 3.1: Photo of experimental setup for metastable contact angles measurements.

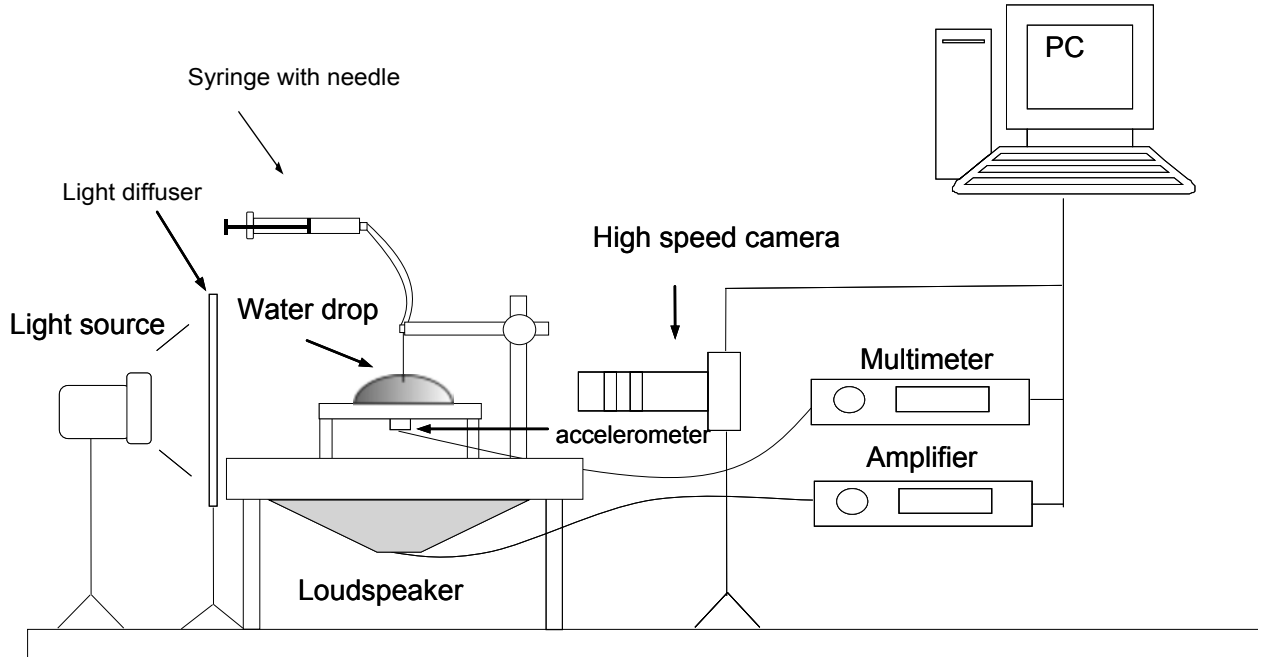


Figure 3.2: Schematic of experimental setup for metastable contact angles measurements.

Figures 3.1 and 3.2 show the experimental setup for measuring metastable contact angles. A loudspeaker (VRP-10, Velodyne) was fixed under an adjustable table to provide the vibration. The sound signal was generated from a PC and amplified by an amplifier (Harman Kardon, DPR 2005). The amplifier was also used to control the amplitude of the vibration. If we set the maximum output of the amplifier to be 0 dB, 5 different vibration strength levels of 0 dB,  $-6$  dB,  $-12$  dB and  $-18$  dB were selected, and the corresponding vibration amplitude ratios were found to be 1, 0.79, 0.50, 0.25 and 0.125.

In order to examine the metastable contact angles by controlling the free energy of the water drop from the initial contact angle of the advancing contact angle, water drop in 1 cm diameter was deposited onto the testing surface using a 25 G stainless steel needle (Hamilton) remotely controlled by a 1 ml syringe (Hamilton). Subsequently, more water

was injected slowly into the existing sessile water drop to cause the drop to expand on the surface. As soon as the drop dimension has reached approximately 1.5 *cm*, I carefully removed the needle from the top and started the vibration by generating signal from the computer. Experiments for metastable contact angles of water drop from the initial angle of receding contact angle was following similar procedures, except that a larger water drop was deposited on the polymer surface and water was then slowly retrieved from the needle in order to cause the drop to shrink.

The water drop diameter was carefully controlled to be around 1.5 *cm*. A very large water drop is sensitive to environmental interference, producing more errors and noises into the observation. On the other hand, Gaydos and Neumann [92] stated that line tension is dependent on the drop size. When the drop is too small, the measurement of contact angles would be affected by line tension.

Image sequences of water drops during the vibration process were captured by a high speed camera (DRS inc., Lightning RDT 16000) with a zoom lens. The record rate was 25 fps (frames per second) and the resolution of caption was  $768 \times 256$ . All images were recorded by a computer using a video caption card.

### 3.2.3 Contact angle measurements

The APF method was chosen to measure contact angles because it is relatively straight forward to programme. Two parameters, polynomial order  $M$  and number of points  $n$ , used in the APF method in this work were selected by comparing the results of PMMA advancing contact angles from APF method to the existing value from the literature [67, 68].

Figure 3.3 shows the effect of polynomial order  $M$  on polynomial fitting accuracy when applying different  $M$  values of 3, 4 and 5 in the calculation. As the advancing contact angle

value measured by Kwok et al. [67] is  $73.7^\circ$ , the polynomial fitting using  $M = 3$  failed to provide correct contact angle values. The results calculated by using  $M = 4$  and  $M = 5$  are both acceptable. The use of higher order polynomial used to fit the drop profile will not bring significant improvements and will cause a waste of computational time.

Figure 3.4 shows the effect of the number of points chosen from the drop profile to do the polynomial curve fitting. It is obvious that using 30 points to do the curve fitting will yield an advancing contact angle around  $77 - 78^\circ$ , which is too large when compared to the literature value, while the usage of 70 points yields a smaller value of the advancing contact angle .



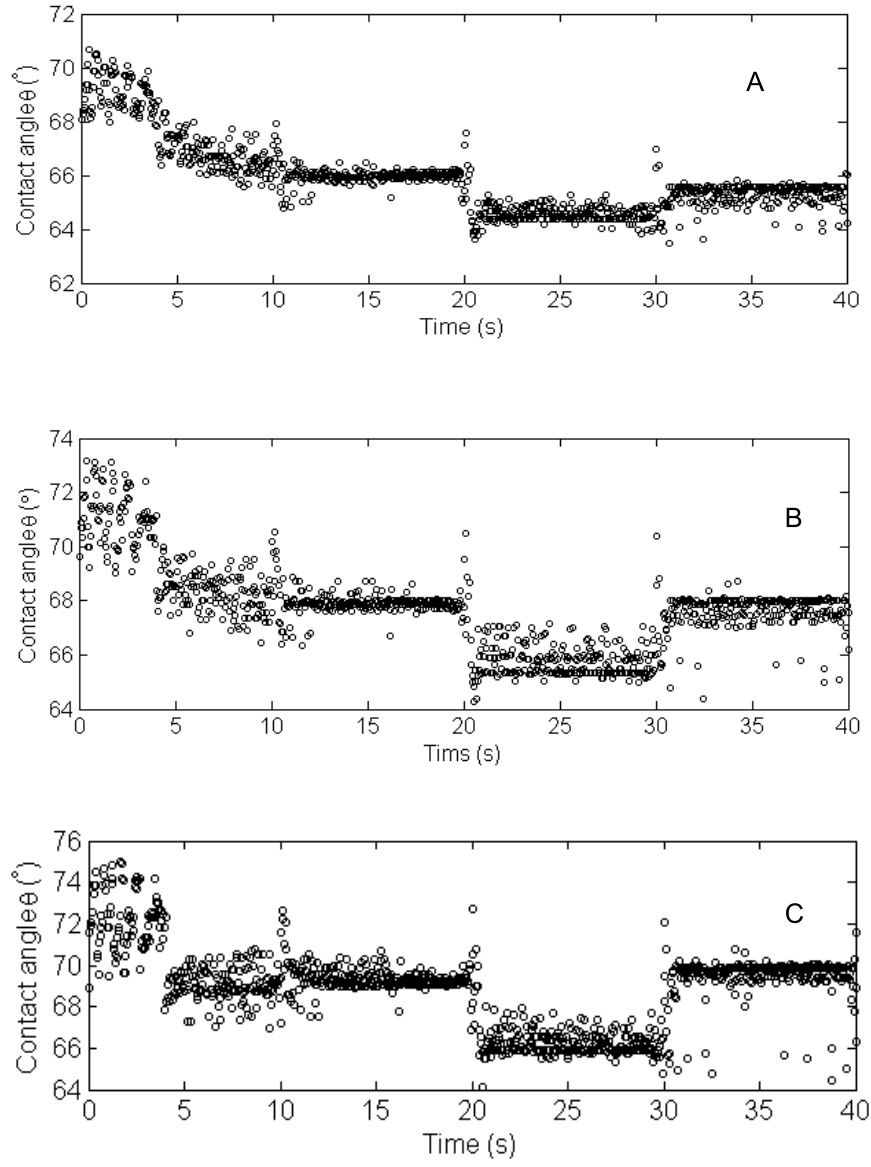


Figure 3.3: Effect of different polynomial orders used to calculate the contact angle value using one of the image sequences of water drop released from advancing on PMMA solid surface, A:  $M = 3$ , B:  $M = 4$ , C:  $M = 5$  while  $n$  is fixed at  $n = 50$ .

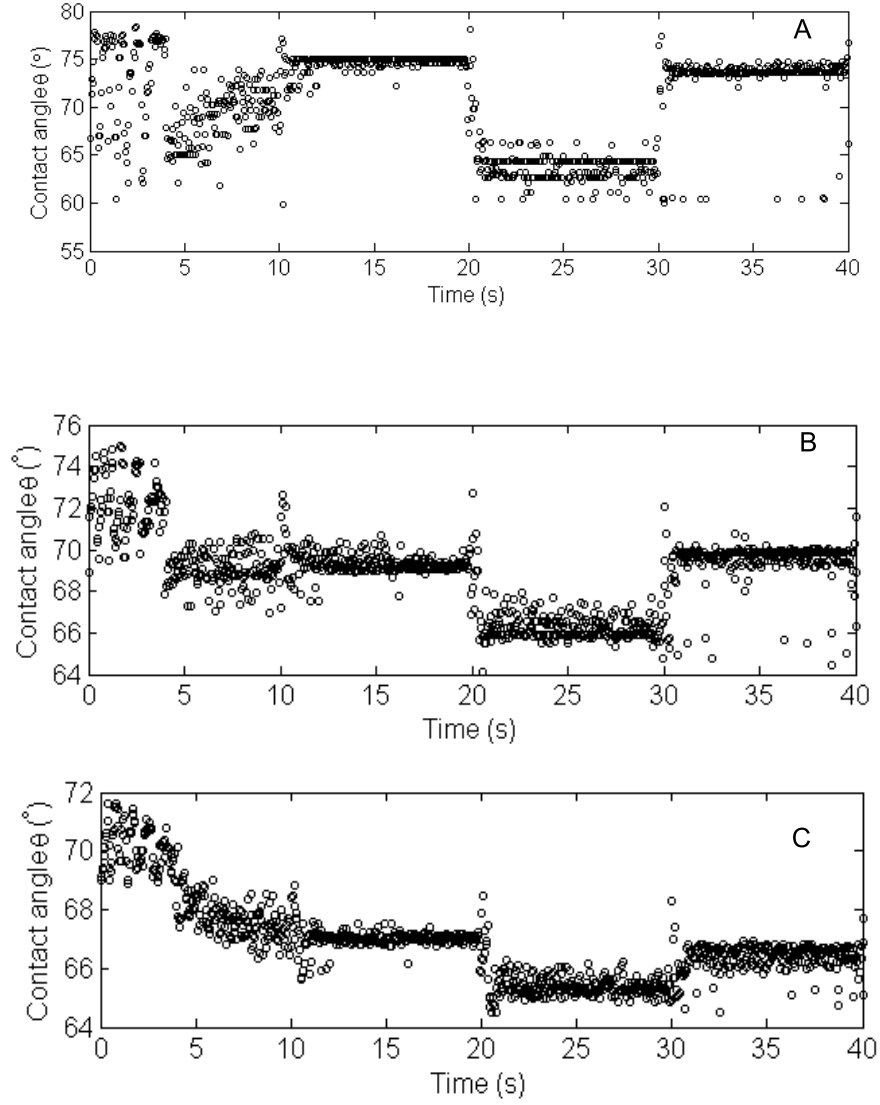


Figure 3.4: Effect of different amount of points used to calculate the contact angle value using one of the image sequences of water drop released from advancing on PMMA solid surface, A:  $n = 30$ , B:  $n = 50$ , C:  $n = 70$  while  $M$  is fixed at  $M = 5$ .

As shown in Figure 3.6, all image sequences captured by the high speed camera were cropped into a suitable size before the adjustment of contrast and brightness using the open software ImageJ. All the adjusted images were then processed by Matlab <sup>1</sup> with the Image

Processing Toolbox. Pictures were firstly digitized into matrices, and the edges of drop profiles were then computed using the Sobel method.

Figure 3.5 compares the edges calculated using different edge-finding methods. It appears that the Canny and the Laplacian of Gaussian methods provide extra information but may also affect the calculation of the edges. Other edge-finding methods are all acceptable for the calculation.

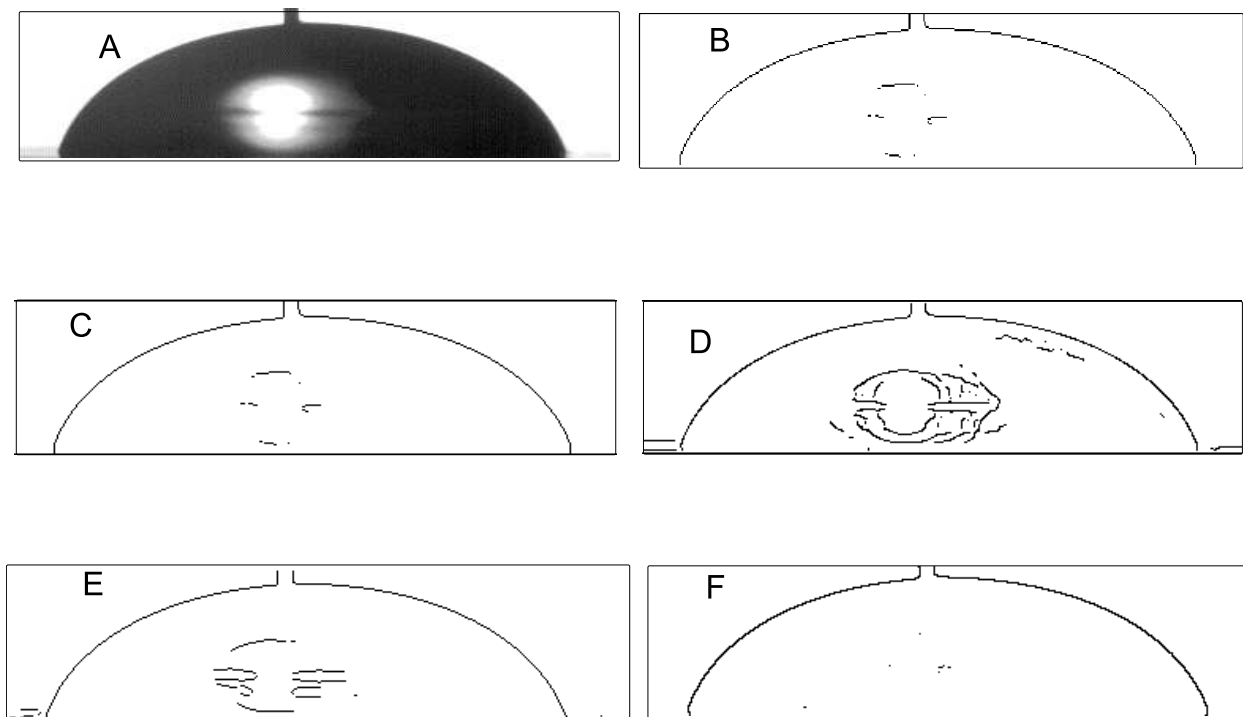


Figure 3.5: The effect of different edge-finding methods, A: raw data, B: Sobel method, C: Prewitt method, D: Canny method, E: Laplacian of Gaussian method, F: Roberts method.

A 5th order polynomial and 50 points on the drop profile were used to fit the drop profile in each figure. As shown in Figure 3.6, a tangent line for the polynomial was then used to calculate the contact angle value for each figure. Both the contact angles from the left and right side of drop profile were calculated, and the resulting contact angle is the average of

the two. The Matlab programming code is provided in Appendix.1.

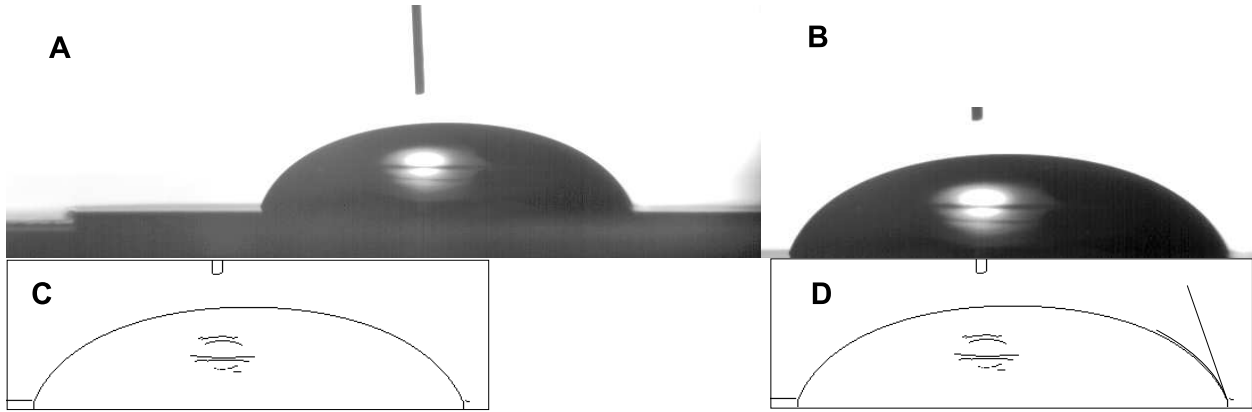


Figure 3.6: A sample of image process, A: raw jpeg image from the recorded video clip, B: cropped and adjusted using ImageJ, C: finding drop edge using the Sobel method, D: polynomial fitting and contact angle measurements.

### 3.2.4 Vibration signals generation

All audio signals were generated from a computer to the amplifier by playing audio clips with the format of Waveform Audio File Format (.wav). All the audio clips were generated and edited by using the open source software Audacity. Mainly two kinds of sound samples were used to generate the vibration: white noise and drum pulse. Figure 3.7 shows the sound waveform of these two kinds of samples. For the drop sitting on the solid surface, the drum sound sample provides a pulse vibration compared to continuous vibration from the white noise sound sample. The audio clips were generated by combining these sound samples.

Figure 3.8 shows the audio clip which was used most frequently in metastable contact angle experiments to generate vibration. This audio clip is the combination of four 50  $Hz$  sound samples with a 0.5 s length and 5 silence sound samples. 5 seconds of silence from

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<sup>1</sup>Matlab are registered trademarks of The MathWorks.

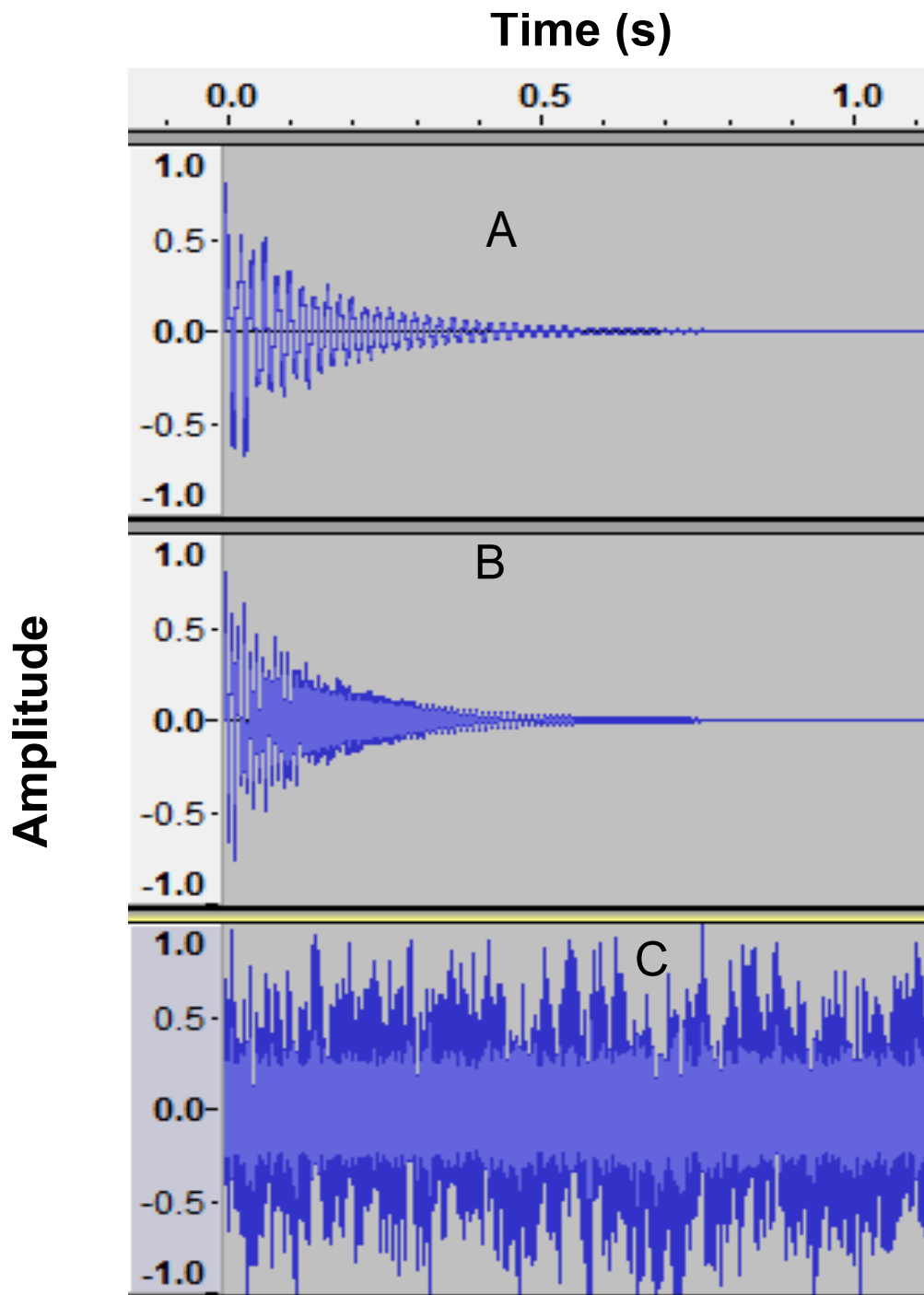


Figure 3.7: Sound sample generated by Audacity, A: 50  $Hz$  drum sample, B: 100  $Hz$  drum sample, C: white noise sample.

the beginning was used to allow the drop to relax after the removing of the needle, and 9.5 seconds of silence was used after each pulse from the drum signal.

