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Static and dynamic contact angle measurement on rough surfaces using sessile drop profile analysis with application to water management in low temperature fuel cells

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By

Vinaykumar Konduru

A THESIS

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

(Mechanical Engineering)

MICHIGAN TECHNOLOGICAL UNIVERSITY

2010

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This thesis, "Static and Dynamic Contact Angle Measurement on Rough Surfaces Using Sessile Drop Profile Analysis with Application to Water Management in Low Temperature Fuel Cells," is hereby approved in partial fulfillment for the requirements for the Degree of MASTER OF SCIENCE IN Mechanical Engineering.

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ABSTRACT

Fuel Cells are a promising alternative energy technology. One of the biggest problems that exists in fuel cell is that of water management. A better understanding of wettability characteristics in the fuel cells is needed to alleviate the problem of water management. Contact angle data on gas diffusion layers (GDL) of the fuel cells can be used to characterize the wettability of GDL in fuel cells. A contact angle measurement program has been developed to measure the contact angle of sessile drops from drop images. Digitization of drop images induces pixel errors in the contact angle measurement process. The resulting uncertainty in contact angle measurement has been analyzed. An experimental apparatus has been developed for contact angle measurements at different temperature, with the feature to measure advancing and receding contact angles on gas diffusion layers of fuel cells.

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CHAPTER 1. INTRODUCTION

In a proton exchange membrane (PEM) fuel cell, hydrogen and oxygen react to form electricity, water and heat. The basic assembly of a PEM fuel cell consists of polymer electrolyte membrane which is sandwiched between two electrodes. These electrodes which are called gas diffusion layers (GDL) are made up of carbon cloth or carbon paper. A catalyst layer is bonded to the polymer membrane. This catalyst layer helps in accelerating the rate of reactions. The GDL is coated with poly(tetrafluoroethylene) (PTFE) to make the surface hydrophobic. This aides in the removal of water to the surface of GDL. Such an arrangement of GDLs with a polymer electrolyte membrane with catalyst forms a single fuel cell and is commonly called as membrane electrode assembly (MEA). Different cells are connected together by means of bipolar plates. The bipolar plates have channels built into them that carry the reactants to the fuel cell and also collect the water produced in the fuel cell (Figure 1.1).



Figure 1.1. PEM Fuel Cell Assembly

During operation, hydrogen in passed over anode and oxygen over cathode. At anode, hydrogen gas dissociates producing protons and electrons. Protons travel through the electrolyte membrane while electrons travel through the circuit. At cathode, they react with oxygen to form water. These reactions are given in Equations (1.1)-(1.3).

At Anode:
$$H_2 = 2H^+ + 2e^-$$
 (1.1)

At Cathode:
$$O_2 + 4H^+ + 4e^- = 2H_2O$$
 (1.2)

Net cell Reaction:
$$2H_2 + O_2 = 2H_2O$$
 (1.3)

Water management in a fuel cell plays a vital role for the optimal performance of a fuel cell. Water that is formed at cathode during the fuel cell operation is removed by the reactant flow. The membrane is kept hydrated as the proton conductivity increases with water content. If excess water is withdrawn, the membrane will dry out and thereby increasing the resistance to the motion of protons reducing the fuel cell performance. If the water removal rate is slow, the excess water that is produced forms plugs in the channels and thereby blocking the path of reactant gases and reducing the number of available reaction sites severely hampering fuel cell operation [Larminie and Dicks, 2003].

To solve the problem of water management, an understanding of wetting characteristics of GDLs is essential. One way to characterize the GDLs is by virtue of analyzing the contact angle it makes with water. The contact angle is defined as the angle made by the liquid in contact with solid surface and measured from the liquid side (Figure 1.2). The static contact angle between a liquid drop and a smooth solid surface is given but the Young's Equation (1.4) which essentially is the force balance between the interfacial tensions at the solid-liquid-vapor interface.

$$\sigma_{LV}\cos(\theta) = \sigma_{SV} - \sigma_{SL} \tag{1.4}$$

In the fuel cell, dynamic conditions exist. Water drops that are formed on the GDL move over the GDL in the channels and for this reason dynamic contact angle needs to be measured.