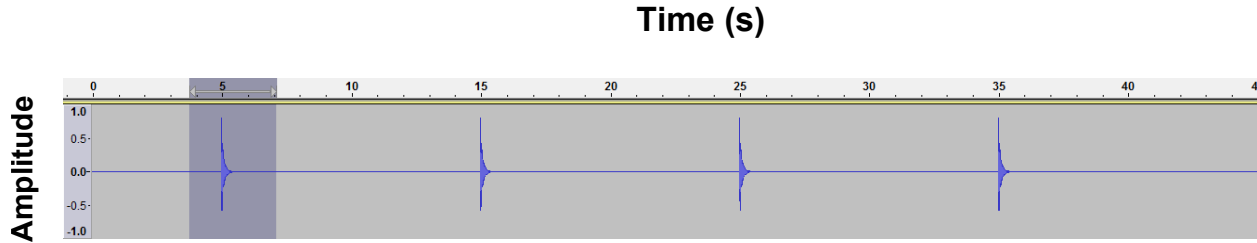


Figure 3.8: The waveform of the most frequently used audio clip.

### 3.3 Results and discussions

#### 3.3.1 Drop shape observations

Cropped images of water drop on polymer surfaces before and after acoustic vibration (with large amplitude) are placed together for both advancing and receding angles as initial contact angles in Figure 3.9, for PMMA solid surface and in Figure 3.10, for PnBMA solid surface.

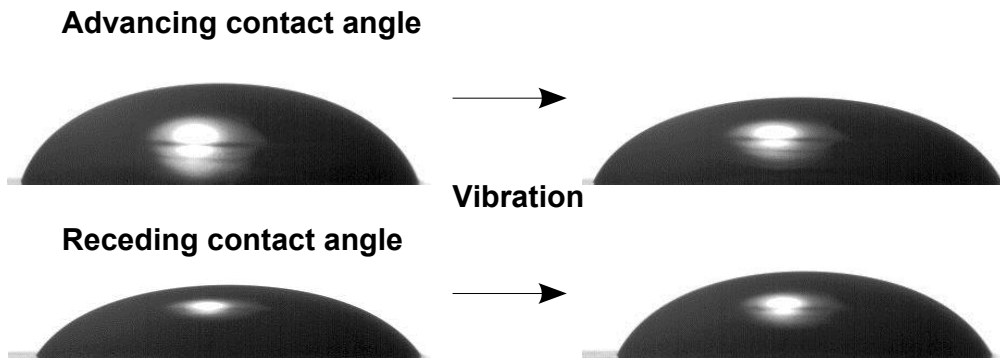


Figure 3.9: Initial and final states of drop on PMMA surface subject to vibration from both advancing and receding contact angles.

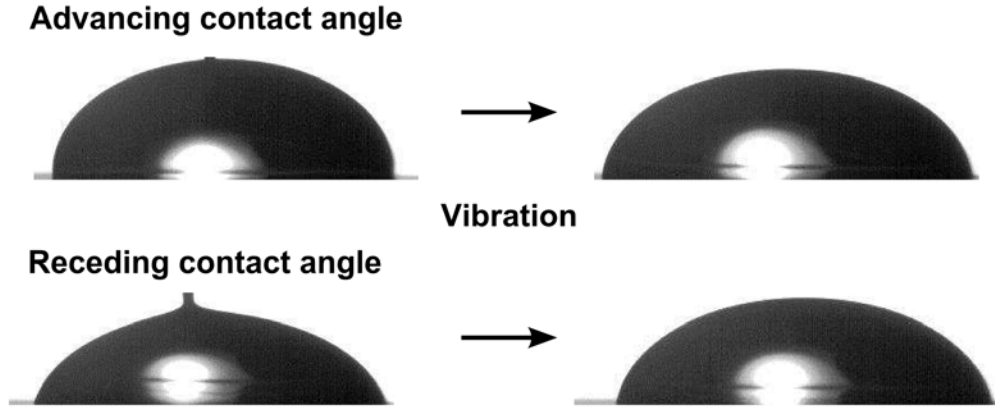


Figure 3.10: Initial and final states of drop on PnBMA surface subject to vibration from both advancing and receding contact angles.

Both figures show the same trend that after the vibration, the advancing angle decreases and the receding angle increases. Similar shape of drops after the vibration shows that vibration causes the drops to reach the states with global minimum free energy. All the contact angle values are shown in figures in next subsection.

### 3.3.2 Contact angle values in vibration-relaxation cycles

After using the polynomial fitting method for each video frame captured by the high speed camera, the calculated contact angles were plotted as a function of time. In Figure 3.11, 3.12, 3.13 and 3.14, metastable contact angle values of water drops from both advancing and receding angles on the PMMA and PnBMA surfaces show responses similar to the vibration generated from the audio clip (Figure 3.8 ) using two different amplitudes,  $0\text{ dB}$  and  $-12\text{ dB}$ . It is noted that the amplitude of  $-12\text{ dB}$  is about 25% the amplitude of  $0\text{ dB}$ .

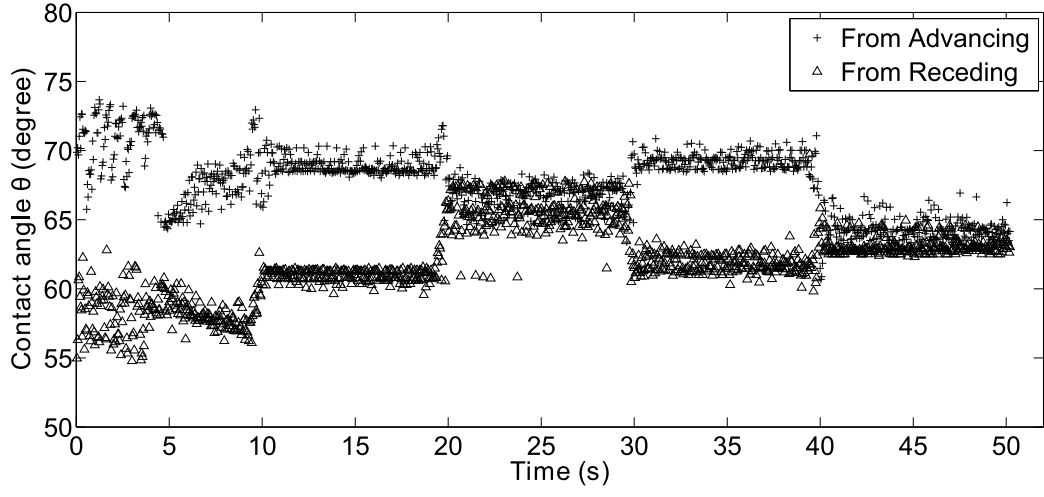


Figure 3.11: Metastable angles of water drop on PMMA surface with high vibration amplitude of 0 *dB* versus time.

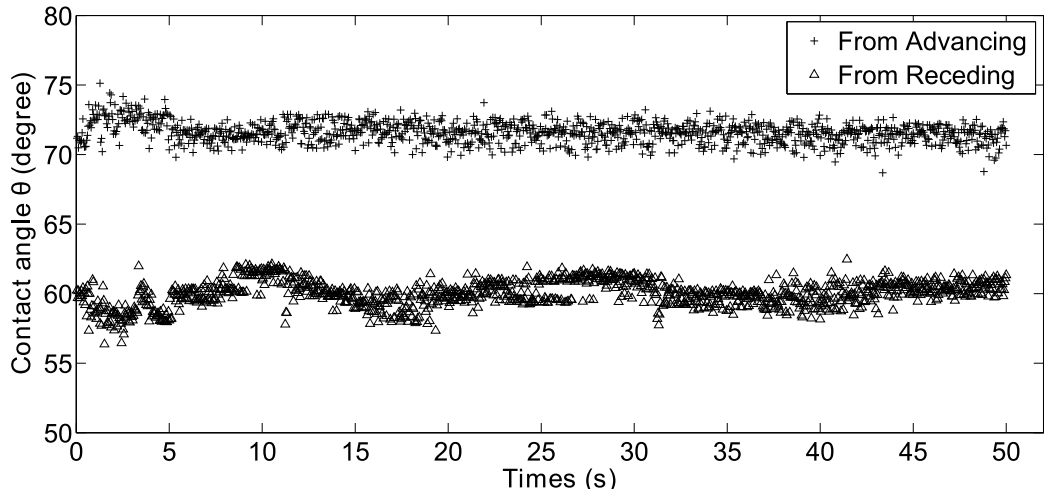


Figure 3.12: Metastable angle of water drop on PMMA surface with low vibration amplitude of  $-12$  *dB* versus time.



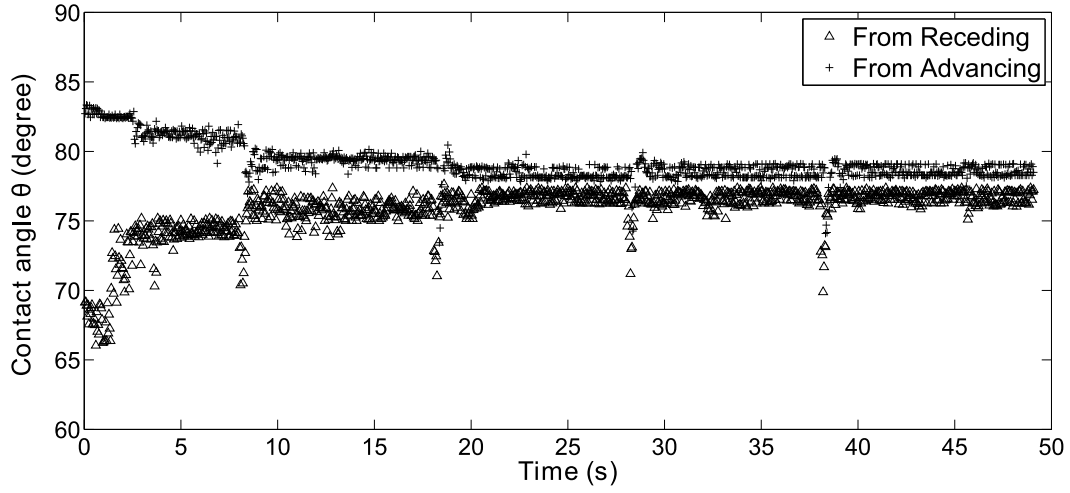


Figure 3.13: Metastable angle of water drop on PnBMA surface with high vibration amplitude of 0 *dB* versus time.

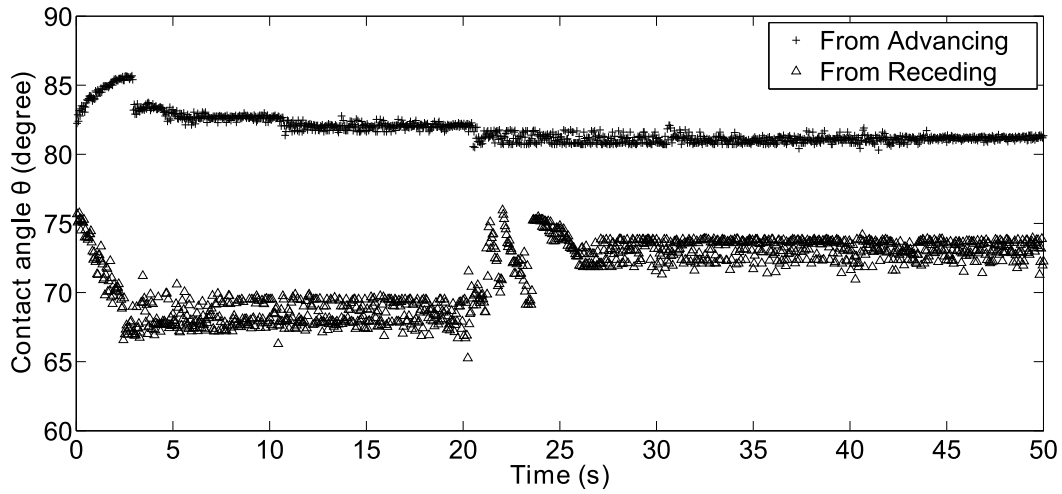


Figure 3.14: Metastable angle of water drop on PnBMA surface with low vibration amplitude of -12 *dB* versus time.

From the results of this experimental investigation, the predictions to metastable states of contact angles from Neumann and Good's vertical plate model have been illustrated

even though the experimental solid surface is much more complicated than the solid surface consisting of vertical or horizontal strip patterns. It is also obvious from the figures that advancing contact angle and receding contact angle are respectively, the maximum and minimum values of the contact angle that the system can achieve.

The vibration amplitude strongly affects the ability of water drops jumping from the high energy metastable state to the low energy state. For metastable states of the solid-liquid-vapor, there exists a energy barrier to prevent the system from reaching its minimum. The effect of the acoustic vibration is to force the drop to change its boundary so that it can reach a state with lower system energy. The assumption here is that the closer the metastable contact angle approaches to the contact angle at the global minimum system energy, the larger value of energy barrier that the metastable state has. The assumption shows good agreement to the experimental results. For the vibration with higher amplitude, the minimum contact angle from the initial advancing angle and the maximum contact angle from the initial receding angle can be very close. For water drop on the PMMA solid surface, these two angles can even overlap. On the other hand, when the vibration amplitude is about 75% lower, these two angles mentioned above only approach slightly, leaving a larger discrepancy between each other.

### 3.3.3 Selection of vibration signals

Three different kinds of sound samples were used to generate the acoustic vibration, and resulting metastable contact angles versus time are shown in Figure 3.15. The three different sound signals are 50Hz drum, 100Hz drum and white noise. The waveforms of these sound signals are shown in figure 3.7. The aim of this comparison is to investigate the effect of vibration frequency, pulse and continuous vibration on the metastable contact angles.

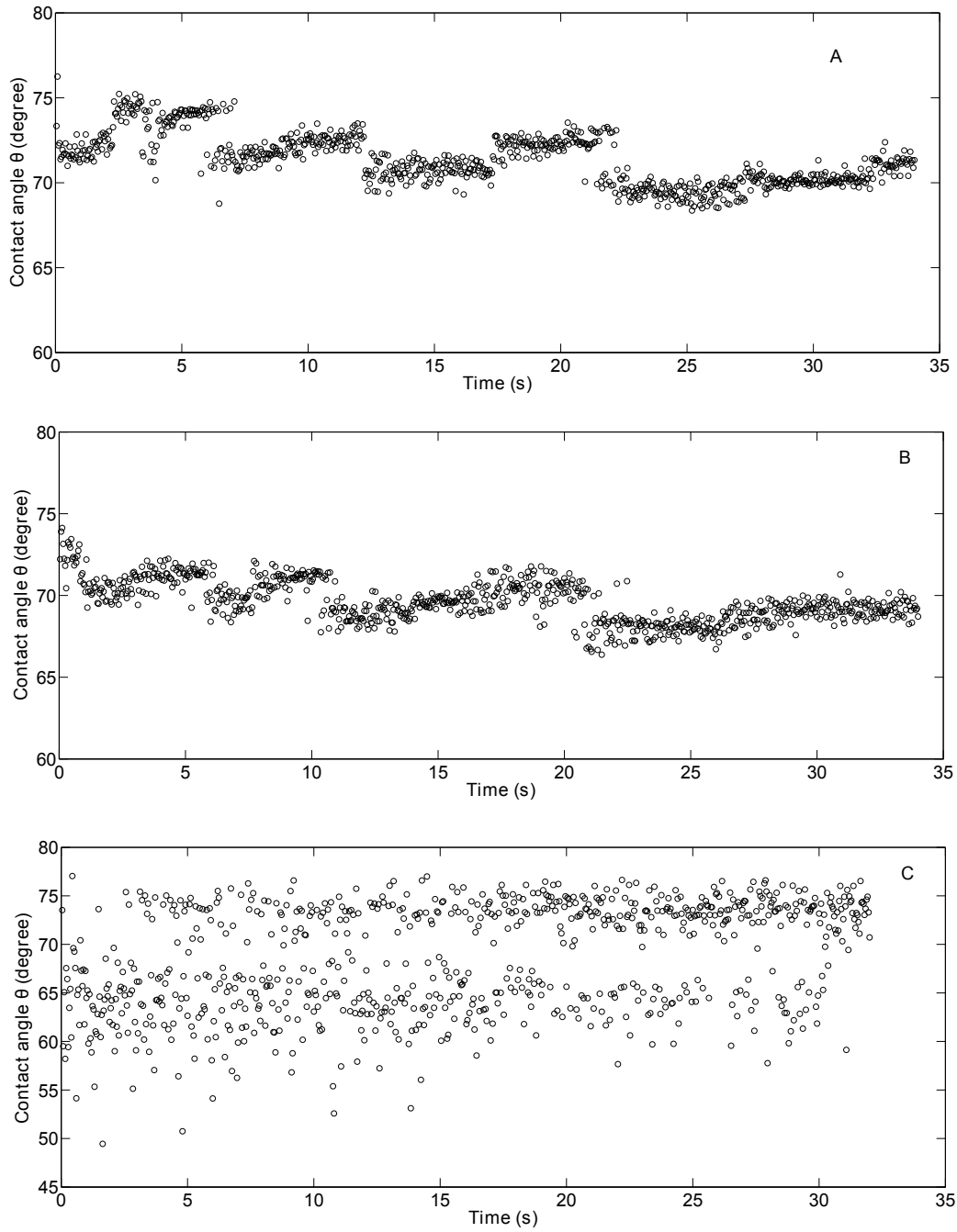


Figure 3.15: The effect of different sound signals to metastable contact angles, A: 50  $Hz$  drum pulse, B: 100  $Hz$  drum pulse, C: white noise.

It has been reported by Mettu and Chaudhury [46] that white noise is effective to the relaxation of contact line. They chose the white noise vibration in order to avoid the randomness from the pulse vibration. However, by comparing the metastable contact values subjected to the white noise vibration and those subjected to the pulse vibration, the white noise vibration in my experimental setup only causes the contact angle value to change with time by a very large range (Figure 3.15C). The pulse vibration, on the other hand, remains effective in overcoming the energy barrier, as long as pulse vibration was allowed for the drop to settle.

The results for the vibration frequency of 50  $Hz$  and 100  $Hz$  from Figure 3.15A and 3.15B show similarity in the metastable contact angle patterns. It does appear that the vibration amplitude plays a more important role than the vibration frequency in affecting the metastable contact angles of the drop for the system we have investigated. However, it is difficult to conclude that the sound frequency could have no effect to metastable contact angles. Larger vibration frequency leads to higher energy density of vibration. However, the frequency range of the loudspeaker used in my experiment was limited. Higher frequency vibration could be performed by using other types of loudspeakers.

### 3.3.4 Dependence of metastable contact angles on vibration amplitudes

By controlling the vibration amplitudes, different amount of the external energy can be input into the water drop, so as to overcome the energy barriers and to decrease the free energy of the system. It is obvious that liquid drop with larger external energy has larger possibility to overcome energy barriers and reach their states at the global minimum of free energy. As mentioned previously, the assumption here is that the metastable state with smaller free energy will have larger energy barrier.

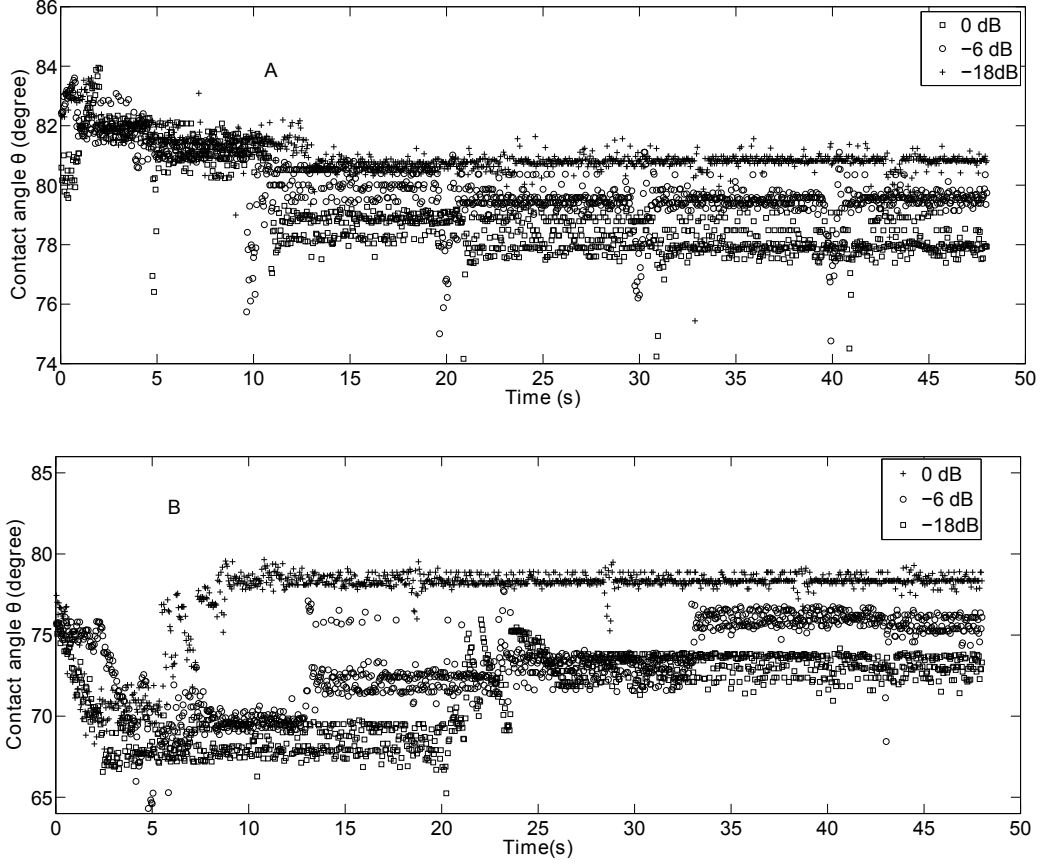


Figure 3.16: Metastable angles of water drop on PnBMA surface with different vibration amplitude of 0 *dB*, -6 *dB*, and -18 *dB* for A: advancing initial angles, B: receding initial angles.

The Figure 3.16 for PnBMA solid surface shows that vibration excitation with higher amplitude have a larger effect on contact angles while the vibration with smaller amplitude has little or no effect on contact angles. The metastable states of PnBMA surface appears to be quite stable. When the system reaches a metastable state, the only direction it can go further is the direction of decreasing its system's free energy.

Compared to the metastable contact angles of PnBMA surface, contact angles of PMMA follow the similar trend that stronger excitation results in a state with smaller free energy as shown in Figure 3.17. For water drop on PMMA surface with high external energy, there

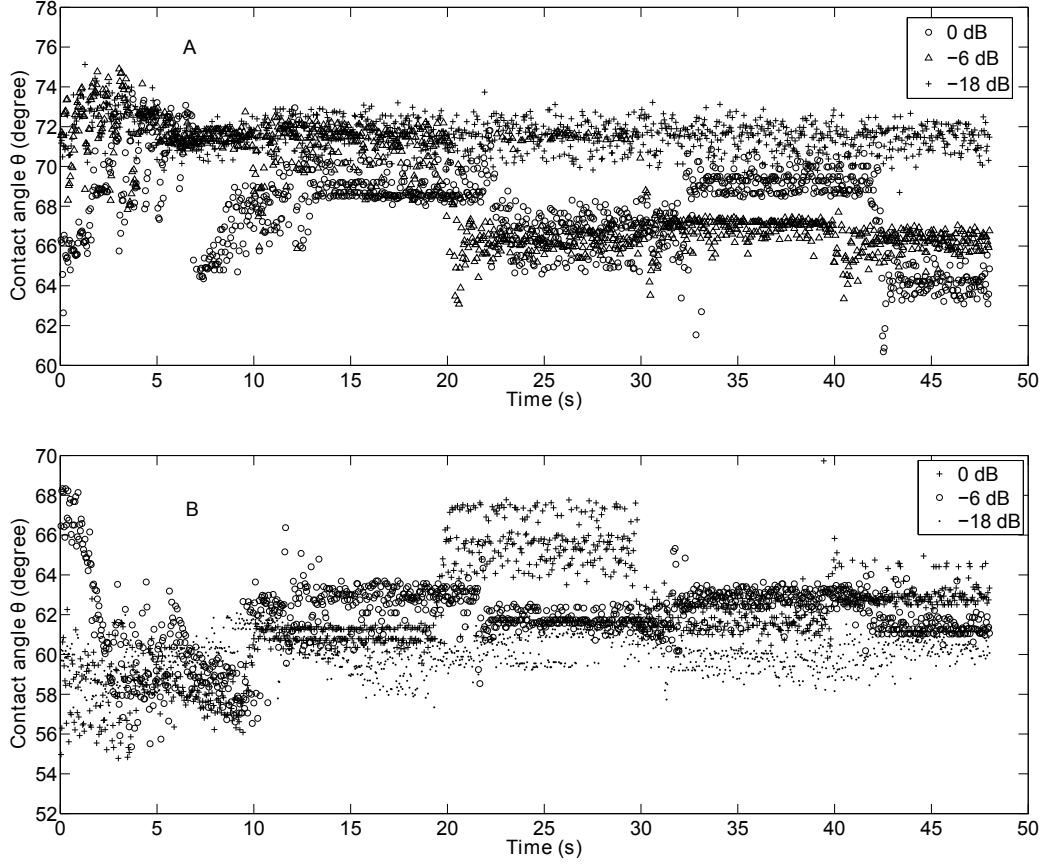


Figure 3.17: Metastable angles of water drop on PMMA surface with different vibration amplitude of 0 *dB*, -6 *dB*, and -18 *dB* for A: advancing initial angles, B: receding initial angles.

is a possibility that the contact angle could jump from the low free energy state to the high free energy state.

Some studies suggest that the purpose of introducing acoustic vibration is to force the sessile drop in overcoming the energy barrier and decreasing the system free energy [36, 83]. Let me examine this closely.

Whenever there is acoustic vibration, the position of the solid surface will change vertically, making the water drop on top to deform because of inertia and fluidity. As shown in

Figure 3.18, ascension of solid surface decreases the apparent drop contact angle, and the descent of solid surface yields a larger apparent contact angle. Figure 3.19 gives the evidence for the existence of the water drop deformation in both directions.

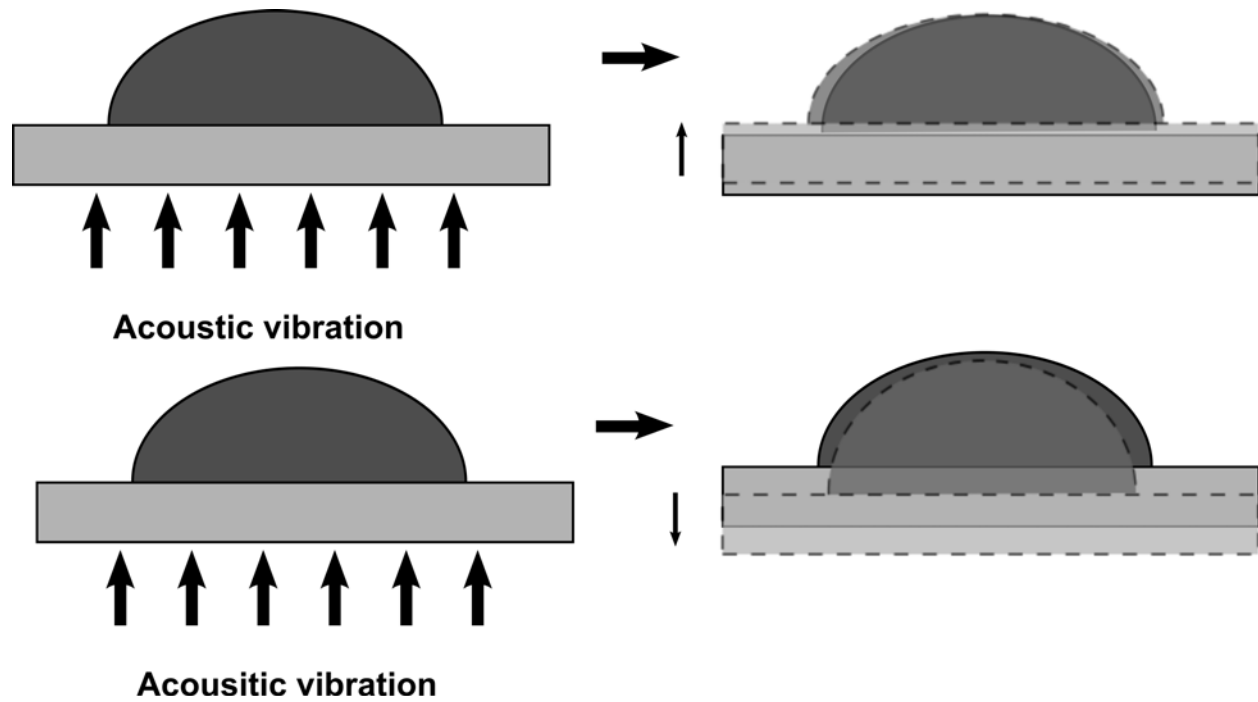


Figure 3.18: Schematic of drop deformation after the vibration.

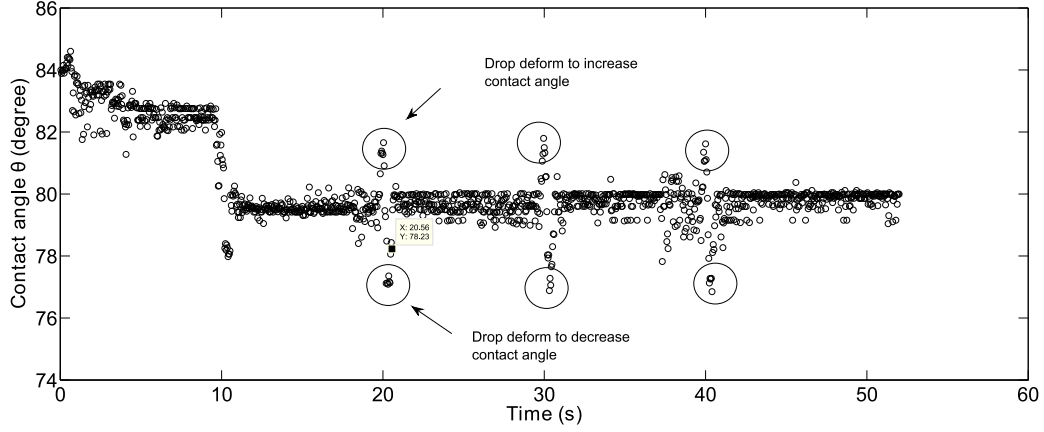


Figure 3.19: Metastable contact angles of water drop on PnBMA surface with an advancing initial angle. Both kinds of drop deformations are marked by the dashed circles.

The deformation of water drop would change the surface area of interfaces as well as the system free energy. The dependence of free energy change and the vibration amplitude deviating from the equilibrium position can be estimated by a simplified model.

As shown in Figure 3.20, assuming the shapes of the sessile drop are sphere caps before and after the vibration, the vibration changes the drop height  $h$ . We assume the sessile drop to be in spherical cap before and after the vibration and that vibration changes the drop height  $h$ , as shown in Figure 3.20. The surface free energy can be calculated as the volume of the drop should be a constant.

$$V = \pi h^3 \frac{2 + \cos \theta}{3(1 - \cos \theta)} \quad (3.1)$$

The free energy change is then:

$$\Delta G = \gamma_{lv} \Delta A_{lv} + (\gamma_{sl} - \gamma_{sv}) \Delta A_{sl} \quad (3.2)$$



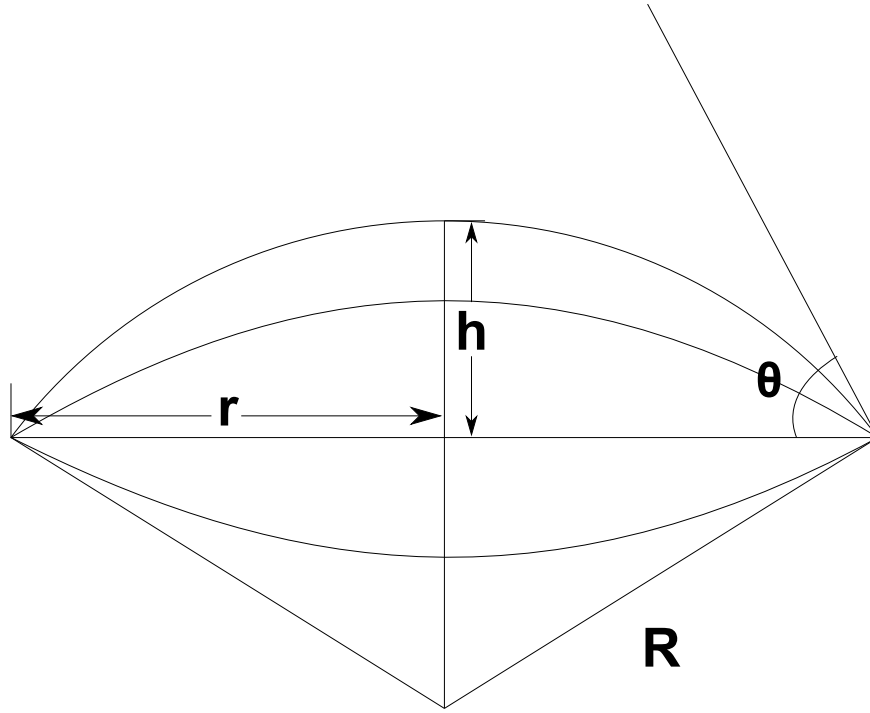


Figure 3.20: Schematic of free energy estimation by assuming the drop shape is a sphere cap.

Using the water drop on the PMMA as an example, with the equilibrium states,  $\theta_e = 64^\circ$ ,  $h = 1 \text{ cm}$ ,  $\gamma_{lv} = 72.7 \text{ mJ/m}^2$ , the free energy change with the vibration amplitude can be calculated and is shown in Figure 3.21

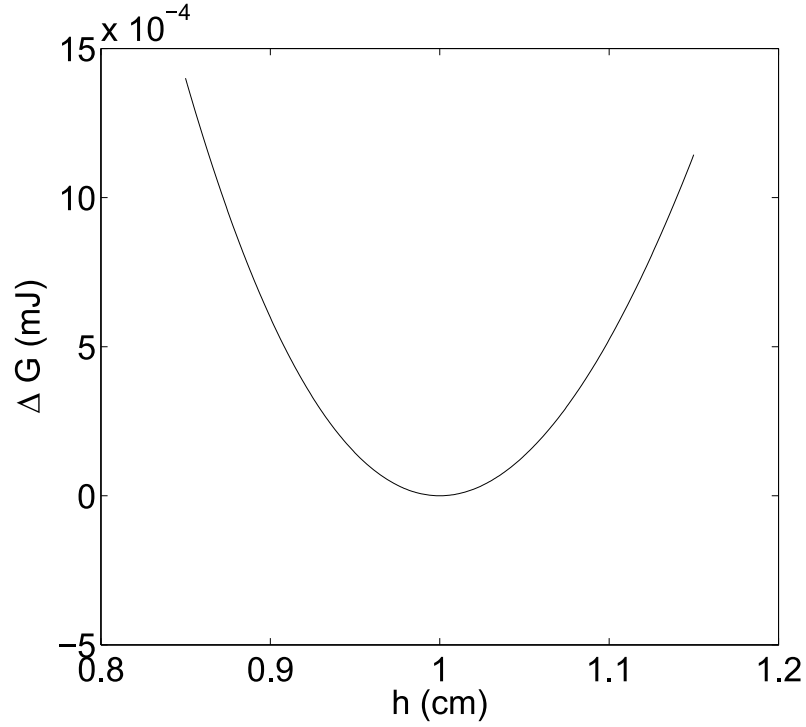


Figure 3.21: Estimated free energy as a function of drop height  $h$ .

The deformation caused by either enlarging or decreasing the drop contact area would change the system's free energy. If the free energy change is relatively small, the drop might be able to overcome one or several energy barriers in order to reach a metastable state. If increased free energy is sufficiently large to overcome all the energy barriers, drop will then be able to move back to the opposite direction from the deformation, more like a spring repelling to the external force. After much of the extra energy is consumed due to dissipation, and if that amount of energy is not sufficient enough to overcome energy barrier corresponding to the contact line position, the drop will settle in the equilibrium state that corresponds to the global minimum free energy or be trapped inside one of the metastable energy states.

We conclude that the vibration usually deforms the drop and provides the extra system

free energy. It is this extra free energy which could drive the drop to the opposite direction from the deformation, resulting in the drop landing onto one of the metastable energy or the global minimum states. If we consider the case for the PMMA and PnBMA. For the same amount of extra free energy, the energy barrier for PMMA is larger and more difficult to overcome. Hence, the drop on the PMMA surface can result more metastable states after the vibration with a higher amplitude.

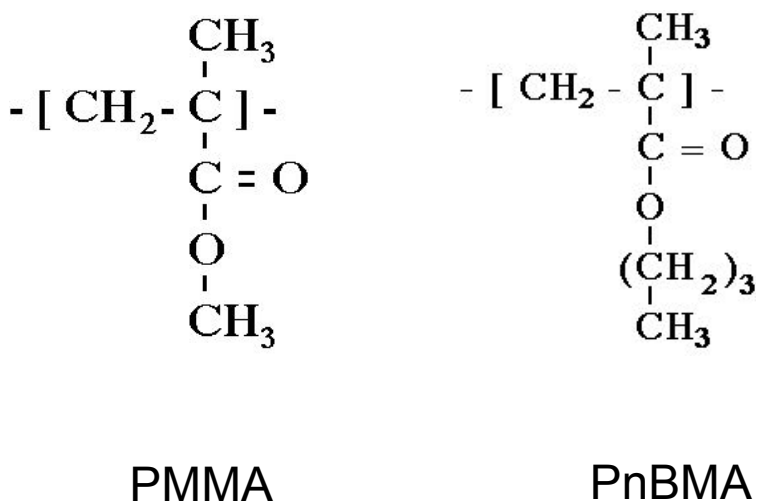


Figure 3.22: Structural formulas for PMMA and PnBMA.

### 3.3.5 Theoretical explanations using Neumann and Good's model

In this section, the vertical plate model of Neumann and Good's [33] is used to explain the experimental results. The vertical plate model was established by Neumann and Good in order to improve the cylindrical drop model from Johnson and Dette [32, 54]. By considering a vertical plate with an infinite length dipping into liquid, there is capillary rise along the wall on the vertical plate. When compared to the contact angle measured using the sessile drop method, the measurements of contact angle via the capillary rise is similar.

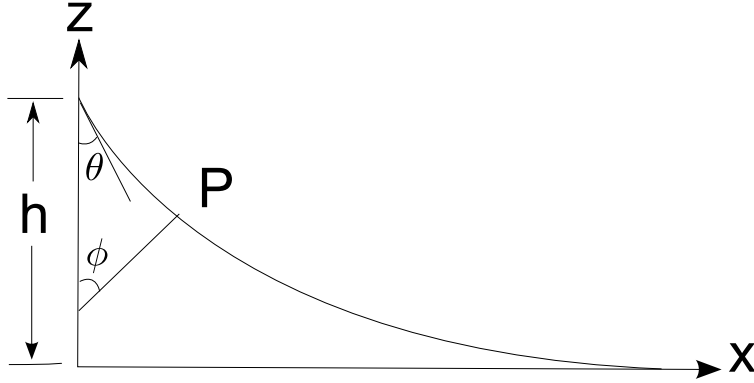


Figure 3.23: Schematic of the vertical plate model.

A schematic of the vertical plate model is shown in Figure 3.23. One advantage of the vertical plate model, is when the contact angle  $\theta = 90^\circ$ , the total energy of the system is 0. As Neumann and Good described in the paper, there are three different energy changes related to the capillary rise.

- $\Delta G_1$  comes from the variation of the solid-vapor interface to the solid-liquid interface, when the contact angle is less than  $90^\circ$ . For contact angle larger than  $90^\circ$ , the solid-liquid interface turns into the solid-vapor interface.
- $\Delta G_2$  is the term reflecting the energy variation of liquid-vapor interface due to changes in the liquid-vapor interfacial area.
- $\Delta G_3$  is the work done against the gravitational force.

The analytic expressions for these three energy terms are summarized below:

$$\Delta G_1 = -L\gamma_{lv} \cos \theta_e \sqrt{\frac{2\gamma_{lv}}{\Delta\rho g}} \sqrt{1 - \sin \theta} \quad (3.3)$$

$$\Delta G_2 + \Delta G_3 = \frac{1}{3}L\gamma_{lv} \sqrt{\frac{2\gamma_{lv}}{\Delta\rho g}} [2\sqrt{2} - (1 + \sin \theta)^{\frac{3}{2}}] \quad (3.4)$$

Where  $L$  is the unit length used for calculation with the direction perpendicular to the  $xz$  plane;  $\theta$  is the contact angle of the capillary rise;  $\theta_e$  is the intrinsic contact angles of the vertical plate;  $\gamma_{lv}$  is the liquid-vapor interfacial tension;  $\Delta\rho$  is the density difference between liquid and vapor;  $g$  is the gravitational acceleration. I used the above equations directly in my calculations.

In the calculation for the PMMA surface, the vertical plate is considered to consist of two types of horizontal strips with the same width of  $1^\circ$ . One type of strip having the equilibrium contact angle  $\theta_{e1} = 74^\circ$ , the advancing contact angle of PMMA surface. The other strip having the angle  $\theta_{e2} = 54^\circ$ , the receding contact angle of PMMA.  $\gamma_{lv}$  is the surface tension of water at  $25^\circ\text{C}$ ,  $\gamma_{lv} = 72.7 \text{ mJ/m}^2$ , and  $\Delta\rho = 1 \times 10^3 \text{ kg/m}^3$ ,  $g = 10 \text{ m/s}^2$

In the calculation for PnBMA surface, the vertical plate is considered to consist of two types of horizontal strips with different widths. One type of strip with the width of  $3^\circ$  having the equilibrium contact angle  $\theta_{e1} = 86^\circ$ . The advancing contact angle of PnBMA surface, the other strip with a width of  $1^\circ$  having the angle  $\theta_{e2} = 66^\circ$ , the receding contact angle of PnBMA. As discussed in the previous section, the surface of PnBMA has more coverage for the hydrophobic hydrocarbon group.

The results of my calculations are shown in Figure 3.24 for PMMA and Figure 3.25 for PnBMA. The free energy curve for PMMA is symmetrical and the global minimum free energy state lies between the receding and advancing angles. The curve for the PnBMA surface is asymmetrical and the global minimum free energy state moves towards the direction of the receding angle. From both figures, it can be found that the energy barrier increases when the metastable angles are near the global minimum. It is also note that the energy barrier vaule for the PMMA surface is about 2 – 3 times larger than that of the PnBMA surface. These results as calculated form the Neumann and Good's vertical plate model are

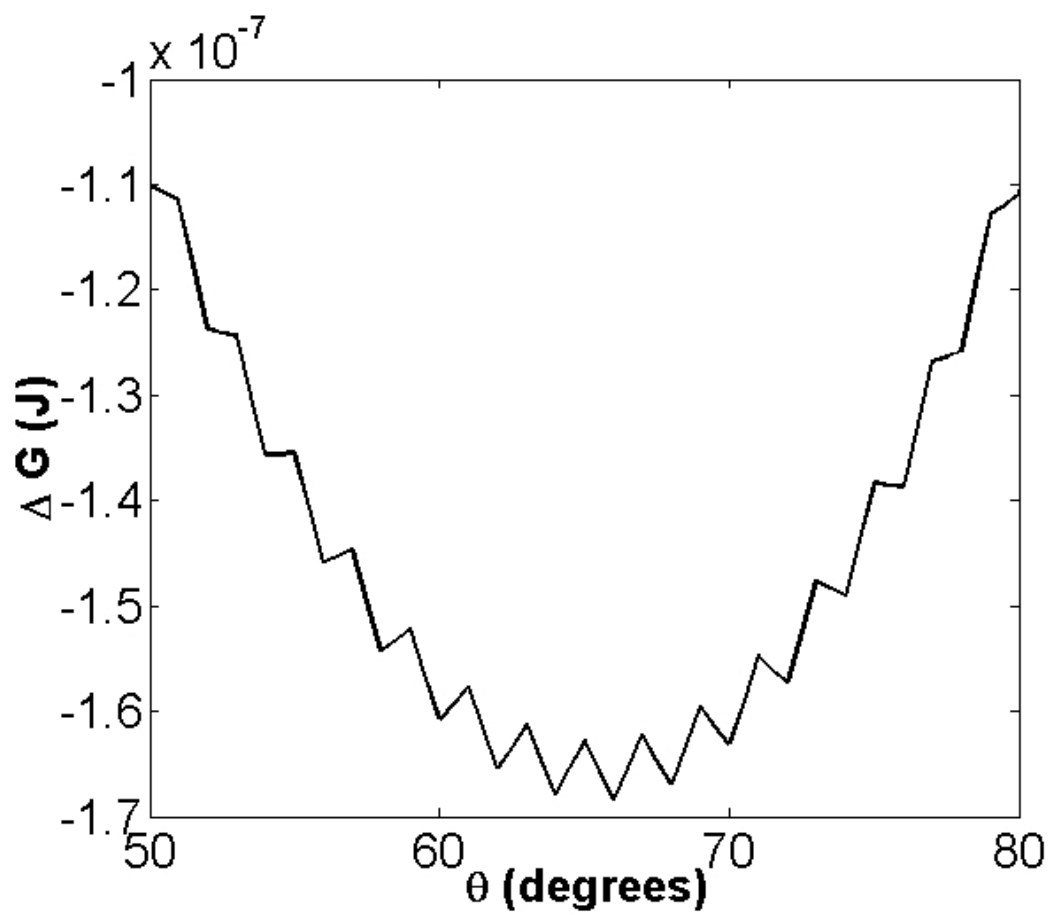


Figure 3.24: Calculated free energy curve for PMMA surface.