Figure 1.2. Young's Model of Sessile Drop showing relationship between Interfacial Tensions

1.1 Techniques for Measuring Contact Angle

Several techniques exist to determine the contact angle, principal among them being the Wilhelmy Plate method and goniometry.

1.1.1 Wilhelmy Plate Method

This technique can be used to measure the contact angle if the surface tension of the liquid is known. Similarly, if the contact angle for the given solid-liquid pair is known, surface tension of the liquid can be obtained with this method. Wilhelmy plate method essentially consists of a rectangular plate on which angle is to be measured and a reservoir of the fluid kept below the plate. To measure the contact angle, the fluid is raised towards the plate until it touches the plate (Figure 1.3). The change in the weight of the plate (ΔW) occurs because of the liquid adhering to the plate. This change in weight is measured and with the knowledge of the wetted perimeter (p), the contact angle (θ) is measured from Equation 1.5.

$$\sigma\cos(\theta) = \frac{\Delta W}{p} \tag{1.5}$$

This method of measuring the contact angle is not suitable for rough and porous substrates such as GDLs. The fibrous surface of a GDL coupled with pores makes it difficult to measure the perimeter and may also result in wicking of the fluid into the GDL which result in incorrect weight measurements producing incorrect contact angle results. A modification of the Wilhelmy plate method is the Single Fiber Wilhelmy method in which the plate is replaced by a single fiber of the substrate. The single fiber however is not an accurate representation of the actual GDL surface.



Figure 1.3. Contact angle measurement using Wilhelmy Plate method

1.1.2 Goniometry

In goniometry, an image of the drop is obtained and contact angle is measured from the drop image. An elementary method is to draw a tangent and the solid-liquid interface along the drop profile and measure the contact angle. This method is very crude and the obtained angle is dependent on the judgement of the user and hence this method is not suitable for scientific applications.

For very small drops with Bond number (Bo) less than 1, spherical cap approximation can be applied in which the drop shape is approximated to that of a sphere by neglecting the effects of gravity. This approximation fails if the Bond number becomes greater than 1 as the effects of gravity cannot be neglected. The small slope approach [Allen, 2003] presents a simple model to obtain contact angles which are less than 30° but can be applied to drops of any size.

$$\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\sigma = \Delta P \tag{1.6}$$

Contact angle measurement by fitting a curve to the drop edge gets rid of the size constraints imposed by previous methods. Multiple points on the drop edge are selected from the images and a B-spline [Stalder et al., 2006] or any other curve is fitted to these profile points. Another approach is to model the drops using the Laplace-Young equation (1.6). A numerical solution to this equation was first developed by Bashforth and Adams [1883]. Hartland and Hartley [1976] solved the Laplace-Young equation numerically using the fourth order Runge-Kutta method and obtained the exact drop profile for different drop parameters. Cheng et al. [1990] followed a similar approach and developed a technique called Axisymmetric Drop Shape Analysis (ADSA), to fit the obtained theoretical drop profiles to the drop edge obtained from the images.

Young's equation (1.4) is applicable to systems with smooth and homogeneous surfaces only. On rough and heterogenous surfaces as found on GDLs, contact angles obtained using Young's correlation would be incorrect. Modifications to the Young's equation have been established previously and will be discussed in Section 1.2

1.2 Contact Angle on Rough Surfaces



Figure 1.4. Wetting on Rough Surfaces

A drop of liquid on a rough surface can take either of the two forms a) Total wetting (Figure 1.4a), where the liquid wets the entire rough surface; or b) Partial wetting (Figure 1.4b), where vapor is trapped between the liquid and the troughs of the rough surface. For the case of total wetting, Wenzel [1936] developed Equation 1.7 to model the apparent contact angle (θ_W) on rough surfaces. Roughness factor (r) is the ratio of the true surface area and the projected surface area. For non-wetting surfaces ($\theta > 90^{\circ}$), an increase in roughness would increase the apparent contact angle and for wetting surfaces ($\theta < 90^{\circ}$), increased surface roughness would reduce the apparent contact angle.