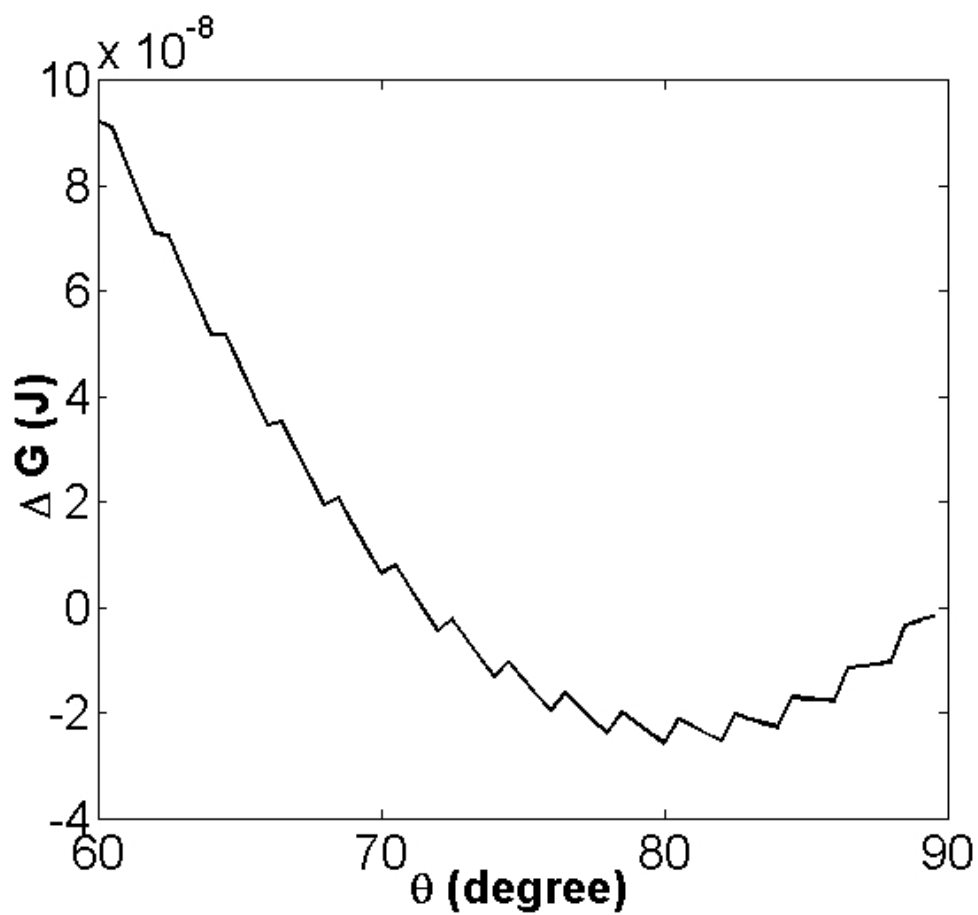


Figure 3.25: Calculated free energy curve for PnBMA surface.

consistent with my experimental results.

These calculated results provide a better understanding to the thermodynamics of contact angles with the context of my PMMA and PnBMA surfaces. For example, the equilibrium angles employed to construct the PMMA free energy curve are  $74^\circ$  and  $54^\circ$  for the two different types of strips, while those for the PnBMA surface are  $86^\circ$  and  $66^\circ$ . From the calculated free energy curve of the PMMA surface in Figure 3.24, there exist many metastable contact angles. The maximum metastable angle corresponds to  $74^\circ$  and the minimum metastable angle is  $54^\circ$ . Since real surface should contain some degree of impurities, the majority of its surface components should also be low energy. Therefore, the largest angle ( $74^\circ$ ) should reflect the hypothetical anticipated solid surface for the low energy component, while that  $54^\circ$  would be for those hypothetical higher energy component on the surface such as impurity. Therefore, the largest contact angles from the metastable angles should reflect the anticipated solid surface if we are to use Young's equation for the determination of solid surface tensions. This angle is the advancing contact angle  $\theta_a$ . The minimum angle is the receding angle but it is of no use for the determination of the anticipated solid surface tension.

There also exist many metastable contact angles including the contact angle that corresponds to the global minimum of the system. For the case of the PMMA surface in Figure 3.24, this is the equilibrium angle of they system  $\theta_{ES}$  and is about  $66^\circ$ . This is the contact angle that many researchers attempted to obtain by means of the acoustic vibration. However, even if we are able to obtain this value, there is no use of this angle in conjunction with Young's equation for the determination of the anticipated solid surface tensions.

$$\theta_{ES} \neq \theta_Y$$

Similar interpretation can also be obtained from the results for the PnBMA surface in Figure 3.25 We conclude that the advancing contact angle is a very good approximation of



the  $\theta_Y$  in Young's equation. Attempts to include  $\theta_{ES}$  in Young's equation for the calculation of the anticipated solid surface tension can be misleading.

### 3.4 Conclusions

Experiments have been carried out by using a loudspeaker with an amplifier to generate excitations to the water drop on solid surfaces. With the aid of a high speed camera and software, instantaneous contact angles for the entire vibration cycles were recorded and calculated. Metastable contact angles have been successfully observed on both PMMA and PnBMA solid surfaces by careful controlling of the vibration amplitude. After plotting the time dependence of contact angles, their responds to the acoustic vibration can be clearly observed.

As predicted by the theoretical model and some experimental studies of other researchers, the higher vibration amplitude will increase the possibility of overcoming the energy barrier. The global minimum energy states can also be obtained with sufficient vibration.

By comparing the time dependence of the contact angles for PMMA and PnBMA solid surfaces, it is interesting to find that there exists possibilities that water drop on PMMA surface can jump from low energy states to high energy states when the vibration amplitude is large. This inconsistency of the two polymer surfaces has been carefully analyzed. It turns out that instead of the early interpretation that the PMMA surface has lower metastable energy barrier and easy to jump randomly, the PMMA surface has higher metastable energy barrier which can sustain their position at high energy state.

We conclude that the advancing contact angle is a very good approximation of the  $\theta_Y$  in Young's equation. Attempts to include  $\theta_{ES}$  in Young's equation for the calculation of the anticipated solid surface tension can be misleading.

# Chapter 4

## Experimental and Theoretical Investigations to Droplet Impact onto Solid Surfaces

### 4.1 Introduction

The studies of droplet impact onto solid surfaces are of great importance to many technical applications, such as metal solidification [93, 94], spray coating, spray cooling [95] and jet-ink printing [96, 97]. While some researchers have more interests in impacting processes involving heat transfer, such as molten metal drop solidification [93, 94] and droplets impacting onto hot surfaces [98], fundamental understanding of droplet impacting process at room temperature is far from completed and attract attention from many researchers.

The fundamental research on droplet impact includes three main aspects:

- Numerical simulations. Numerical studies of drop impact mainly focus on solving the hydrodynamic equations (i.e. Navier–Stokes equations ) numerically. Different numerical approaches have been used for the simulation, including finite difference method [99], finite element method (FEM) [100], lattice-Boltzmann methods (LBM) [101, 102], and molecular dynamics (MD) [103, 104].
- Analytical studies. Simplified models as well as assumptions are established to provide the approximate predictions analytically [105, 106, 107, 108, 109, 110, 111]. Research interest in this aspect is the precise prediction of the

maximum spreading diameter  $D_{max}$ , which describes the largest spreading area the droplet can cover after impacting on a solid surface. The dimensionless number maximum spreading ratio  $\beta_{max}$ , results from normalizing  $D_{max}$  with the initial droplet diameter  $D_0$ , is more often used in the literature [93, 109, 108, 110, 111]. More details will be given in the next subsection.

- Experiments. Considering that the impact of droplets onto solid surfaces is a dynamic process having small time scales, experimental studies involve imaging the impacting process with the aid of a high speed video camera.

#### 4.1.1 Analytical models for droplet impact

Numerical simulations have their advantage of providing detailed physic properties, such as temperature, pressure and velocity for the entire impacting process. However, the simulations require professional programming skills and long computational time. To provide a simple estimation of maximum spreading ratio  $\beta_{max}$ , several analytical models have been developed [105, 106, 107, 108, 109, 110, 111].

Almost all the analytical models include two dimensionless parameters: Reynolds number ( $Re = \rho u D / \mu$ ) and Weber number ( $We = \rho u^2 D / \gamma_{lv}$ ). Here  $\rho$  is the liquid density,  $u$  is the impacting velocity,  $D$  is the drop diameter,  $\mu$  is the liquid viscosity and  $\gamma_{lv}$  is the liquid-vapor interfacial tension. The contact angle  $\theta$  is also of significant importance for the models as  $\theta$  relates the interfacial tensions through Young's equation.

In the works of Kendall and Rohsenow [105], Bechtel et al. [106] and Kim et al. [107], they assume the geometry of the deforming droplet, and obtained the simplified differential equations to describe the droplet impacting dynamics. They all utilize variational principle instead of Navier-Stokes equations for the hydrodynamics. However, different approaches

are applied for wetting and viscous effect for the drop dynamics.

In the model of Roisman [108] et al, the behaviour of drop is simplified by models with different geometries for each step after the impact. Analytical solution was provided by considering the conservation of mass, momentum and energy. In this model, inertia, surface tension, viscous dissipation, and the effect of wettability via contact angle were considered.

Some models even avoid the analysis of hydrodynamics for the droplet behaviour. These models utilize the energy conservation principle to analyze the initial state and the state when the drop is at its maximum spread. Bennet and Poulikakos [112] examined the model of Jones [113], Collings [114] et al., Chandra and Avedisian [109] and Madejski [93] for predicting  $\beta_{max}$ . It was concluded that the first two models were oversimplified and failed to predict  $\beta_{max}$ . The models of Chandra and Avedisian and Madejski showed promise and were included in his own model. The reason was due to the fact that these two models provide good estimation of viscous energy dissipation as well as surface energy.

In the recent study of Ukiwe and Kwok [115], the theoretical prediction for  $\beta_{max}$  from models of Madejski [93], Roisman et al. [108], Kurabayashi-Yang [111] and Pasandideh-Fard [110] et al. have been compared. They concluded that the Pasandideh-Fard model provided the best estimation of the experimental data for  $\beta_{max}$ . This model was then modified to include different surface energy terms, resulting in a new model.

#### 4.1.2 The effect of contact angle selection in the literature

Analytical models for the effect of contact line and capillary force on drop spreading have been completed by Haley et al. [116] and Hocking et al. [117]. The analytical models from Madejski [93] and Bechtel et al. [106] neglected the effect of contact angles and led to poor agreements with the experimental results. Fukai et al. suggested that at the beginning of the

impact, the droplet behavior is mainly controlled by initial impacting velocity and inertial force. After the mechanical energy is released due to the friction (by the viscous force) and outside droplet (with the solid surface), the capillary force becomes more important [118].

Other models from Chandra et al. [109] and Pasandideh-Fard et al. [110] employed directly measured experimental contact values. However, as discussed in the previous chapter of this thesis, the measurements of contact angle is complicated and may lead to inaccurate prediction if the contact angle is not measured with extreme experimental care.

The experimental study of Ukiwe and Kwok [115] were carried out on well prepared polymer surfaces. The contact angle value used in their analytical model were from the well-characterization completed by Kwok et al. [67, 68]. Thus the experimental data and the model prediction have good agreement when comparing with other models. The apparent defect for this work is that the energy dissipation term contributed from the contact angle hysteresis has been neglected.

In this work, Ukiwe's model of predicting the maximum spreading ratio  $\beta_{max}$  has been improved by adding an energy dissipation term contributed by the contact angle hysteresis. In addition, the minimum spreading ratio  $\beta_{min}$ , the spreading ratio of droplet during the first recoil, has been predicted and compared with the experimental data.

## 4.2 Experimental methods and procedures

### 4.2.1 Polymer surfaces preparation

Microscopic slides were cut into 2.5 *cm* by 2.5 *cm* square pieces before cleaning in acetone ( $\geq 99.5\%$ , Sigma-Aldrich) under sonication for 10 *min*. Square slides were then rinsed with deionized ultrafiltered (DIUF, from Fisher Scientific ) water and dried in the oven at 200 °C for 2 *hr*. These were used as substrates after they cooled off to room temperature. Two dif-

ferent polymer solutions were prepared by dissolving PMMA ( $M_w = 350,000$ , purity  $\geq 95\%$ , Sigma-Aldrich) powder and PnBMA ( $\eta = 0.5$ , purity  $\geq 95\%$ ,  $M_w = 180,000$  Polyscience) powder into chloroform ( $\geq 99.8\%$ , Sigma-Aldrich) respectively with the same weight percentage of 1%. Polymer films were then prepared by spin-coating the polymer solutions onto glass substrates using a spin-coater (Model WS-400B-6NPP-LITE, Laurell inc.) with the maximum spinning speed of 3000 *rpm*.

#### 4.2.2 Droplet impact experiments

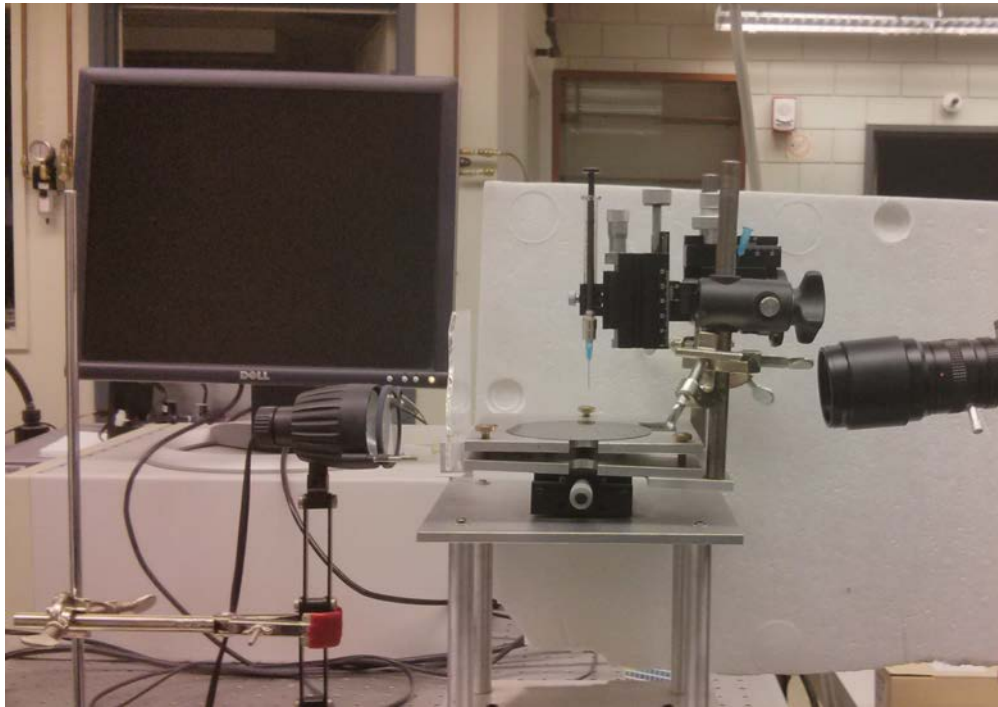


Figure 4.1: Photo of the setup for droplet impacting experiment.

Figure 4.1 and 4.2 show the experimental setup for the droplet impact experiments. DIUF water was the only testing liquid. All equipments were set up on a vibration free table to minimize the environmental interference, although a metastable contact angle measurements have been setup by using loudspeakers. Water droplets were generated from the tip of a 25

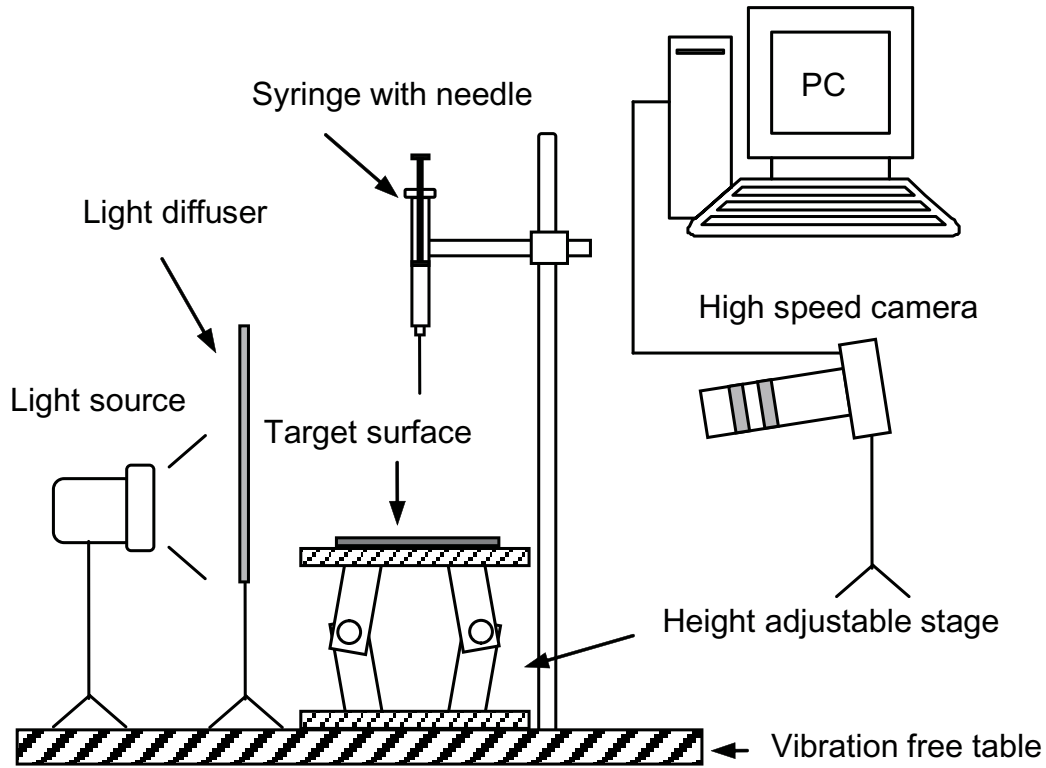


Figure 4.2: Schematic of the setup for droplet impacting experiment.

G stainless steel needle by using a 1 *ml* glass syringe (Hamilton). Droplet size (2.3 *mm*) was calculated by weighting a fixed amount of droplets with a digital balance. The impacting velocity of the droplets was controlled by adjusting the impacting height with the aid of a height adjustable stage. A high speed camera (DRS inc., Lightning RDT 16000 ) with a zoom lens was used to capture the motion of droplets. The camera was positioned at an angle of inclination of approximately  $10^\circ$  with a fixed distance of approximately 50 *cm* away from the testing solid surface. Illumination was provided by a combination setup using a floodlight and a light diffuser. Images were taken at 2500 frames per second (i.e., a 0.4 *ms* interval between each frame). The Sequence of these images was recorded by a computer via

a video capture card. A  $256 \times 204$  image resolution was selected because of the limitation of the video capture rate under a frame rate of 2500 frames per second.

#### 4.2.3 Contact angle measurements

The wettability of polymer surfaces were characterized by measuring the advancing and receding contact angles. The experimental setup was similar to droplet impacting experiment where the needle tip was fixed at several millimeters above the polymer surface. The angle of camera was also adjusted to a small inclination so that very small part of the reflection can be seen and be used to determine the contact line from image. The advancing angle measurements started with the deposit of a small sessile drop of DIUF water on the testing surface. A needle tip was then pierced into the sessile drop at the very top and more water was then injected into the droplet from the glass syringe to cause the contact line to advance. The rate of water supply was slow and roughly constant so as to minimize vibration. The measurements of receding angle were based on the same setup as the advancing but instead of injecting water, water was sucked back into the syringe to cause the three phase contact line to recede. Pictures of the sessile drop were taken successively at intervals of 10 ms during the advancing/receding process.

Contact angles were then measured from the drop profile by using the automated polynomial fitting method, which is described in the previous chapter.

#### 4.2.4 Spreading ratio calculation

As shown in Figure 4.3, the captured video clips including the drop impacting process were then cropped and transferred into Tagged Image File Format (.tiff) series by using the open software ImageJ. The droplet profiles were then calculated by Matlab with the Image



Processing Toolbox using the Sobel edge-finding method. The first image from the image sequence was used to determine the initial drop diameter, and the 14th image, approximately at the maximum spreading, was used to determine where the spreading width is measured. The spreading ratio for each frame of the image sequence is then calculated by Matlab. The program used to calculate is provided in Appendix C.

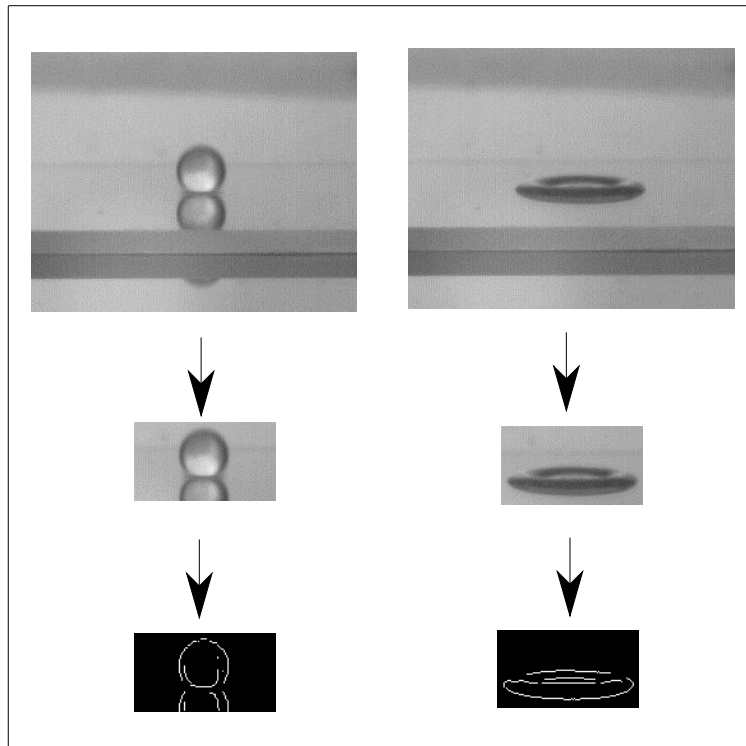


Figure 4.3: Procedures of image processing and the images used to calculate spreading ratio.

#### 4.2.5 Impacting velocities of the droplets

Four impact heights were selected for the droplet impacting experiments: 1.00 *cm*, 2.00 *cm*, 4.00 *cm*, 8.00 *cm*. The initial impacting velocities were then calculated by considering the buoyancy and drag forces.

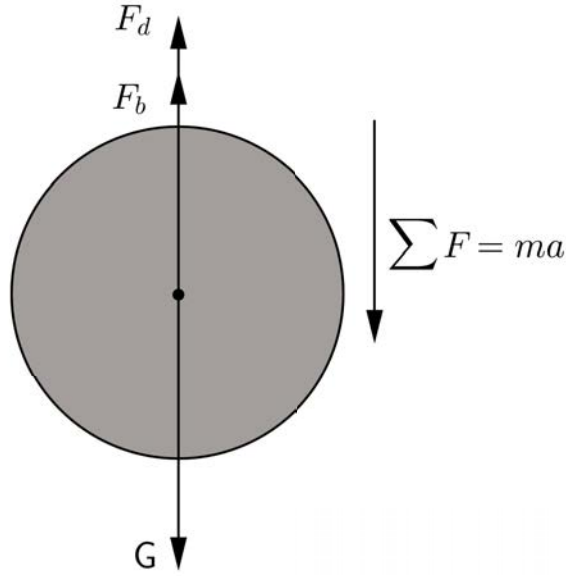


Figure 4.4: Forces applying on falling droplet.

Figure 4.4 is a schematic of drop falling through air with the forces that account for its motion. Assuming that force balance applying on the drop has not been reached (i.e., the droplet is still accelerating with  $a$  as the acceleration), the following equation can be directed from Newton's second law:

$$\sum F = G - F_b - F_d = ma = m \frac{dU}{dt} \quad (4.1)$$

Where  $U$  is the velocity of the drop,  $m$  is the mass of the drop,  $G$  is the gravitation:  $G = mg$ ,  $F_b$  is the buoyancy force:  $F_b = mg \frac{\rho_a}{\rho}$  ( $\rho_a$  is the mass density of air and  $\rho$  is the mass density of the liquid drop), and  $F_d$  is the drag force:  $F_d = bU$ , where  $b$  is drag coefficient defined as  $b = 6\pi\mu D_0/2$  ( $\mu$  is the viscosity of air and  $D_0$  is the droplet diameter). The differential equation (Equation 4.1) can be solved analytically and gives the impacting velocity  $U$  as:

$$U = \frac{mg}{b} \left(1 - \frac{\rho_a}{\rho}\right) (1 - e^{-bt/m}) \quad (4.2)$$

Table 4.1 summarize the calculation results of the impacting velocities of the droplet as well as some dimensionless numbers of the water droplet at impacting. In this table,  $Re$  is the Reynolds number:  $Re = \rho U_0 D_0 / \mu$ , and  $We$  is the Weber number:  $We = \rho U_0^2 D_0 / \gamma_{lv}$ , where  $\gamma_{lv}$  is the surface tension of liquid-vapor interfaces.

Table 4.1: Impact velocities and other dimensionless parameters for water droplets.

| impacting height $H$ (cm) | impacting velocity $U_0$ (m/s) | $Re$ | $We$ |
|---------------------------|--------------------------------|------|------|
| 1.00                      | 0.453                          | 1160 | 6.53 |
| 2.00                      | 0.646                          | 1660 | 13.3 |
| 4.00                      | 0.925                          | 2380 | 27.3 |
| 8.00                      | 1.33                           | 3420 | 56.6 |

### 4.3 Modelling for prediction of $\beta_{max}$ and $\beta_{min}$

#### 4.3.1 Energy dissipation during the advancing and receding process

Assuming that the difference between an equilibrium contact angle and advancing/receding contact angle is from the friction between solid-liquid interface. For an advancing process, using the force balance on the horizontal direction, yields,

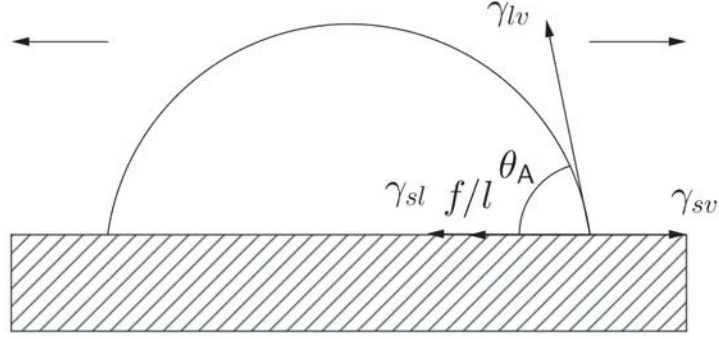


Figure 4.5: Force balance at three phase interfaces when droplet is advancing.

$$\gamma_{sv} - \gamma_{sl} - f/l = \gamma_{lv} \cos \theta_a \quad (4.3)$$

so,

$$f/l = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} \cos \theta_a \quad (4.4)$$

Substitute Young's equation:  $\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta_Y$ , into Equation 4.4 yields

$$f/l = (\cos \theta_Y - \cos \theta_a) \gamma_{lv} \quad (4.5)$$

the total energy dissipation is:

$$E_f = \int (f/l) l dx = \int f/l dA = \int (\cos \theta_Y - \cos \theta_a) \gamma_A dA \quad (4.6)$$

For the receding process, the total energy dissipation is

$$E_f = \int (\cos \theta_r - \cos \theta_Y) \gamma_A dA \quad (4.7)$$

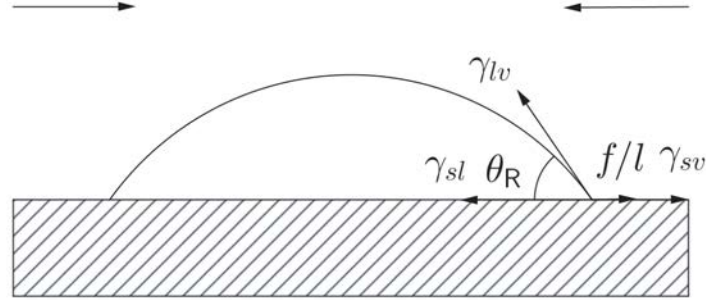


Figure 4.6: Force balance at three phase interfaces when droplet is receding.

#### 4.3.2 Ukiwe's model for predicting $\beta_{max}$

Ukiwe's model is based on the assumption that at the maximum spreading, the shape of the droplet is a flat plate on the solid surface,



Figure 4.7: Schematic of our old model for maximum spread.

Based on energy conservation, we obtain

$$\frac{1}{2}(\frac{1}{6}\rho\pi D_0^3)U_0^2 + \pi D_0^2\gamma_{lv} + \frac{\pi}{4}D_{max}^2\gamma_{sv} = \pi D_{max}h\gamma_{lv} + \frac{\pi}{4}D_{max}^2\gamma_{lv} + \frac{\pi}{4}D_{max}^2\gamma_{sl} + W_v \quad (4.8)$$

where  $W_v$  is the work done against viscosity [110]

$$W_v = \frac{\pi}{3}\rho U_0 D_0 D_{max}^2 \frac{1}{\sqrt{Re}} \quad (4.9)$$

After using Young's equation, we obtain

$$\frac{1}{12}\rho\pi D_0^3 U_0^2 + \pi D_0^2\gamma_{lv} = \pi D_{max}h\gamma_{lv} + \frac{\pi}{4}D_{max}^2(1 - \cos\theta_Y)\gamma_{lv} + \frac{\pi}{3}\rho U_0 D_0 D_{max}^2 \frac{1}{\sqrt{Re}} \quad (4.10)$$

Equation 4.10 can be written as

$$(We + 12)\beta_{max} = 8 + \beta_{max}^3[3(1 - \cos\theta_Y) + 4\frac{We}{\sqrt{Re}}] \quad (4.11)$$

#### 4.3.3 Modification of Ukiwe's model with the $E_f$ term

From the moment droplet when starts to contact the solid surface to the moment when it reaches its maximum spread , the total energy dissipation from friction is

$$E_f = \int_0^{\pi D_{max}^2/4} (\cos\theta_Y - \cos\theta_a)\gamma_{lv} dA = \frac{\pi}{4}D_{max}^2(\cos\theta_Y - \cos\theta_a)\gamma_{lv} \quad (4.12)$$

and using the the energy conservation principle,

$$\begin{aligned} \frac{1}{12}\rho\pi D_0^3 U_0^2 + \pi D_0^2\gamma_{lv} &= \pi D_{max}h\gamma_{lv} + \frac{\pi}{4}D_{max}^2(1 - \cos\theta_Y)\gamma_{lv} \\ &+ \frac{\pi}{3}\rho D_0 U_0 D_{max}^2 \frac{1}{\sqrt{Re}} + \frac{\pi}{4}D_{max}^2(\cos\theta_Y - \cos\theta_a)\gamma_{lv} \end{aligned} \quad (4.13)$$

Equation 4.13 can be written as:

$$(We + 12)\beta_{max} = 8 + \beta_{max}^3[3(1 - \cos\theta_a) + 4\frac{We}{\sqrt{Re}}] \quad (4.14)$$

#### 4.3.4 Models for predicting $\beta_{min}$

After the maximum spreading diameter, the droplet will rebound till it reaches its minimum spreading diameter. The shape of the droplet at this point depends on both hydrodynamics and the Laplace equation of capillarity and is very difficult to model.

In my model, I assume that the shape of the droplet at the minimum spreading diameter is between the shape of a cylinder and a cone as shown in Figure 4.8

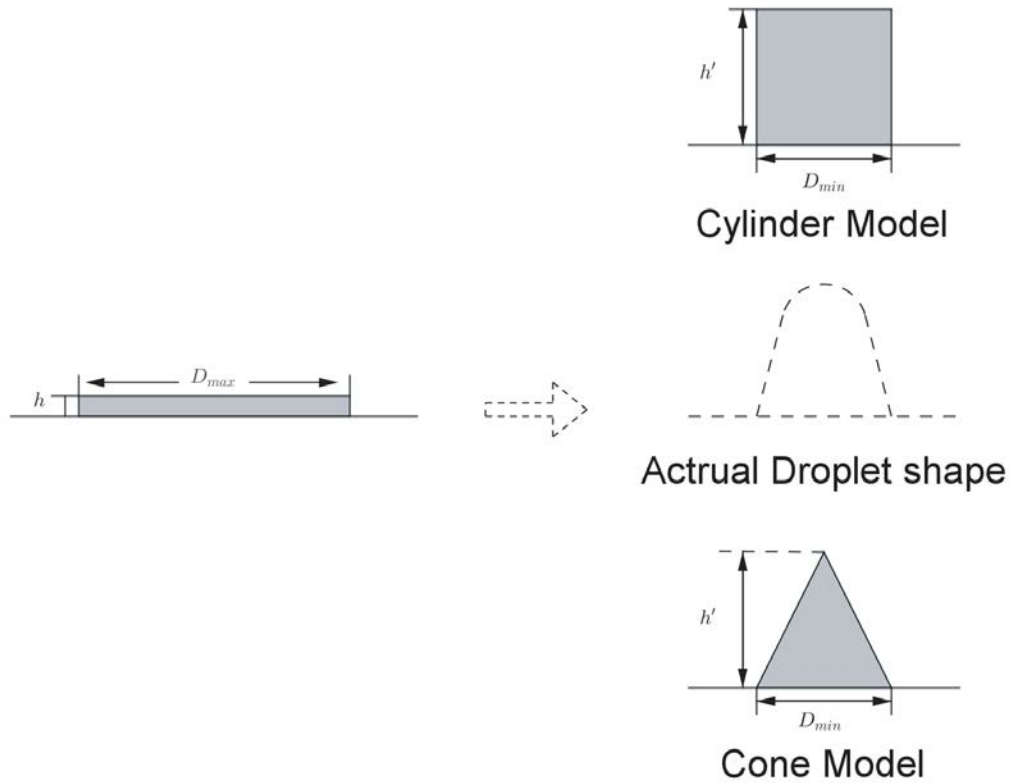


Figure 4.8: Two simplified models for actual droplet at minimum spread.

For the cylinder model, as presented in Figure 4.8,  $D_{min}$  is the minimum spreading diameter for the droplet,  $h'$  is the cylinder height at the minimum spread.

From energy conservation, we obtain

$$\begin{aligned} \frac{\pi}{4}\gamma_{sl}D_{max}^2 + \frac{\pi}{4}\gamma_{lv}D_{max}^2 + \pi D_{max}h\gamma_{lv} &= \frac{\pi}{4}\gamma_{sv}(D_{max}^2 - D_{min}^2) \\ + \frac{\pi}{4}\gamma_{lv}D_{min}^2 + \frac{\pi}{4}\gamma_{lv}D_{min}^2 + \pi D_{min}h'\gamma_{lv} &+ W_g + W_v + E_f \end{aligned} \quad (4.15)$$

where

$$h = \frac{\pi D_0^3/6}{\pi D_{max}^2/4} = \frac{2D_0}{3\beta_{max}^2} \quad (4.16)$$

$$h' = \frac{\pi D_0^3/6}{\pi D_{min}^2/4} = \frac{2D_0}{3\beta_{min}^2} \quad (4.17)$$

$W_g$  is the work done against gravity force:

$$W_g = m_0 g \left( \frac{h'}{2} - \frac{h}{2} \right) = \frac{\pi}{18} g D_0^4 \left( \frac{1}{\beta_{min}^2} - \frac{1}{\beta_{max}^2} \right) \quad (4.18)$$

$W_v$  is the work done against viscosity [109]

$$W_v \approx \mu \left( \frac{U}{L} \right) \Omega t_c \quad (4.19)$$

Where  $\Omega$  is the volume of the liquid,  $t_c$  is the time taken,  $\mu$  is the liquid viscosity,  $U$  is the velocity of the liquid,  $L$  is the dimension of the liquid. In my experiment with water droplets,  $W_v$  is negligible, as its value is very small compared to  $W_g$  and  $E_f$ .  $E_f$  can be obtained from Equation 4.7:

$$E_f = \int_{D_{min}^2/4}^{D_{max}^2/4} (\cos \theta_r - \cos \theta_Y) \gamma_{lv} dA = \frac{\pi}{4} (D_{max}^2 - D_{min}^2) (\cos \theta_r - \cos \theta_Y) \quad (4.20)$$

Substituting Equations 4.16, 4.17, 4.18, 4.20 and Young's equation (Equation 2.7) into Equation 4.15, yields,

$$\begin{aligned} &\frac{\pi}{4}\gamma_{lv}D_0^2(\beta_{max}^2 - \beta_{min}^2)(1 - \cos \theta_r) + \\ &\frac{2\pi}{3}D_0^2\gamma_{lv}\left(\frac{1}{\beta_{max}} - \frac{1}{\beta_{min}}\right) + \frac{\pi}{18}gD_0^4\left(\frac{1}{\beta_{max}^2} - \frac{1}{\beta_{min}^2}\right) = 0 \end{aligned} \quad (4.21)$$



In the cone model, as presented in Figure 4.8,  $D_{min}$  is the minimum spreading diameter for the droplet,  $h'$  is the cone height at the minimum spread. From energy conservation:

$$\begin{aligned} \frac{\pi}{4}\gamma_{sl}D_{max}^2 + \frac{\pi}{4}\gamma_{lv}D_{max}^2 + \pi D_{max}h\gamma_{lv} &= \frac{\pi}{4}\gamma_{sv}(D_{max}^2 - D_{min}^2) + \\ \frac{\pi}{4}\gamma_{sl}D_{min}^2 + \frac{\pi}{4}\gamma_{lv}D_{min}^2 + \frac{\pi}{2}\gamma_{lv}D_{min}\sqrt{\frac{D_{min}^2}{4} + h'^2} &+ W_g + W_v + E_f \end{aligned} \quad (4.22)$$

where

$$h' = 3\frac{\pi D_0^3/6}{\pi D_{min}^2/4} = \frac{2D_0}{\beta_{min}^2} \quad (4.23)$$

$W_g$  is the work done against gravity force:

$$W_g = m_0g(0.206h' - 0.5h) = \frac{\pi}{6}gD_0^4\left(\frac{0.413}{\beta_{min}^2} - \frac{1}{3\beta_{max}^3}\right) \quad (4.24)$$

Substituting Equations 4.16, 4.23, 4.24, 4.20 and Young's equation (Equation 2.7) into Equation 4.22, yields,

$$\begin{aligned} \frac{\pi}{4}\gamma_{lv}D_0^2\beta_{max}^2 + \frac{2\pi D_0^2\gamma_{lv}}{3\beta_{max}} - \frac{\pi}{4}\gamma_{lv}D_0^2\cos\theta_r(\beta_{max}^2 - \beta_{min}^2) - \\ \frac{\pi}{4}\gamma_{lv}D_0^2\beta_{min}\sqrt{\beta_{min}^2 + \frac{16}{\beta_{min}^4}} - \frac{\pi}{6}gD_0^4\left(\frac{0.413}{\beta_{min}^2} - \frac{1}{3\beta_{max}^3}\right) = 0 \end{aligned} \quad (4.25)$$

## 4.4 Results and discussion

### 4.4.1 Contact angle measurements

The contact angle measurements and pictures are shown in Figure 4.9 and 4.10. The maximum value from the plot of advancing drop is the advancing contact angle, while the minimum value from the plot of receding drop is the receding contact angle.

For the PMMA surface, the advancing and receding angles are, respectively,  $\theta_a = 74^\circ$  and  $\theta_r = 54^\circ$ . For the PnBMA surface, the advancing and receding angles are, respectively,  $\theta_a = 86^\circ$  and  $\theta_r = 66^\circ$ .

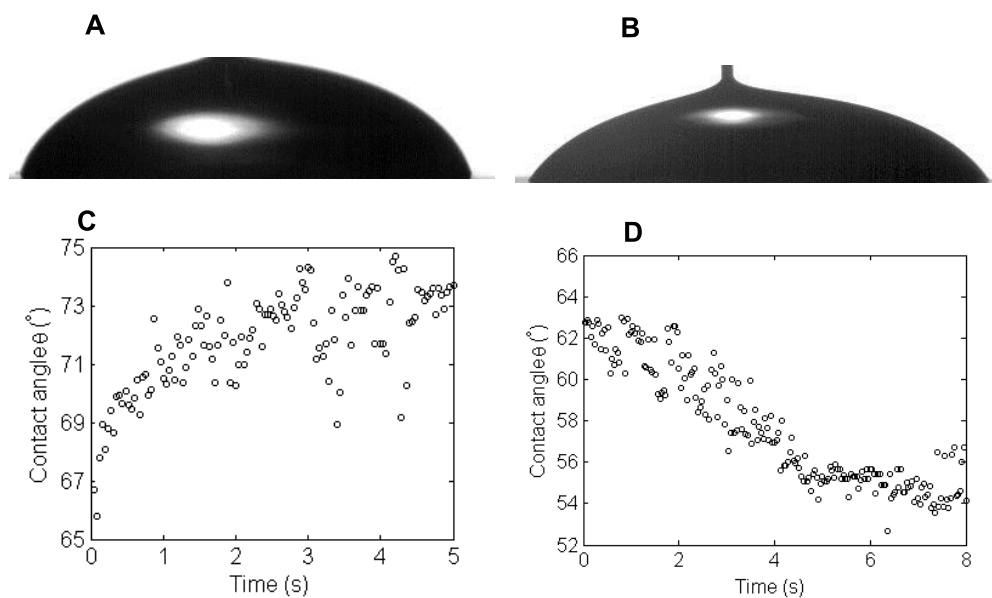


Figure 4.9: PMMA contact angle measurements, A: picture of the advancing drop; B: picture of the receding drop; C: contact angle value of the advancing drop; D: contact angle value of the receding drop.

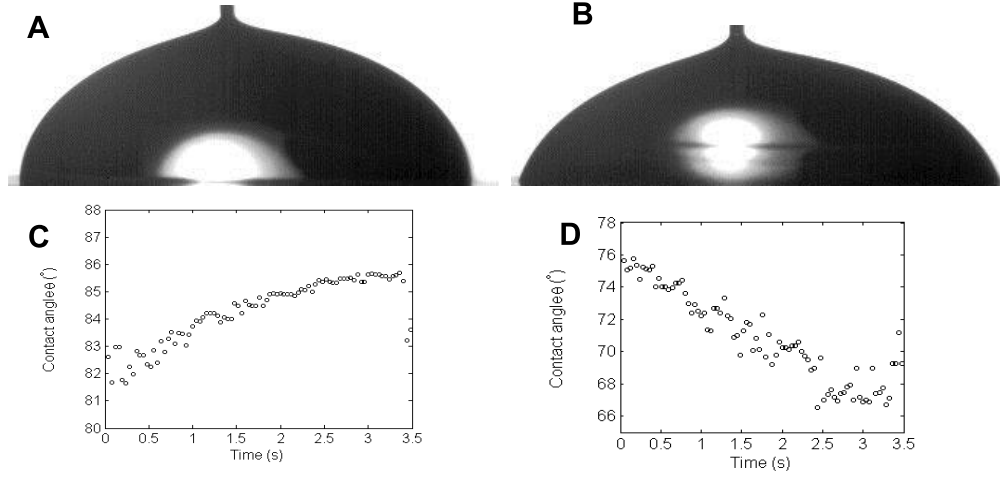


Figure 4.10: PnBMA contact angle measurements, A: picture of the advancing drop; B: picture of the receding drop; C: contact angle value of the advancing drop; D: contact angle value of the receding drop.

#### 4.4.2 Droplet impacting dynamics

Images of water droplet impacting onto PMMA and PnBMA solid surfaces from 4 different selected impacting height (1 cm, 2 cm, 4 cm and 8 cm) are summarized in Table 4.2 and 4.3. The droplet collision dynamics can be described with three main steps: After the droplet coming into contact with the solid surface, it quickly spreads to a maximum diameter on the solid surface and then recoils to a maximum height, which also brings a minimum spreading diameter. By comparing sequential images between two different polymer surfaces with different wettabilities, the dynamics of droplets impacting onto the two polymer surfaces show more difference in the recoiling process than spreading.

To provide a clear description of the impacting dynamics, the instantaneous droplet spreading ratio is plotted in Figure 4.11. By comparing the maximum spreading ratio in Figure 4.11, it can be found that droplets reach their maximum spreading ratio  $\beta_{max}$  at

Table 4.2: Images of water droplets impacting on PMMA and PnBMA surfaces from the impacting heights of 1 *cm* and 2 *cm*.