$$\cos(\theta_W) = r\cos(\theta_Y) \tag{1.7}$$

Cassie and Baxter [1944] developed Equation 1.8 to model contact angle on heterogenous surfaces, where f_i is the fraction area of each surface under the liquid and θ_{Y_i} is the contact angle for the same surface. For the case of partial wetting with vapor trapped between the solid and liquid, 1.8 takes the form of Equation 1.9, where f_1 is the fractional area for the solid-liquid interface and f_2 is the fractional area for the pores.

$$\cos(\theta_C) = \sum f_i \cos(\theta_{Y_i}) \tag{1.8}$$

$$\cos(\theta_C) = f_1 \cos(\theta_Y) - f_2 \tag{1.9}$$

The Wenzel 1.7 and Cassie-Baxter 1.9 do not consider the irregularities that occur at the solid-liquid-vapor contact line. Several modifications to these equations have been published. Drelich and Miller [1993], have suggested modifications to the above equations for different configurations of the surface at the contact line. However, due to the lack of a uniform surface on a GDL, these equations are not applicable on GDLs.

CHAPTER 2. SESSILE DROP PROFILE ANALYSIS

The Laplace equation of capillarity is the mathematical balance between the surface tension forces and gravitational forces, for two fluids separated by an interface.

$$\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\sigma = \Delta P \tag{2.1}$$

where σ is the interfacial tension, ΔP is the pressure difference across the interface, R_1 and R_2 are the two principal radii at the apex. The pressure difference consists of two components, the hydrostatic pressure (P_g) and the pressure due to the curvature (P_{σ}) . These are expressed as

$$\Delta P_g = \rho g z \tag{2.2}$$

$$\Delta P_{\sigma} = \frac{2\sigma}{b} \tag{2.3}$$

Thus for any sessile drop, at a height of z from apex, the Laplace equation can be expressed as

$$\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\sigma = \frac{2\sigma}{b} + \rho gz \tag{2.4}$$

At apex of the drop, due to symmetry of an axisymmetric drop, $R_1 = R_2 = b$ where b is the radius of curvature at the apex. The two radii of curvature can be expressed in terms of the arc length and the angle of the tangent to the interface by recognizing that

$$\frac{1}{R_1} = \frac{d\theta}{ds} \tag{2.5}$$

$$\frac{1}{R_2} = \frac{\sin(\theta)}{x} \tag{2.6}$$

Equation (2.4) is then expressed as

$$\frac{d\theta}{ds} = \frac{2}{b} + \frac{\rho g z}{\sigma} - \frac{\sin(\theta)}{x}$$
(2.7)

To solve equation (2.7), it is non-dimensionalized using the capillary constant, c, which is the ratio of physical properties of the fluid, namely the density, surface tension and gravity and has the dimensions of $1/\text{length}^2$.

$$c = \frac{\rho g}{\sigma} \tag{2.8}$$

The non-dimensionalized parameters that are needed to define the drop profile are

$$X = xc^{\frac{1}{2}} \tag{2.9}$$

$$Z = zc^{\frac{1}{2}} \tag{2.10}$$

$$B = bc^{\frac{1}{2}} \tag{2.11}$$

$$S = sc^{\frac{1}{2}} \tag{2.12}$$

In non-dimensionalized form, equation (2.7) is expressed as

$$\frac{d\theta}{dS} = \frac{2}{B} + Z - \frac{\sin(\theta)}{X} \tag{2.13}$$

Equation (2.13) with the geometric definitions, equations (2.14) and (2.15) form a set of first order differential equations which are solved numerically to obtain the required drop profile.

$$\frac{dX}{dS} = \cos(\theta) \tag{2.14}$$

$$\frac{dZ}{dS} = \sin(\theta) \tag{2.15}$$

In order to solve the above set of equations, different solvers exist in MATLAB[®]. The ode45 solver, which utilizes the Runge-Kutta method, was selected to obtain the drop profile. To validate the obtained profile, a comparison is made between the profile obtained from ode45 and the numerical data published by Hartland and Hartley [1976]. Data points at $\theta = 90^{\circ}$ are selected for comparison (Table 2.1). The obtained profile points are accurate and deviate only in the fourth digit, which enables us to conclude that an accurate drop profile is generated.