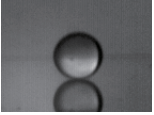
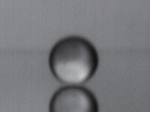
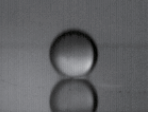
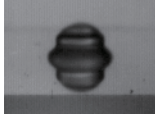
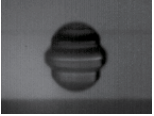
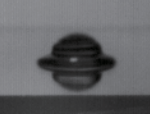
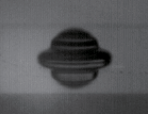
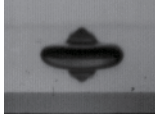
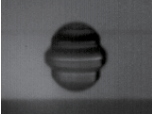
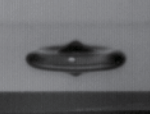
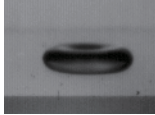
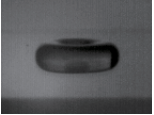
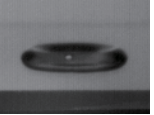
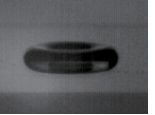
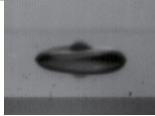
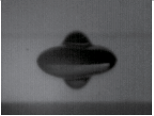
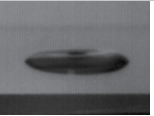
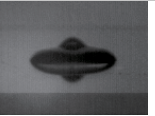
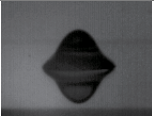
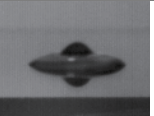
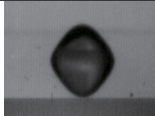
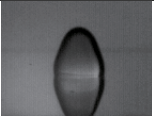
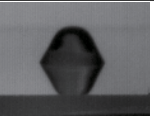
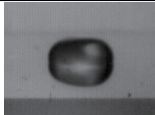
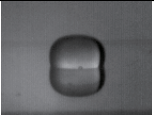
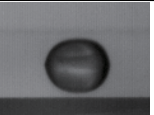
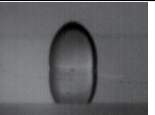
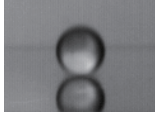
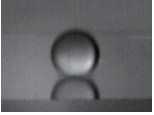
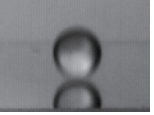
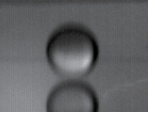
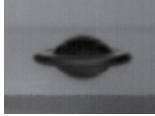
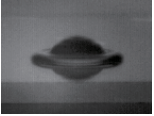
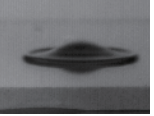
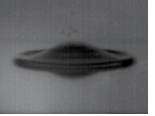
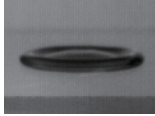
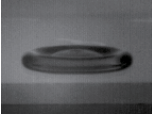
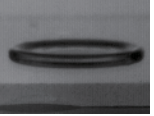
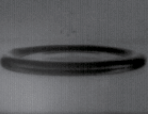
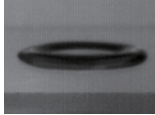
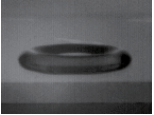
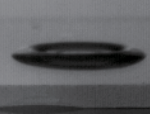
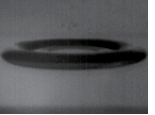
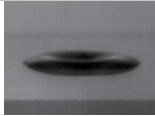
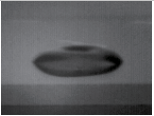
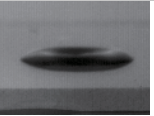
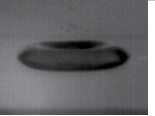
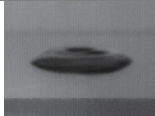
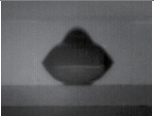
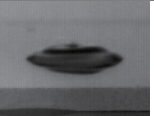
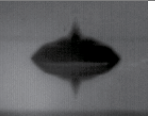
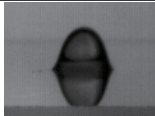
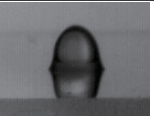
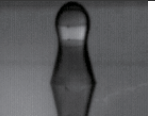
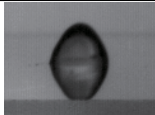
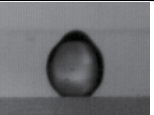
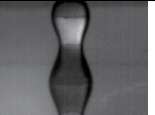
| Time<br>( <i>ms</i> ) | Height : 1 <i>cm</i>                                                                |                                                                                     | Height : 2 <i>cm</i>                                                                 |                                                                                       |
|-----------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
|                       | PMMA                                                                                | PnBMA                                                                               | PMMA                                                                                 | PnBMA                                                                                 |
| 0.0                   |    |    |    |    |
| 1.6                   |    |    |    |    |
| 3.2                   |   |   |   |   |
| 4.8                   |  |  |  |  |
| 8.0                   |  |  |  |  |
| 9.6                   |  |  |  |  |
| 14.4                  |  |  |  |  |
| 17.6                  |  |  |  |  |

Table 4.3: Images of water droplets impacting on PMMA and PnBMA surfaces from the impacting heights of 4 *cm* and 8 *cm*.

| Time<br>( <i>ms</i> ) | Height : 4 <i>cm</i>                                                                |                                                                                     | Height : 8 <i>cm</i>                                                                 |                                                                                       |
|-----------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
|                       | PMMA                                                                                | PnBMA                                                                               | PMMA                                                                                 | PnBMA                                                                                 |
| 0.0                   |    |    |    |    |
| 1.6                   |    |    |    |    |
| 3.2                   |   |   |   |   |
| 4.8                   |  |  |  |  |
| 8.0                   |  |  |  |  |
| 9.6                   |  |  |  |  |
| 14.4                  |  |  |  |  |
| 17.6                  |  |  |  |  |

approximately the same time. This is because of the small time interval of the spreading step. The differences of  $\beta_{max}$  for PMMA and PnBMA at the same impacting height of 1 cm, 2 cm and 4 cm suggest that surface properties affect  $\beta_{max}$  when the surface energy is comparable to the initial kinetic energy of the droplets. This is also suggested in the model for  $\beta_{max}$ . The initial kinetic energy will dominate the spreading process at high impacting velocities. The overlap of  $\beta_{max}$  for PMMA and PnBMA at the impacting height of 8 cm illustrate this.

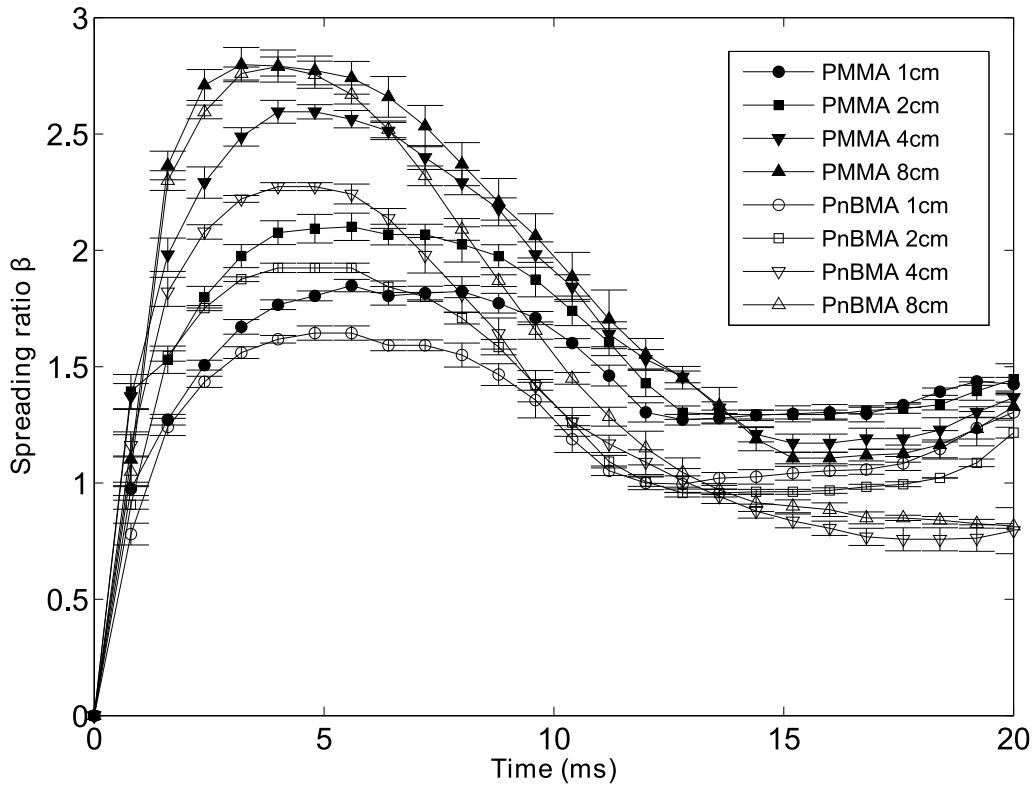


Figure 4.11: The spreading ratio of water droplet impacting onto PMMA and PnBMA solid surfaces from selected impacting heights of 1 cm, 2 cm, 4 cm and 8 cm versus the spreading time.

The recoiling process of the droplets are more difficult to compare because of the large differences in sessile droplet shape in this step. However, it is clear that surface properties are more sensitive in this process than the spreading. It can be found in Figure 4.11 that all the four minimum spreading ratio  $\beta_{min}$  for PMMA have larger values than their four values for PnBMA, while the same trend cannot be found for the maximum spreading ratio  $\beta_{max}$ .

#### 4.4.3 Comparison of model predictions with experimental data

The model prediction of Equation 4.14 for  $\beta_{max}$  together with our experimental data is plotted in Figure 4.12. The relative mean error of the model was calculated to be about 9.8% with a standard deviation of 6.1%. This is a better result when compared to Ukiwe's model [115] which yields an error of 11.3% with a standard deviation of 7.1% using with my experimental data.

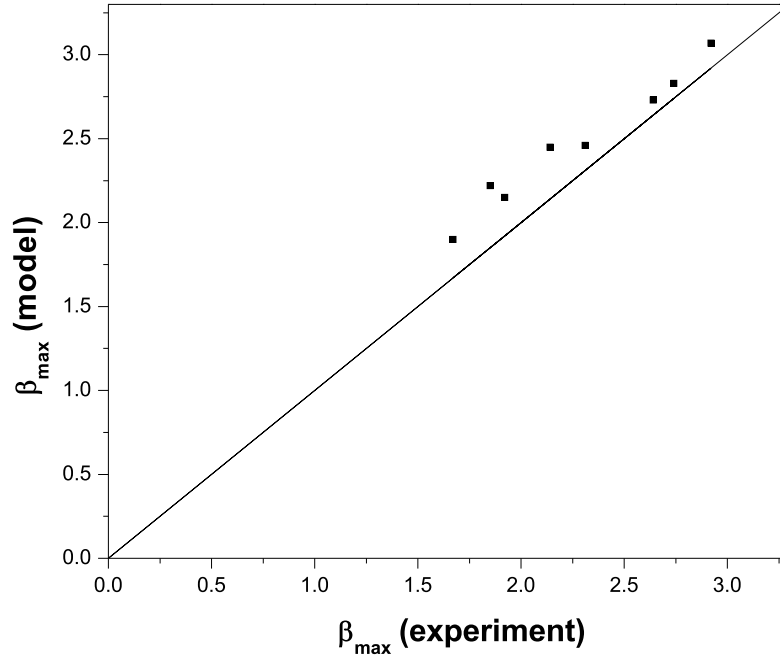


Figure 4.12: The comparison of experimental data for  $\beta_{\max}$  with the prediction from Equation 4.14.

In Ukiwe's paper, the mean error was claimed to be 5.09% with a standard deviation of 5.05%, which seems to be better when compared with our results. However, a large portion of his experimental data was collected with much larger impacting velocities. The high initial kinetic energy minimizes the effect of surface energy to  $\beta_{\max}$  and results in a small prediction error eventually.

Using the cylinder model for predicting the minimum spreading ratio  $\beta_{\min}$ . We found a prediction error to be about 11.1% with a standard deviation of 9.3%. Using the cone model, we found an error of about 4.1% with a standard deviation of 16.3%.



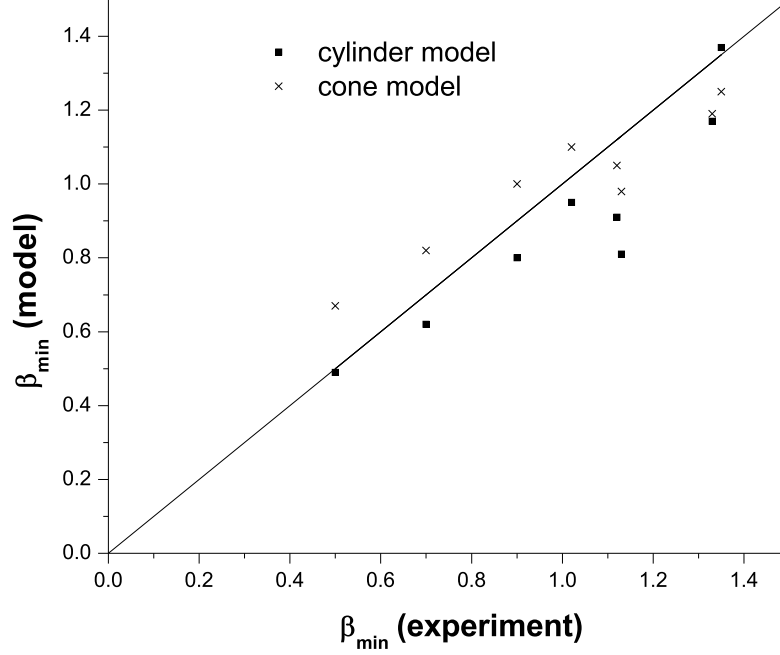


Figure 4.13: The comparison of experimental data for  $\beta_{min}$  with the prediction from Equation 4.21 for the cylinder model and Equation 4.25 for the cone model.

The main contribution to the prediction error can be summarized as follows:

- The energy loss term  $E_f$  in my model is based on the assumption that the work done by the frictional force is independent of the advancing or receding velocities of the droplet. As the droplet spreads and recoils during impacting within the 10 *ms*, energy loss is underestimated in my model without taking into account of the energy difference coming from the advancing/receding velocity.
- The droplet shape at either maximum or minimum spread was simplified in

my model. When droplet impacts onto a hydrophobic solid surface with a large impacting velocity, the shape of the droplet at the minimum spread can be substantially different from either a cylinder or a cone. In some cases, the droplet could bounce off the solid surface. The relatively larger standard deviation using the cone model could arise from the oversimplification of the shape of droplet impacting onto PnBMA from the height of 8 *cm*.

## 4.5 Conclusions

The model of Ukiwe and Kwok [115] for the prediction of the maximum spreading ratio has been modified with the introduction of the energy dissipation from the friction between solid and liquid interfaces. A model for the prediction of the minimum spreading ratio  $\beta_{min}$  has been established based on the energy conservation principle. In this model for  $\beta_{min}$ , the droplet shape at the minimum spread has been simplified with a cylinder model and a cone model. Experimental results have been obtained from the impact of water droplets (original diameters  $D_0 = 2.3mm$ ) and onto two carefully prepared polymer surfaces (PMMA and PnBMA) from four controlled impacting heights (1 *cm*, 2 *cm*, 4 *cm*, 8 *cm*). Observation of our experimental results also shows that drop impact dynamics is influenced by the initial energy of the droplet at impact, physical properties of the liquid droplets, and solid surface tensions. The surface properties play a more important role for the recoiling process than the spreading process. By comparing with the experimental data, the modified model yields good improvement in the determination of the maximum spreading diameter with a mean error of 9.8% with standard deviation of 6.1%. For the minimum spreading diameter, the cylinder model gives a mean error of 11.1% with a standard deviation of 9.3%, and the cone model gives a mean error of 4.1% with a standard deviation of 16.3%. However, the complications

involved in deriving the minimum spreading diameter remain largely unresolved since my model still underestimates the energy dissipation and the simplified cylinder and cone has their limitation in estimating the shape of actual droplets. These theoretical models are based on the general conditions of droplet impacting behaviors and can be used to interpret other experimental behaviors of droplet impact.

## Chapter 5

# Droplet Impact Experiments for Carbon/Polymer Composite

### 5.1 Introduction

Carbon materials with high surface area have been applied in various fields, including both industrial production and academic research. They can be used as adsorbent [119, 120], catalyst support [121, 122], and so on because of their low specific gravity, low manufacturing cost, chemical stability, good electrical conductivity. A carbon material with high surface area can be a carbon black, which is commercially available in large quantity, for example, Vulcan <sup>TM</sup>carbon (VC, Carbot). It also can be one kind of carbon nanotubes (CNTs) or mesoporous/nanoporous carbons, both of which have been widely and extensively studied in the past decades [123, 124, 125, 126, 127].

The composites of carbon material with polymers also received great interests from researcher. Taking carbon nanotubes(CNTs) as an example, because of their unique physical properties, including its high mechanical strength and elastic moduli [128, 129], good thermal conductivity [130, 131] and excellent conductivity [132, 133], researchers have been trying to embed carbon nanotubes into polymer matrix to reinforce the physical properties of the embedded polymer. It is reported by Ruan et al. [134] that the strain energy density of a polyethylene film was to increase by 150% with the addition of 1wt.% Multi-wall carbon nanotubes. Jia et al. [135] reported that the weight percentage of CNTs added into PMMA will affect the mechanical properties of the composites. Biercuk et al. [136] fabricated single-

walled carbon nanotubes(SWNTs)-epoxy composites and the thermal conductivity of the industrial epoxy was increased by 70% with only 1 *wt.%* SWNTs added into the epoxy. Carbon black-Nafion composites is also widely used in fuel cell [137, 138], while carbon black acts as the catalyst support and electron conductor, and Nafion acts as proton conductor.

However, the surface properties of carbon materials have not been completely investigated, particularly the surface wettability of high surface area carbons as carbon particles and porous carbon. This is mainly attributed to the variable valences of carbon atom, resulting that different functional groups can form on the surface of carbon materials, so the surface property of carbons can vary from hydrophilic to hydrophobic [139]. In the mean time, the surface properties of carbon materials are of great importance to their applications. For example, a superhydrophilic carbon with high surface area might be used as desiccant [140], while a superhydrophobic nanoporous carbon can be applied in the removal of spilled oil on water body [141]. Another very important usage of nanoporous carbons is to serve as catalyst support in low temperature fuel cells, e.g., polymer electrolyte membrane fuel cell (PEMFC), where the surface wetting property of carbons have to be balanced. A hydrophilic surface of carbon could retain water in the electrode, which is helpful if a PEMFC is running under a low humidity condition, since the retained water facilitates the transport of protons through the electrode and thus improve the performance of the PEMFC. However, a hydrophilic carbon surface can also make the electrodes flooded when a PEMFC is running at a high current density or under a high humidity condition. In this condition, a hydrophobic carbon surface is preferred, which accelerates the evaporation of water products and thus improves the performance of PEMFC.

The research difficulty of measuring the contact angles and surface properties of particles and porous materials also greatly affects the investigation into surface properties of carbon

materials. The difficulty lies on lacking of direct approach of the measurements and becoming even more complicated with the high surface heterogeneity in terms of the size and shape for particles and porous materials. As the direct measurements of contact angles is impossible and thus Young's equation is also not applicable, the capillary penetration method may be one of the mostly used approach to characterize the surface properties of particles and porous quantitatively [74, 75]. In the capillary penetration method, a microbalance is used to measure the capillary force of liquid penetrated into the particle packs or the porous materials. The surface tension is then calculated by so called Washburn equation [142]. However, this method has its disadvantage that there is a high possibility that the particle bed will collapsing during the early stage of liquid penetration.

Both experimental and theoretical studies of metastable and dynamic contact angles on heterogeneous but smooth polymer surfaces in the previous chapters provide better understandings to the contact angle hysteresis and the idea of characterizing the surface properties of carbon powders quantitatively by mixing them with the well characterized polymers with different weight ratios. The procedures developed in previous chapters for the droplet impact dynamics in terms of both the maximum spreading ratio  $\beta_{max}$  and the minimum spreading ratio  $\beta_{min}$  for different solid surfaces can also be used. The reasons that the impacting droplet method has been chosen instead of the direct contact angle measurements are that the increased surface heterogeneity of the mixture may rise the difficulty of the contact angle measurements and thus Young's equation is also inapplicable in this situation.

In this chapter, the surface wettabilities of two commercial carbons with high surface areas, CNTs and VC were characterized by using droplet impacting method. The dynamics of the droplets impacting onto carbon/polymer composites with different component ratio have been compared. The theoretical free energy model from Good and Neumann has also

been used to interpret the experimental results.

## 5.2 Experiments

### 5.2.1 Materials

Three different kinds of carbon/polymer composite were prepared as the targeting surface. They are CNTs/PMMA, VC/PMMA and VC/Nafion composite. The as prepared (AP) grade SWNTs purchased from Carbolex Inc., with purity from 50 to 70wt.% were purified by refluxing in 3mol/L HNO<sub>3</sub> (ACS grade, Aldrich) for 20hr. This purification method is from the work of Dai et al. [143]. The resulting suspension was then repetitively washed with Deionized ultrafiltered water (DIUF water), and then centrifuged until a neutral supernatant solution is obtained. The SWNTs in the sediment were then dried at 120°C before use. Poly(methyl methacrylate)(PMMA) powder ( $M_W = 350\,000$ ) was purchased from Aldrich. Vulcan Carbon was from Cabot and dried overnight at 120°C before use. Nafion from DuPont was purchased in the form of 5wt.% Nafion/alcohol stock solution.

### 5.2.2 Carbon/polymer composite film preparation

The suspensions were made by dissolving PMMA in chloroform ( $\geq 99.8\%$ , Sigma-Aldrich) into 1% solution or dissolving Nafion in ethanol into 1 % solution before mixing with the carbon powders. A series of mixtures with different carbon powder/polymer weight ratios were prepared and ultrasonicated for 1 hour to get a better dispersion. Surfaces were prepared on clean glass microscope slides by spin-coating via a spin-coater (Model WS-400B-6NPP-LITE, Laurell inc.) with the maximum spinning speed of 3000 rpm. The coated glass slides were then placed onto a 120°C hot plate for 10 min to minimize any solvent residuals before the droplet impacting experiments.

### 5.2.3 Droplet impacting experiments

For the drop impacting experiments, the experimental setup is similar to the picture and schematic shown in Figures 4.1 and 4.2, except that the impacting height is fixed at 120 *mm* above the solid surface.

The data acquisition is exactly the same with the droplet impacting experiment described in Chapter 4 by using the high-speed camera (DRS inc., Lightning RDT 16000) with a zoom lens at the speed of 2500 frames per second. The captured videos were then analyzed by using the software just as mentioned in Chapter 4.

## 5.3 Results and discussions

### 5.3.1 Purification of SWNTs

Figure 5.1 shows the suspension of purified and unpurified SWNTs in DIUF water. It is very clear the purified one has a much better dispersion in DIUF water. The 20 *hr* reflux in 3 *mol/L* HNO<sub>3</sub> can partially oxidize the outer surface of SWNTs into carboxyl groups and functionalize it with nitro functional groups. The hydrophilicity of nitro and carboxyl groups on the outer surface of CNTs can be one explanation of the better dispersion for purified samples. Another explanation could be the purification process also truncates the SWNTs from the original length of about 1  $\mu m$  to a mean length of about 200 *nm*. The short length reduces the possibility of the tangling of individual nanotubes.





Figure 5.1: Suspensions of purified (left bottle) and unpurified (right bottle) SWNTs in DIUF water.

### 5.3.2 SWNTs/PMMA composite

Figure 5.2 shows the sequential images of water droplets impacting onto the surface of PMMA and 10 – 50% CNTs/PMMA composite films. Since the water droplets have the same size  $D$  and impacting velocity  $u$  for all these tests, any variation in the droplet impacting dynamics comes from the differences among the surface properties of the polymer surfaces. If we compare the droplet behaviour at the same impacting time, it seems like that the time differences of the group of droplets reaching the maximum spreading ratio  $\beta_{max}$  and the minimum spreading ratio  $\beta_{min}$  are very small to distinguish.

In order to compare the spreading process of water droplets on these film surfaces, their spreading ratios were plotted in Figure ?? . As described previously, the spreading process of the droplets are affected significantly by the initial impacting kinetic energy while the recoiling process reflects the difference of the surface properties between solid surfaces. This

spreading ratio dependence of impacting time plot provides good evidence to it. By comparing the  $\beta_{max}$  and  $\beta_{min}$ , the  $\beta_{max}$  from different solid surfaces are of the similar value, while the  $\beta_{min}$  value varies from each other. The minimum spreading ratio values of 10 – 30% CNTs/PMMA surfaces suggest that the presence of purified CNTs has the trend to make the PMMA surface more hydrophilic. The minimum spreading ratio of 50 % CNTs/PMMA is close to that of 30 % CNTs/PMMA, as it should be larger. This is caused by the increased roughness of the surface, which increases the friction of moving water on it and thus declines the kinetic energy of water droplet. The roughness of 50 % CNTs/PMMA film also contributes to the high contact area between water and the film, which increases the conversion of kinetic energy of water droplet into interfacial surface tension between water and the film, and thus decreases the minimum spreading ratio. Both the surface roughness and hydrophilicity of the film surface retard the shrinking/recoiling of water droplets.

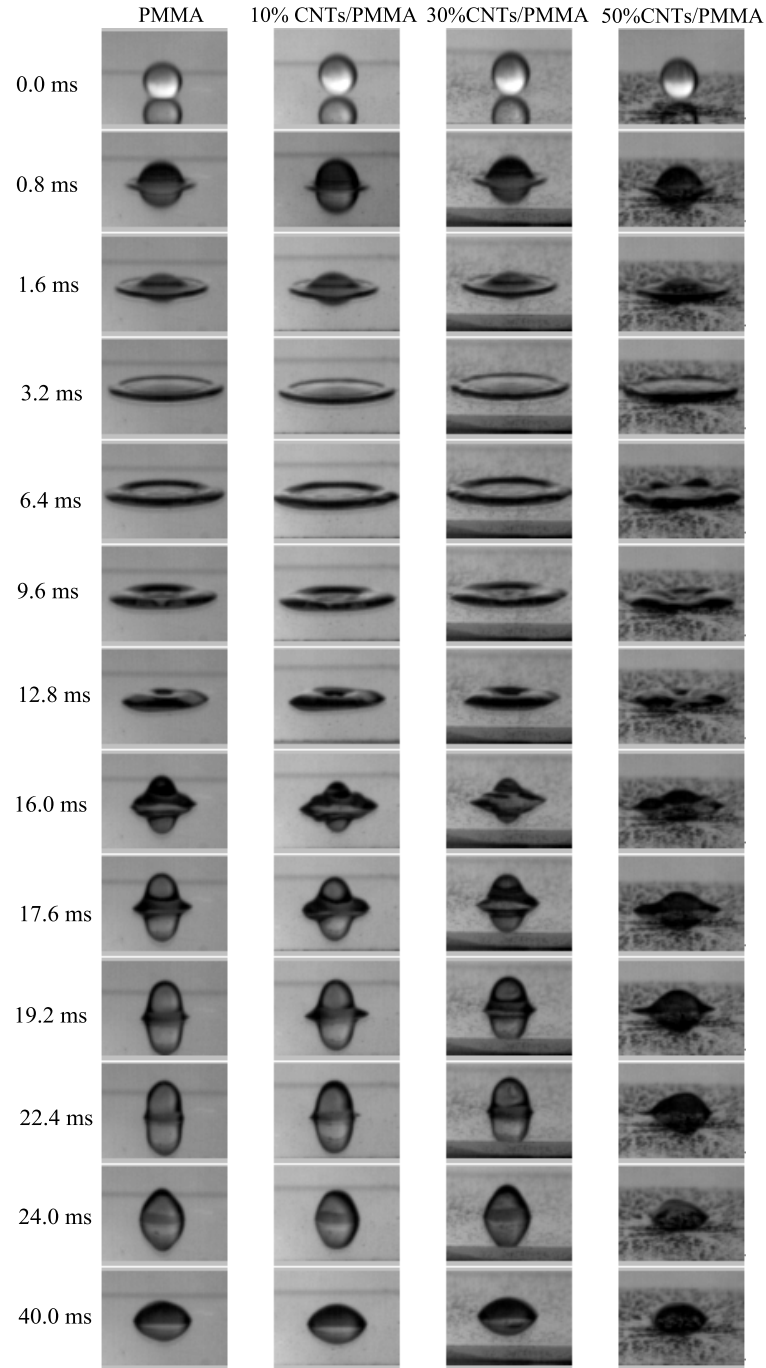


Figure 5.2: Images of water droplets impacting onto PMMA and SWNTs/PMMA composites with 10%, 30% and 50% SWNTs *wt%*.

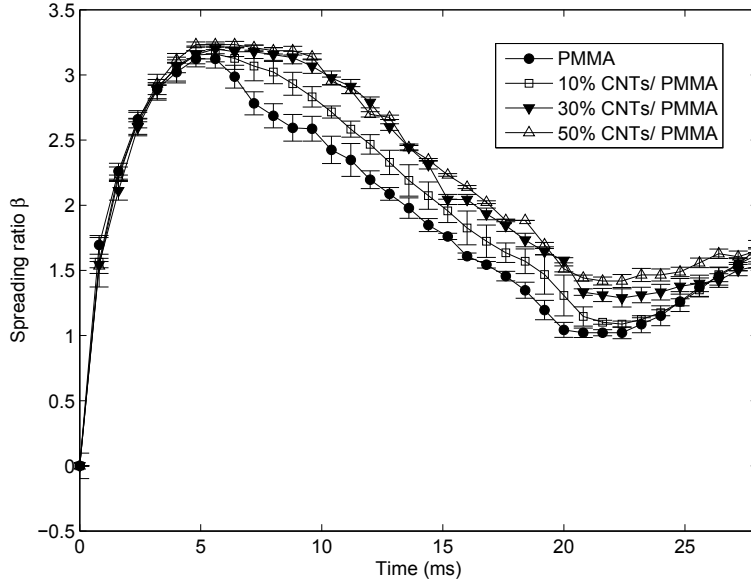


Figure 5.3: Time dependence of spreading ratio  $\beta$  of water droplets impacting onto PMMA and SWNTs/PMMA composites with 10%, 30% and 50% SWNTs *wt%*.

In Figure 5.2, it is obvious that increasing CNTs content up to more than 30% of the composites results in the increase of the surface roughness. This is likely due to the bad dispersion of the purified CNTs in the PMMA/ $\text{CHCl}_3$  solution during the preparation. Longer sonication times were also tried on these CNTs/PMMA/ $\text{CHCl}_3$  mixtures, but the dispersion of CNTs in the solution was still not good. The bad dispersion of purified CNTs in the PMMA/ $\text{CHCl}_3$  solution is likely due to the hydrophilic functional groups on CNTs, such as hydroxyl and carboxyl acid groups. These hydrophilic groups could significantly enhance the interaction between CNTs by forming hydrogen bonds with each other through the hydrophilic groups in the  $\text{CHCl}_3$  solution. Especially at high contents of CNTs in the solution, CNTs have very high chances to interact with each other, leading to their agglomeration, forming big particles shown as the lumps on the surface of 50% CNTs/PMMA composite

in Figure 5.2. The hydrophilic function groups on the outer surface of SWNTs can also be bonded with the hydrophilic function groups on the side chain of PMMA molecules, causing even more agglomerations.

### 5.3.3 VC/PMMA composite

After the surfaces are prepared, different surface appearances can be observed. Good dispersion of VC into PMMA/ $\text{CHCl}_3$  solution leads to smooth surfaces in visual sights. With more Vulcan carbon added into PMMA, the film looks darker. Surface roughness also increases when more Vulcan carbon is added. That may happen because of the aggregation of Vulcan carbon at high concentration of PMMA/Vulcan carbon mixture before coating.

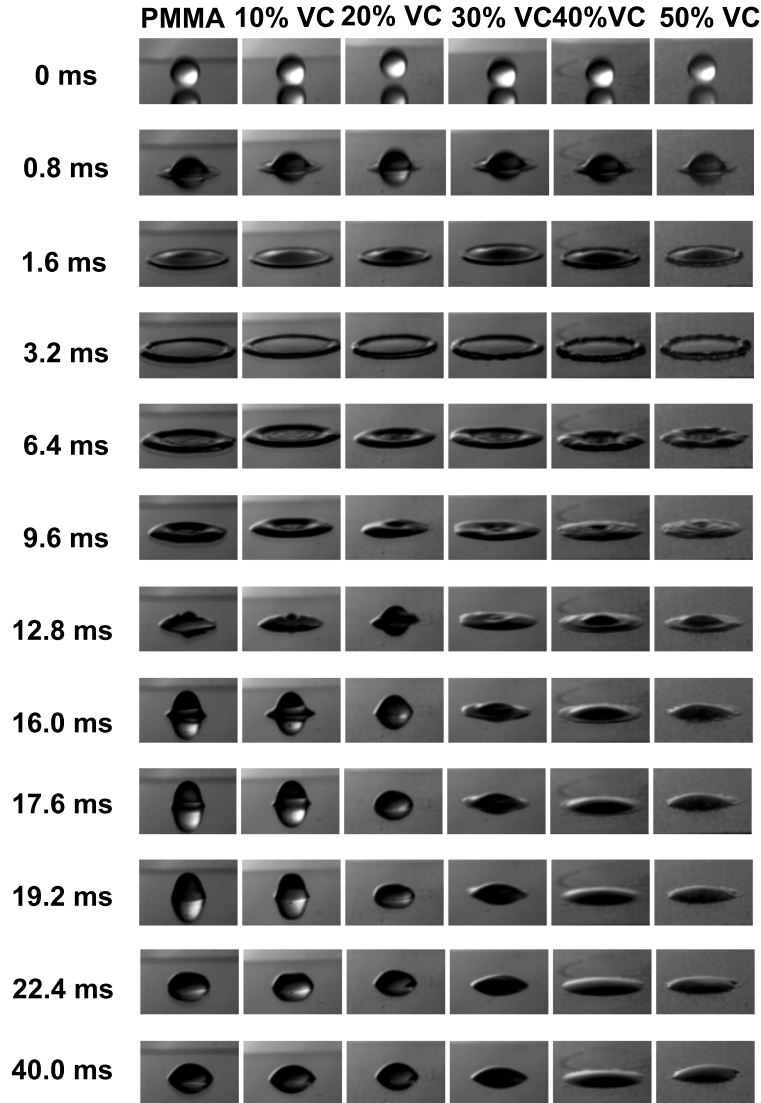


Figure 5.4: Images of water droplets impacting onto PMMA and VC/PMMA composites with 10%, 20%, 30%, 40% and 50% VC *wt%*.

Figure 5.5 provides the spreading ratio with the dependence of the impacting time. If we compare the minimum spreading ratio from different spreading curve, it was found that with more VC added into PMMA, the composite becomes more hydrophilic with larger minimum spreading ratio. When more VC was added into PMMA, the volume ratio of VC

in the composite increased, so the composite surface tends to reflect the wettability of Vulcan carbon particle surfaces. The results here suggested that VC has a more hydrophilic surface compared with PMMA, which is consistent with the literature [144]. However, when the *wt%* of Vulcan carbon weight percentage in the composite increases from 40% to 50%, the composite surface becomes more hydrophobic. This inconsistency is caused by the increase of surface roughness with more Vulcan carbon particles added.

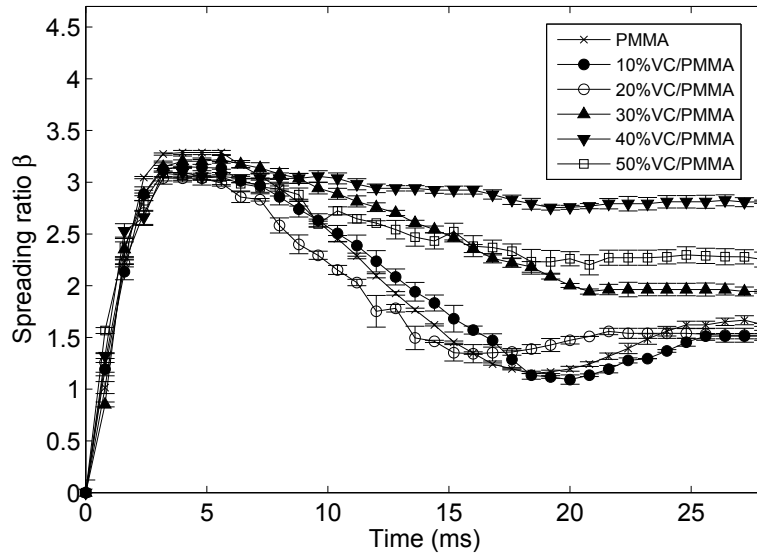


Figure 5.5: Time dependence of spreading ratio  $\beta$  of water droplets impacting onto PMMA and VC/PMMA composites with 10%, 20%, 30%, 40% and 50% VC *wt%*.

#### 5.3.4 The comparison of SWNTs/PMMA composite and VC/PMMA composite

If we compare the minimum spreading ratios  $\beta_{min}$  of water droplet impacting on the SWNTs/PMMA surfaces and the VC/PMMA surfaces with the same amount of carbon content, say 10% 30% and 50% (Figure 5.6), the results are obvious that the VC/PMMA composite surfaces are more hydrophilic compared to SWNTs/PMMA composite surfaces. This may also

lead to the conclusion that the Vulcan carbon particles are more hydrophilic than carbon nanotubes, as both of them are more hydrophilic than pure PMMA surfaces.

However, the latter conclusion may not be one hundred percently correct. Their surface properties also rely on their levels of exposure to the outer surface. As discussed previously, the purification of SWNTs functionalize their outer surfaces with hydrophilic groups. The hydrophilic groups can bond with the hydrophilic groups on the side chain of PMMA molecule, causing the SWNTs on the outside covered by PMMA. The orientation of PMMA could also be changed from the existence of SWNTs, leaving all the hydrophobic group towards the outside.

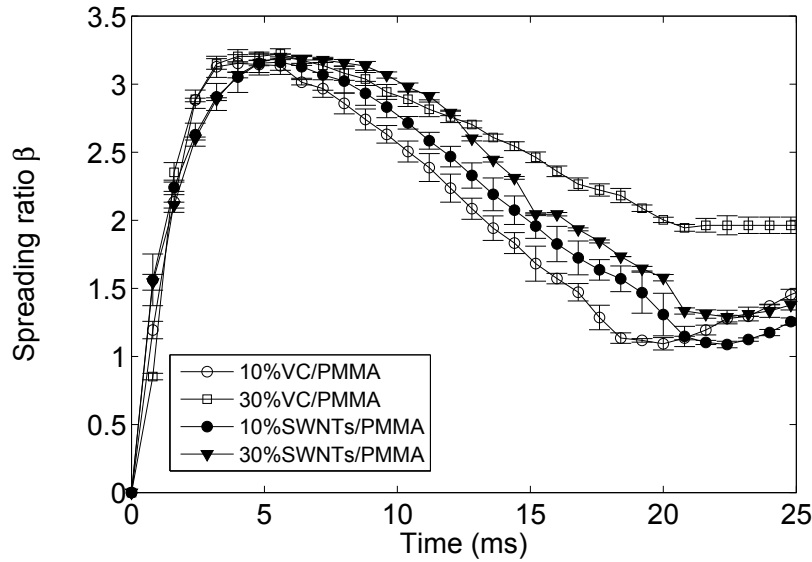


Figure 5.6: Time dependence of spreading ratio  $\beta$  of water droplets impacting onto VC/P-MMA composites with 10% and 30% VC *wt%* and SWNTs/PMMA composites with 10% and 30% SWNTs *wt%*.



### 5.3.5 VC/Nafion composite

Nafion was also used as a binder of VC to prepare VC/Nafion composite films and the VC/Nafion composite can serve as the polymer electrolyte membrane fuel cell (PEMFC). The droplet behaviours of different solid surfaces were shown in Figure 5.7. As we can see, the more involvement of VC, the more hydrophobic the composite is. At high VC content, the composites exhibit superhydrophobic properties, as water droplet rebounds from the impacted surface quickly after spreading to a small maximum contacting diameter, and shows very high contact angles when it comes to static state. These phenomena was explained by Li et al. [145] the surface properties of the composite relies on the orientation of Nafion molecules onto VC carbon surface. As mentioned above, VC has a hydrophilic surface, which would promote the orientation of sulfonic acid groups of Nafion molecules onto the surface, leaving their hydrophobic Teflon backbone outward to air. This makes the composite surface hydrophobic. Along with the roughness from VC particles, the hydrophobicity of the composites results in the superhydrophobicity of 40 – 50%VC/Nafion.

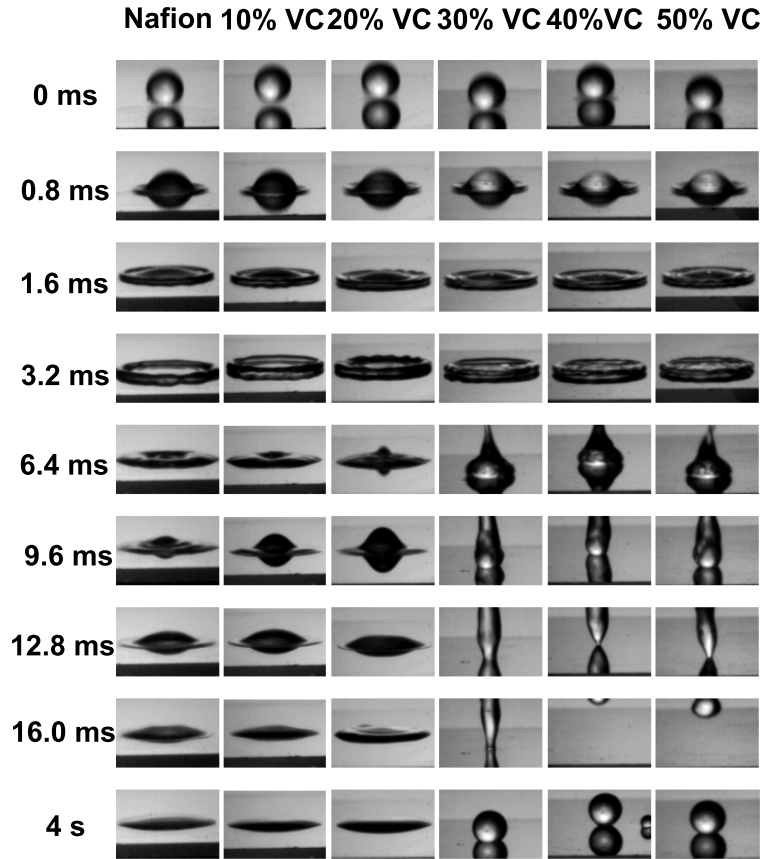


Figure 5.7: Images of water droplets impacting onto Nafion and VC/Nafion composites with 10%, 20%, 30%, 40% and 50% VC *wt%*.

The spreading ratio was shown in Figure 5.8. For pure Nafion film, the water droplet impacting process, big maximum spreading ratio and little recoil occurring, suggests the Nafion has intrinsic hydrophilic property, which is reasonable since Nafion has sulfonic acid groups, which are very polar groups, . The hydrophilicity of Nafion contributes to the hydrophilicity of some VC/Nafion composites with low VC contents, in which the orientation of Nafion onto VC also contributes to the increasing hydrophobicity of these composites with the increase of VC content.

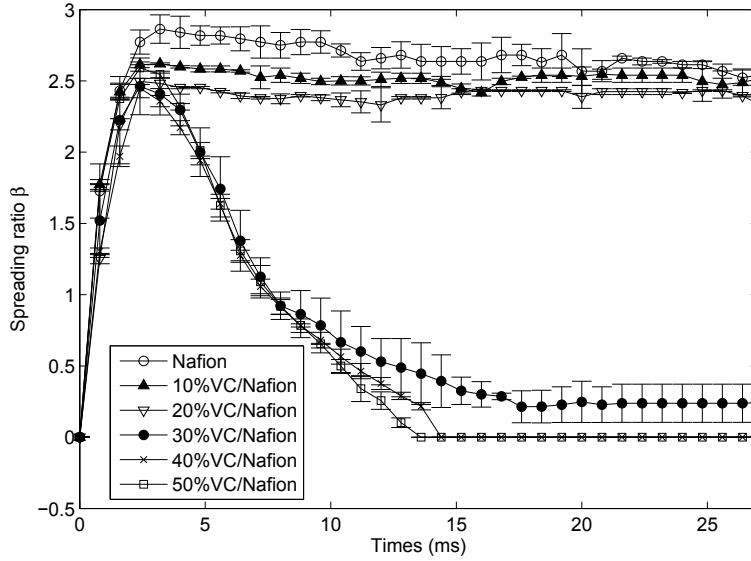


Figure 5.8: Time dependence of spreading ratio  $\beta$  of water droplets impacting onto Nafion and VC/Nafion composites with 10%, 20%, 30%, 40% and 50% VC *wt%*.

### 5.3.6 Theoretical analysis of droplet impacting on to polymer/carbon composite

Some of the results from the previous two chapters can be used in the theoretical analysis. Two important parameters for the droplet impact are the maximum spreading ratio,  $\beta_{max}$  and the minimum spreading ratio,  $\beta_{min}$ . The expressions for  $\beta_{max}$  and  $\beta_{min}$  are given in Chapter 4 as the following:

For the  $\beta_{max}$  calculation,

$$(We + 12)\beta_{max} = 8 + \beta_{max}^3[3(1 - \cos \theta_a) + 4\frac{We}{\sqrt{Re}}] \quad (5.1)$$

it is obvious that  $\beta_{max}$  is controlled by the advancing contact angle when the impacting velocity and drop diameter is fixed.

For the  $\beta_{min}$  calculation, using the cylinder model,

$$\begin{aligned} & \frac{\pi}{4}\gamma_{lv}D_0^2(\beta_{max}^2 - \beta_{min}^2)(1 - \cos \theta_r) + \\ & \frac{2\pi}{3}D_0^2\gamma_{lv}\left(\frac{1}{\beta_{max}} - \frac{1}{\beta_{min}}\right) + \frac{\pi}{18}gD_0^4\left(\frac{1}{\beta_{max}^2} - \frac{1}{\beta_{min}^2}\right) = 0 \end{aligned} \quad (5.2)$$

Using the cone model,

$$\begin{aligned} & \frac{\pi}{4}\gamma_{lv}D_0^2\beta_{max}^2 + \frac{2\pi D_0^2\gamma_{lv}}{3\beta_{max}} - \frac{\pi}{4}\gamma_{lv}D_0^2\cos \theta_r(\beta_{max}^2 - \beta_{min}^2) - \\ & \frac{\pi}{4}\gamma_{lv}D_0^2\beta_{min}\sqrt{\beta_{min}^2 + \frac{16}{\beta_{min}^4}} - \frac{\pi}{6}gD_0^4\left(\frac{0.413}{\beta_{min}^2} - \frac{1}{3\beta_{max}^2}\right) = 0 \end{aligned} \quad (5.3)$$

From these two equations predicting the minimum spreading ratio  $\beta_{min}$ , it can be found that  $\beta_{min}$  is dependent on both the advancing contact angle  $\theta_a$  and the receding contact angle  $\theta_r$ .