B	Hartland	and Hartley	OD	E45
Б	X90	Z90	X90	Z90
-1.50	.0316175	.0316102	0.031627	0.031658
-1.25	.0562045	.0561636	0.056224	0.056221
-1.00	.0998342	.0996054	0.099872	0.099588
-0.75	.176906	.175646	0.176973	0.175620
-0.50	.311216	.304568	0.311345	0.304596
-0.25	.536715	.505309	0.537020	0.505450
0.00	.885291	.766710	0.885116	0.766908
0.25	1.35895	1.02957	1.359368	1.029598
0.50	1.92291	1.23563	1.923322	1.235702
0.75	2.53445	1.370590	2.534496	1.370668
1.00	3.16457	1.44869	3.164281	1.448872

Table 2.1. Comparision of data points with numerical data published by Hartland and Hartley [1976]



Figure 2.1. Variation in drop shape with respect to dimensionless radius of curvature at apex, B

To generate a drop profile in non-dimensional co-ordinates, value of only the dependent variable B is needed. Figure 2.1 shows the drop profiles that are obtained for different values of B. The drop profiles are dimensionalised by dividing them with $c^{1/2}$. The capillary constant thus acts as a scaling factor for the generated drop profiles. Figure 2.2 shows drops generated with same B but at different values of capillary constant.



Figure 2.2. Variation in drop shape with respect to $c \, (\text{cm}^{-2})$ at constant B = 0.4

2.1 Numerical Optimization

The error between the Laplacian curve and the drop profile is defined as the sum of the normal distance between the drop profile and the Laplacian curve. By applying suitable edge detection techniques described in Section 3.1 the drop edge is obtained. On this edge, co-ordinates of N number of points are obtained (Figure 2.3). To calculate the error between the Laplacian curve and the actual profile, a normal is drawn from the N points onto the estimated Laplacian curve. The length of the normal gives the magnitude of error at that point. The total error is the sum of magnitude of distances calculated for all points. The distance is positive if the data point on the drop lies on one side of the the Laplacian curve and negative if it lies on the other side.

If B is kept constant and only fluid properties are changed by varying c, the error obtained for a given drop is minimum only for one value of c. This c would then be the optimal capillary constant corresponding to that value of B. The error obtained for this B-c pair would be the absolute minimum error that exists for B. Thus for different values of B, the error is obtained and the one that yields minimum error gives the solution from which contact angle is determined. Following is the procedure that is utilized to obtain accurate drop profiles:

- 1. Guess the initial value of *B*, which is close to the actual value. The program **Initial guess** performs this function and utilizes the algorithm developed by Stacey [2009].
- 2. Five values of B, two on each side of the initial guess, are selected. Obtain



Figure 2.3. Calculation of error over the drop profile. (offsets are exagerrated)

the capillary constant for each that results in minimum error by employing the bisection method (Figure 2.4).

3. Out of these five, the value that yields minimum error and adjacent two values



Figure 2.4. Variation of error vs capillary constant at same non-dimensionalized radius of curvature at apex, *B*. Actual drop B = 1.467, c = 13.45 (cm^{-2})

are retained and the other two values are discarded. The span between the remaining three values is divided equally to obtain 2 more values of B where the error is calculated again. This procedure is repeated till the limit of error in B is within $\pm 5e^{-5}$ (Figure 2.5 and 2.6). Typically 10 iterations are required to achieve this accuracy.



Figure 2.5. Error optimization (First iteration). (True B = 1.467, $c = 13.45 \ cm^{-2}$) Points 1-5: Error at initial values of B. Points 1 and 5: Discarded after step 1. Points 6 and 7: New guessed values.



Figure 2.6. Error optimization (Second iteration). (True B = 1.467, $c = 13.45 \text{ cm}^{-2}$) Points 2 and 4: Discarded after step 2. Points 8 and 9: New guessed values.

Figure 2.5 shows the results from the first iteration. Circles (points 1-5) represent the initially guessed values while the squares (points 6-7) represent the new values for the next iteration. (Figure 2.6) shows the results from second iteration. Circles represent data from previous iteration while the squares represent new data points. Comparing the two figures, it is seen that the error in the drop profile reduces for each iteration.

2.2 Code Verification

To test the accuracy with which the code determines the contact angle, a drop profile was generated using the Laplace-Young equation. Twenty one points selected from this profile and the co-ordinates of these points were supplied to the program. The program can be said to operate accurately if the obtained values of b, c and the contact angle are the same as those that were used to generate the profile. Cheng et al. [1990] discusses the effect of the number of points used for edge detection on the resultant contact angle. Significant improvement in accuracy was not seen when more points were selected. Table 2.2 shows the obtained values of b and c and the actual values. Also the corresponding theta that is obtained from the program is shown. The test validates that for a given drop profile the program yields an accurate contact angle. It also shows that twenty one points are sufficient for contact angle calculation. However, selection of more points would result in a better estimation of the drop edge [Neumann and Spelt, 1996] at the expense of computational time.

Actual	(Obtained	
b	С	b	θ
0.15	13.4506	0.1500	159.94
0.20	13.4502	0.2000	159.99
0.25	13.4497	0.2500	159.98
0.30	13.4504	0.3000	159.99
0.35	13.4501	0.3500	159.99
0.40	13.4500	0.4000	160.00
0.45	13.4497	0.4500	159.99
0.50	13.4502	0.5000	159.99
0.75	13.4501	0.7500	159.99
1.00	13.4499	1.0000	159.99
1.50	13.4500	1.5000	159.99
2.00	13.4500	2.0000	159.99

Table 2.2. Code Verification for $\theta = 160^{\circ}$; c = 13.45 cm⁻²

CHAPTER 3. ACCURACY IN CONTACT ANGLE MEASUREMENT

The accuracy in contact angle measurement depends upon the image processing technique that is applied for extracting the drop edge from the sessile drop images. This chapter explains in details the effect of inaccuracies in edge detection on contact angle measurement.

3.1 Drop edge detection



 (\mathbf{c}) Pixelation in Gray-Scale Image

Figure 3.1. Drop Edge Detection (GDL: Toray T060,9%PTFE(wt))

The drop image (Figure 3.1a) is converted into a gray-scale image (Figure 3.1b) by thresholding. The gray-scale image consists of a dark foreground representing the

drop and a white background. The edge of the drop, however, is not accurate as it consists of step changes in the profile (Figure 3.1c). An actual drop profile is expected to be smooth and continuous. In addition, the obtained profile would depend on the value set for thresholding. To obtain the accurate drop edge [Cheng et al., 1990], intensities of pixels along a normal across the drop edge are found (Figure 3.2). The pixel intensities for 11 pixels along with a cubic spline fit is shown in Figure 3.3. From the figure, we see a sharp drop in pixel intensity as we move from the background into the drop. The edge of the drop is expected to be in a region along the spline where the gradient is high. From Figure 3.3, it is evident that there lies an uncertainty in exact edge detection and the edge is therefore approximated to lie in the region of 2-3 pixels along the normal. The effect of this uncertainty on contact angle measurements in explained in detail in Section 3.2. This procedure of finding the edge along the normal is repeated over the entire drop profile. To further increase the accuracy by eliminating the step changes that occur at the edge, a second-order least square polynomial is fitted to 11 adjacent points along the edge, and the drop edge is obtained from these polynomials.



Figure 3.2. Edge Detection Approximation



Figure 3.3. Change in pixel intensity along normal to drop profile. Pixel intensities for Figure 3.2.