The vertical plate model is then used to calculate the polymer/carbon composite surface. Two pairs of strips were used to calculate the polymer and carbon content respectively. In each pair, the two strip have the same width, but different equilibrium contact angles, which stands for the high energy region and the low energy region of the polymer surface or the carbon surface because they are both chemical heterogeneous. Figure 5.9 shows the schematic of strips to be used in the simulation for different carbon weight percentage. The total width of the four strips for each weight ratio is the same value of  $16^\circ$ . The intrinsic equilibrium contact angles for the polymer strips are  $80^\circ$  and  $60^\circ$ , and  $40^\circ$  and  $20^\circ$  for the carbon strips.  $\gamma_{lv}$  is using the surface tension of water at  $25^\circ\text{C}$ ,  $\gamma_{lv} = 72\text{mJ/m}^2$ , and  $\Delta\rho = 1 \times 10^3\text{kg/m}^3$ ,  $g = 10\text{m/s}^2$ .

The resulting free energy curves for different carbon weight percentages are shown in Figure 5.11, 5.12 and 5.13. The free energy curve for pure polymer surface is shown in Figure 5.10. It is interesting to find out in all these four figures, that the advancing contact angles are quite close. This explains why the maximum spreading ratio does not change

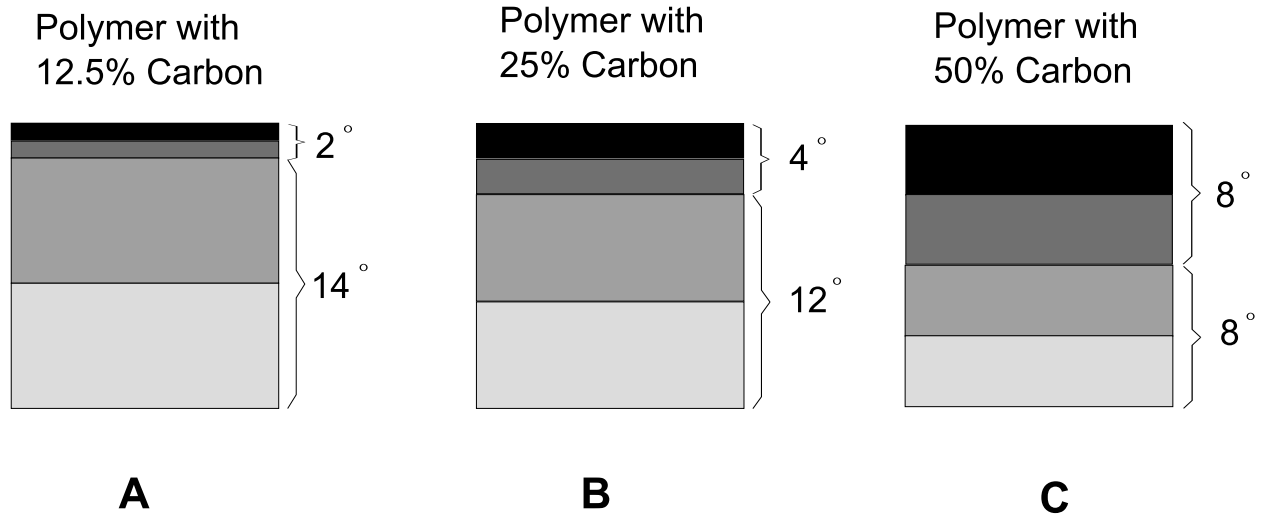


Figure 5.9: Schematic of horizontal strips for polymer/carbon composite with different weight ratio.

too much with the different amount of carbon added. From the above equations, when the advancing angle have the same value, the minimum spreading ratio only depends on the receding contact angle of the surface. From the four figures, it can be concluded that, when more carbon is added into the polymer, the receding angle decreases from  $60^\circ$  to  $20^\circ$ . This provides an explanation why the minimum contact angles have different values corresponding to the carbon weight percentages.

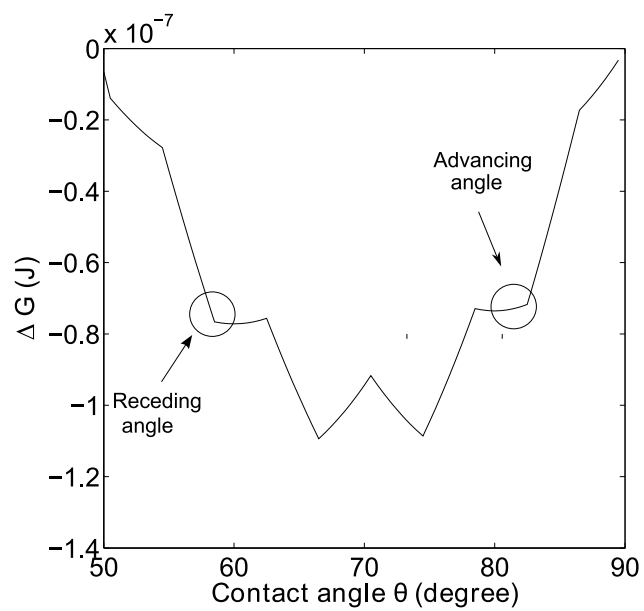


Figure 5.10: Free energy curve for the calculated polymer surface.

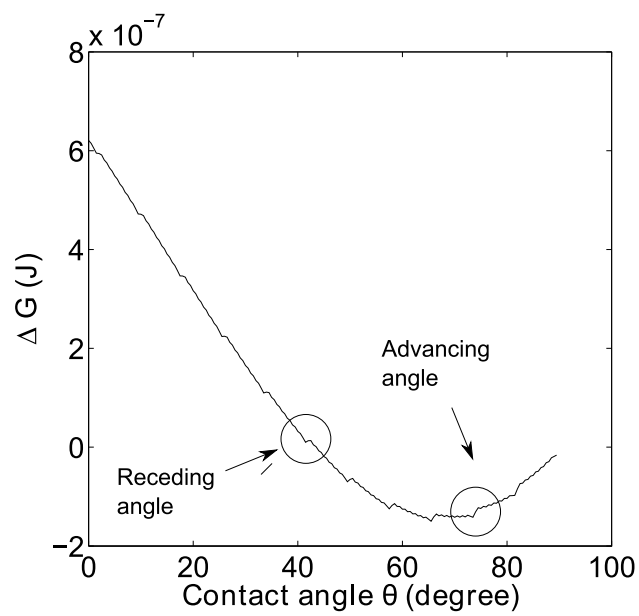


Figure 5.11: Free energy curve for the calculated 12.5wt% of carbon in polymer surface.

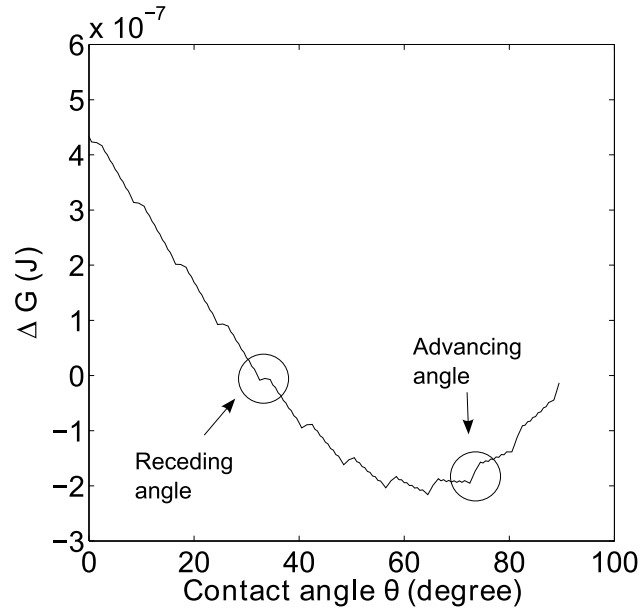


Figure 5.12: Free energy curve for the calculated 25wt% of carbon in polymer surface.

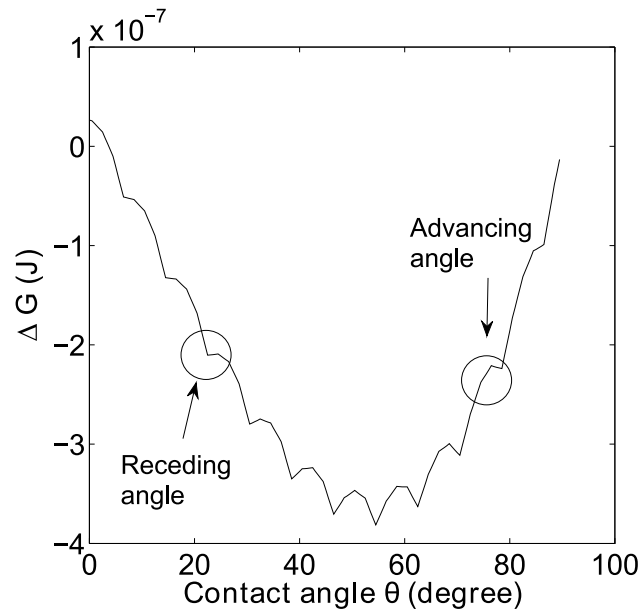


Figure 5.13: Free energy curve for the calculated 50wt% of carbon in polymer surface.

It should be noted here that all the calculations above are based on the assumption that

all the surfaces are smooth but chemical heterogeneous. In reality, with more carbon added into the polymer, the surface becomes rougher. Rough and heterogeneous surfaces are even more complicated and beyond the power of this model. Nafion surface is another special example. Orientation of Nafion may change with the carbon weight ratio, and produce some unpredictable results.

## 5.4 Conclusions

In order to investigate the surface properties of different carbon powders, droplet impact experiments were carried out on CNTs/PMMA, VC/PMMA and VC/Nafion surfaces with different carbon weight percentage. The minimum spreading ratio  $\beta_{min}$  is found to be reliable to the surface properties of composite surfaces. Theoretical analysis also gives good agreement to the experimental results. The surface properties of the carbon powders can be characterized qualitatively by comparing the impacting dynamics of the droplets, especially the comparison of the minimum spreading ratio  $\beta_{min}$ . However, this method suffers from the increased surface roughness corresponding to the increased content of the carbon powders in the composite. The dispersion of carbon powders in the polymer solution as well as the carbon/polymer composite structure may also affect the accuracy of this method.



## Chapter 6

### Conclusions

The measurements of contact angles are of great importance in a wide range of problems in pure and applied science. However, the existence of contact angle hysteresis rises the complexity of measuring contact angles. To explore the intrinsic physic relation of the contact angle hysteresis, different theoretical models have been established by researchers [32, 33]. As predicted in these models, there exists metastable contact angles with in the range between the advancing contact angle and the receding contact angle. However, there lacks systematically experimental investigations into the metastable states of the contact angles.

In this work, in order to examine the experimental evidence of metastable contact angles, experiments have been designed by using acoustic signals to vibrate water drops sitting on PMMA and PnBMA solid surfaces from the starting state of advancing or receding. By carefully controlling the amplitude of the vibration, metastable states have been observed for both polymer surfaces. The different behaviors of water drop responding to the vibration on these two polymer surfaces have been carefully analyzed, and the difference may come from the variation of energy barriers. The simulation results from the vertical plate model developed by Neumann and Good [33] also give good agreement to the experimental observations. It also demonstrate that there exist many metastable contact angles. Even if one obtains the equilibrium contact angles, it is still not applicable to Young's equation.

The above experimental work and the theoretical analysis also provide us a better understanding to the contact angle hysteresis and to the relations between different contact angles such as advancing angle, receding angle, equilibrium angle and Young's angle. It is

important to be able to distinguish which contact angle can be used in Young's equation.

After clarifying these concepts, experimental and theoretical studies have been carried out to examine the droplet behaviors of its impact onto solid surface. Experimental results have been obtained from the impact of water droplets and onto two carefully prepared polymer surfaces(PMMA and PnBMA) from four controlled impacting heights. Observations of our experiments show that drop impact dynamics is influenced by the initial energy of the droplet at impact, physical properties of the liquid droplets, and solid surface tensions. The surface property plays a more important role for the recoiling process than the spreading process. By comparing with the experimental data, the modified model yields good improvement in the determination of the maximum spreading diameter. The cylinder model and cone model also give good predictions to the minimum spreading diameter. However, the complications involved in deriving the minimum spreading diameter remain largely unresolved since my model still underestimates the energy dissipation and the simplified cylinder and cone has their limitations in estimating the shape of actual droplets.

After the theoretical studies, droplet impact experiments were then used to examine the surface properties of carbon powders. Using droplet impacting method instead of direct contact angle measurements is due to the high heterogeneity of the composites surfaces. Carbon powders were mixed with polymer in different weight ratios a targeting surface. The behaviors of droplet impact onto three kinds of carbon/polymer composite: CNTs/PMMA, VC/PMMA and VC/Nafion have been examined by both image sequences and spreading ratio curves. Vulcan carbon powders showed hydrophilicity when compared to PMMA and SWNTs.

The results derived from models used in the previous two chapters were then used to interpret the experimental observations theoretically. Some qualitative results have been

obtained from the droplet impacting experimental result, but it is still not a reliable method of characterizing the surface properties of carbon powders directly and quantitatively. The difficulties come from two aspects: The first one is that with more carbon particles added into the composite, the composite surface becomes rougher, introducing more viable to the interpretation; another one could be that the bondings and interactions between the carbon powder material and the polymer may also affect the validity of this method.

## Chapter 7

### Future Work

#### 7.1 Metastable contact angle measurements

(1) Because of the limitation of the equipments, vibration amplitudes in the experiments were not recorded directly. With the aid of the current Microelectromechanical systems (MEMs) technology, vibration parameters such as acceleration, velocity and displacement, could be measured directly. It could be very interesting to investigate the instantaneous contact angles corresponding to the displacement as well as the kinetic energy.

(2) The effect of vibration frequency can be investigated systematically in any future experiment. Vibration with extremely high frequency, e.g. ultrasound or extremely low frequency, e.g. infrasound may cause the drop act differently. The resonance of the drop excited by continuous acoustic vibration is also of great research interests.

(3) Examination of rough solid surfaces may be another option in future studies. However, according to the theoretical work from Eick and Neumann [55], the metastable states for rough solid surfaces are largely random and can not be predicted thermodynamically. The surface roughness is also difficult to control experimentally.

#### 7.2 Drop impacting models and experiments

(1) The effect of surface roughness and chemical heterogeneous of the solid surface can be examined both by models and by experiments. For rough solid surface, the energy dissipation term could be modified with the consideration of air trapped in the rough surfaces during

drop spreading.

(2) Considering different testing liquids with different viscosities, a viscous term could potentially be added to my model for minimum spreading ratio. More experimental data of spreading ratio for viscous liquids onto selected polymer surfaces can be collected and compared with the prediction of my model.

### 7.3 Drop impacting onto carbon/polymer composites

(1) The advancing and receding contact angles for water on carbon/polymer composite will be measured. Then the estimations of  $\beta_{max}$  and  $\beta_{min}$  for drop impacting onto the composite surfaces could be calculated and then compared to the existing experimental data. The validity of my drop impacting models could be examined and see if they are applicable to composite surfaces.

(2) A series of polymers with a wide range of wettability can be used to characterize the surface properties of particles and powders. The surface properties of the pure polymer surfaces can be characterized firstly and then the testing particles could be mixed with the polymers into composites. After comparing the wettability of different Particles/Polymer surfaces, the surface properties of the particles could be examined indirectly.

## Appendix A

### Matlab program for contact angle measurements

```
% Reading image file sequence with the name starting  
% with character = viable 'name'  
for i1=0:n;  
    if i1<=9;  
        imageName=strcat(name,'000',num2str(i1),'.jpg');  
    elseif i1>=10 & i1<=99;  
        imageName=strcat(name,'00',num2str(i1),'.jpg');  
    elseif i1>=100 & i1<=999;  
        imageName=strcat(name,'0',num2str(i1),'.jpg');  
    elseif i1>=1000;  
        imageName=strcat(name,num2str(i1),'.jpg');  
    end;  
    I_raw = imread(imageName);  
  
% Transform the images into black and white only  
    I_bw=im2bw(I_raw);  
  
    imshow(I_bw);% find and put drop profile into matrices  
    [a,b]=size(I_bw);  
  
for x=1:b;  
    for y=1:a;
```

```

        x1=x;
        y1=a+1-y;
        if I_bw(y1,x1)==0;
            break;
        end;
    end;
end;
    if I_bw(y1,x1)==0;
        break;
    end;
end;
for x=1:b;
    for y=1:a;
        x2=b+1-x;
        y2=a+1-y;
        if I_bw(y2,x2)==0;
            break;
        end;
    end;
end;
    if I_bw(y2,x2)==0
        break
    end;
end
k(1)=x1;
l(1)=y1;

```

```

for i=2:50;
    for j=1:a
        l(i)=y1-i+1;
        k(i)=j;
        if L_bw(l(i),k(i))==0;
            break;
        end
    end

end


    u=k-x1;
    v=y1-l;
    dx=x2-x1;
    dy=y1-y2;
    z=sqrt(u.^2+v.^2);
    theta=atan(v./u)-atan(dy/dx);
    u1=z.*cos(theta);
    v1=z.*sin(theta);
    u1(1)=0;
    v1(1)=0;
    %polynomial fitting
    p=polyfit(u1,v1,5);

```



```
% find the contact angle value
```

```
Ca(i1+1)=atand(p(5));
```

```
end
```

## Appendix B

### Matlab program for vertical plate model

```
%Free energy curve for PMMA
% define variables
ga=72/1000;
g=10;
rho=1000;
F_1=0;
%calculating free energy
for n=0.5:0.5:90;
    F_23=1/3*0.01*ga*(2*ga/g/rho)^0.5* ... ,
(2.828-(1+sind(90-n))^1.5);
    if rem(2*n,4)==1|rem(2*n,4)==2;
        F_11=-0.01*ga*cosd(76)*sqrt(2*ga/rho/g)* ... ,
(sqrt(1-sind(90-n))-sqrt(1-sind(90-n+0.5)));
    else
        F_11=-0.01*ga*cosd(54)*sqrt(2*ga/rho/g)* ... ,
(sqrt(1-sind(90-n))-sqrt(1-sind(90-n+0.5)));
    end
    F_1 =F_1+F_11;
    F(2*n)=F_23+F_1;
end
```

```
x=89.5:-0.5:0
```

```
plot(x,F)
```

```

%Free energy curve for PnBMA
% define variables
ga=72/1000;
g=10;
rho=1000;
F_1=0;
%calculating free energy
for n=0.5:0.5:90;
    F_23=1/3*0.01*ga*(2*ga/g/rho)^0.5* ... ,
        (2.828-(1+sind(90-n))^1.5);
    if rem(2*n,4)==1|rem(2*n,4)==2|rem(2*n,4)==3
        F_11=-0.01*ga*cosd(86)*sqrt(2*ga/rho/g)*... ,
            (sqrt(1-sind(90-n))-sqrt(1-sind(90-n+0.5)));
    else
        F_11=-0.01*ga*cosd(66)*sqrt(2*ga/rho/g)*... ,
            (sqrt(1-sind(90-n))-sqrt(1-sind(90-n+0.5)));
    end
    F_1 =F_1+F_11;
    F(2*n)=F_23+F_1;
end
x=89.5:-0.5:0
plot(x,F)

```

## Appendix C

### Matlab program for spreading ratio measurements

```
clc

%determine the drop diameter

picname=strcat(name,'0000',' .tif')
I=imread(picname)

a=size(I);
length(1)=1;

for i=2:a(1)-30;
    left=0;
    right=0;
    for j=1:a(2);
        if I(i,j);
            left=j;
            break;
        else j=j+1;
        end;
    end
end
```

```

    for k=1:a(2);
        if I(i,a(2)+1-k)
            right=a(2)+1-k;
            break
        else k=k+1;
        end;
    end;

    length(i)=right-left+1;
    i=i+1

end

[ dia , l1 ]=max(length)

%determine the base line using the 14th pic
picname1=strcat(name,'0014',' .tif')
I=imread(picname1)
a=size(I);
length(1)=1;
for i=2:a(1)-10;

```

```

left=0;
right=0;
    for j=1:a(2);
        if I(i,j);
            left=j;
            break;
        else j=j+1;
        end;
    end

    for k=1:a(2);
        if I(i,a(2)+1-k)
            right=a(2)+1-k;
            break
        else k=k+1;
        end;
    end;

    length(i)=right-left+1;
    i=i+1

end

[ma,l]=max(length);

```

*%measure spreading diameter for each frame;*

```
for i1=1:100
    if i1<=9;
        imageName=strcat(name,'000',num2str(i1),'.tif');
    elseif i1>=10 & i1<=99;
        imageName=strcat(name,'00',num2str(i1),'.tif');
    elseif i1>=100 & i1<=999;
        imageName=strcat(name,'0',num2str(i1),'.tif');
    end

    I = imread(imageName);
    a=size(I);
    spread(1)=1
    i=1
    for j=1:a(2);
        if I(i,j);
            left=j;
            break;
        else j=j+1;
    end;
end

for k=1:a(2);
    if I(i,a(2)+1-k)
```



```

        right=a(2)+1-k;

        break

    else k=k+1;

    end;

end;

spread(i1+1)=right-left+1;

if spread(i1+1)<.8*spread(i1)

    i=l-1

    for j=1:a(2);

        if I(i,j);

            left=j;

            break;

        else j=j+1;

        end;

    end

end

for k=1:a(2);

    if I(i,a(2)+1-k)

        right=a(2)+1-k;

        break

    else k=k+1;

    end;

end;

spread(i1+1)=right-left+1;

```

```
end

ratio(i1+1)=spread(i1+1)/dia;
end;
x=1:101
figure , plot(x,ratio)
dlmwrite('ratio.txt',ratio)
```

## Appendix D

### Matlab program for drop edge finding, calculating 95 confidence interval error and plot figures with error bar

*%this code automatically find the edge for each picture*

*%in the image sequence if the file name is input as a valuable.*

```
for i1=0:100;
    if i1<=9;
        imageName=strcat(name,'000',num2str(i1),'.tif');
    elseif i1>=10 & i1<=99;
        imageName=strcat(name,'00',num2str(i1),'.tif');
    elseif i1>=100 & i1<=999;
        imageName=strcat(name,'0',num2str(i1),'.tif');
    end
    I = imread(imageName);
    BW1 = edge(I,'sobel');
    edged=strcat('e',imageName);
    imwrite(BW1,edged)
end;
```

*%this code calculates the 95% confidence interval*

*%when the sample number is 4*

```

a=[y1;y2;y3;y4]
y=mean(a,1)
x=1:100
for i=1:100;
    stdy(i)=std(a(:,i));

    intv(i)=1.96.*stdy(i)./2;
end
errorbar(x,y,intv)
dlmwrite( 'error.txt',intv)
dlmwrite( 'mean.txt',y)

%this code reads the data from text files
%and then plots the figures with error bar

clear
a1=dlmread( 'mean.txt')
e1=dlmread( 'error.txt')
x=0:99
for i=1:50
    a1_=a1(2*i-1)
end
for i=1:50

```

```

a1_(i)=a1(2*i-1)
end
for i=1:50
e1_(i)=e1(2*i-1)
end
for i=1:50
x_(i)=x(2*i-1)
end
a=x_./2.5
errorbar(a,a1_,e1_)

```

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