3.2 Edge Detection Accuracy

The uncertainty that exists in drop edge detection causes the obtained contact angles to become a function of the methodology that is used for edge detection. The edge, can be defined to lie anywhere along spline with a high gradient (Figure 3.3). To analyze this effect, the region along the spline with steep pixel intensity gradient was selected. The lower limit was obtained by averaging the pixel intensity for the darkest 4 pixels (Pixels 1-4 in Figure 3.3). This limit corresponds to the lowest illumination intensity where the drop can be located. A similar upper limt was set by the 4 brighest pixels (pixels 8-11 in Figure 3.3). However, from Figure 3.3, it is seen that there exists 5 pixels (7-11) that have the intensity of 255 and hence the resulting average of the 4 pixels would also be 255. To eliminate the possibility of an error that could occur when this average intensity is 255, the maximum value upper limit is set at 253. The resulting difference in drop edge co-ordinates as well as the contact angle was found to be miniscule and hence this approximation is considered valid. For situations when the average of the 4 brightest pixels is different from 255, the obtained average is set as the upper limit. Three more equally spaced locations were selected in the region between the upper and lower limits. Figure 3.2 shows the drop edge that is obtained for each approximation. The drop edge obtained by each method would move deeper into the drop as the pixel intensity level is lowered in the algorithm. For this reason, edge obtained by the approximation corresponding to *Position 5* is not appropriate for accurate contact angle determination, but is considered in the analysis.



Figure 3.4. Distribution of $\Delta \theta$ between Position 3 and Positions 1, 2, 4 and 5 for samples in Table 3.1

Different sessile drop images with contact angle varying from 30° to 160° were selected and were processed with these approximations for edge detection and the corresponding contact angle for each method was obtained. Table 3.1 gives details of the samples used to obtain the images for this analysis. Figure 3.4 shows the distribution of error in contact angle that is obtained for positions 1, 2, 4 and 5 when compared with the contact angle obtained for *Position 3*. Table 3.2 summarizes the statistical parameters of the error in contact angle measurements. An explanation for this change in contact angle can be attributed to the change in the drop profile shape that occurs as different edge detection schemes are implemented. For the purpose of edge calculation, data points corresponding to *Position 3*, i.e. midway between the upper and lower limits, are selected following an analogy similar to Cheng et al. [1990].

Substrate	Fluid	Average obtained θ
Plexiglass	80% Tripropylene Glycol - 20% Water	$38^{\circ}\pm2$
Plexiglass	40% Tripropylene Glycol - 60% Water	$57.5^{\circ} \pm 1.8$
Plexiglass	20% Tripropylene Glycol - 80% Water	$67.5^{\circ}\pm 5.5$
RainX	Water	$100^{\circ} \pm 3$
EGC1720	Water	$109^{\circ}\pm 5$
Toray	Water	$158^{\circ} \pm 3$

 Table 3.1.
 Samples used for pixel error estimation

Table 3.2. Variation of Contact Angle with Edge Detection for samples in Table 3.1

	Moon Frror	ean Error Standard Deviation -	95% Region of Certainty		
	Mean Entor		lower limit	Upper limit	
Position 1	0.21	0.65	-0.86	1.28	
Position 2	0.05	0.26	-0.38	0.48	
Position 4	-0.11	0.55	-1.01	0.79	
Position 5	-0.05	2.13	-3.33	3.45	

3.3 Uncertainty in Exact Scale Calculation

The program Scale calculates the scale by analyzing the images of the stage micrometer. The program accounts for any vertical mis-alignments of the micrometer. However, pixelation of image creates an inherent error in scale calculation and the error is of the order ± 1 pixel. To test the effect of this error on contact angle measurements, drop images with different contact angles were analysed by inducing error in the obtained scale. Error of ± 1 , ± 2 pixels per millimeter was induced in the scale calculation and the results were compared with actual calculated scale.



Figure 3.5. Error in Contact Angle Measurements with Error in Scale Calculation

Mea	Moon Frror	Standard Doviation	ndard Deviation 95% Region of Certa	of Certainty
	Mean Entor Stan	Standard Deviation	Lower limit	Upper limit
± 1 Pixel	3.2e-4	0.03	-0.05	0.05
± 2 Pixels	5.5e-5	0.03	-0.06	0.06

Table 3.3. Variation of Contact Angle with Edge Detection

Figure 3.5 shows the distribution of error of ± 1 and ± 2 pixels per millimeter, calculated against the contact angles obtained with no error in scale. Table 3.3 shows the statistical data for the same test. From the results it is evident that errors in the estimation of the scale for the drop images have no effect on contact angle measurements. This is because the the drops are non-dimensionalized using the capillary constant and it accommodates errors in absolute scale calculation. However, with an incorrect scale physical drop properties cannot be calculated accurately.

3.4 Illumination Control

Apart from estimation required to select the cutoff point for edge detection discussed in Section 3.2, the brightness of the source of illumination affects the obtained profile and hence the contact angle measured by ADSA. If the source is too bright, it causes the drop edge to move inside the drop when compared to the image with ideal brightness. To minimize this effect, an image of a needle of known outer diameter is taken and its diameter is measured. The gain of the camera is changed until the calculated diameter of the needle from the images compare to the actual diameter of the needle.

3.5 Solid-Liquid Interface Detection

The accuracy with which the solid-liquid interface, i.e. the surface of the substrate is detected plays a very important part in determining an accurate contact angle. After the fit between the Laplacian curve and the drop profile is made, the co-ordinates of the substrate's surface are used to cut-off the Laplacian curve and at this point the angle is calculated. For smooth surfaces, reflection from the surface aids in better detection of the solid-liquid interface (Figure 3.6a). The rough and porous surface of GDL makes it difficult to detect the interface (Figure 3.6b). In addition, very high contact angles found on GDLs further hampers the ability to detect the exact interface and unless it becomes almost impossible to detect the interface within an accuracy of ± 1 pixel.

An attempt has been made to test the effect of error in solid-liquid interface detection in contact angle measurement. For this purpose, theoretical drop profiles



(a) Sessile Drop on Smooth Surface

(b) Sessile Drop on GDL

Figure 3.6. Error in Contact Angle Measurements with Error Solid-Liquid Interface Detection. Scale = 2μ m/pixel

were generated using different values of b. Error of ± 0.5 and ± 1 pixels was induced.. Error of -1 pixel indicate the location of interface was detected above the original location by 1 pixel. Simply, it means the drop height reduced by 1 pixel. Similarly, error of +1 pixel indicates an increase of 1 pixel in drop height.

Before the comparison is made, it is important to note that different magnifications used for capturing the drop images alter the dimensions of pixels in the image. Thus different drops will have a different resultant error even if they have a same magnitude of pixel error. The effect of inaccuracies in solid-liquid interface determination was calculated by generating drops of different sizes by varying b from 0.1 to 1 cm. Figures 3.7 and 3.8 show the error in contact angle calculation when the error in interface detection was varied from -1 pixel to +1 pixel. Figure 3.7 shows the error when the magnification is 2μ m/pixel while Figure 3.8 corresponds to a magnification 5μ m/pixel. These values of magnification were selected as they approximately represented the maximum and minimum magnification that could be obtained in the experimental apparatus. A discrepency is seen in Figure 3.8d for $\theta = 170^{\circ}$. This is because at $\theta = 170^{\circ}$, an error of +1 pixel causes the resulting contact angle to exceed 180°. As 180° is the maximum contact angle that can exist, error is restricted to 10°. Following points can be asserted from these figures:

- For constant magnification and solid-liquid pair and the same error in interface estimation
 - Smaller drops result in a larger error as compared to bigger drops at constant contact angle.

- Contact angle regimes of $\theta < 30^{\circ}$ and $\theta > 140^{\circ}$ are largely dependent on the accuracy of interface detection
- Beyond θ =50° the calculated contact angle becomes highly sensitive to the calculated interface. In this regime, accurate calculation of the solid-liquid interface is of utmost importance.
- Higher magnifications, i.e., more pixels per mm yield a smaller error than lower magnifications



Figure 3.7. Error in Contact Angle Measurements with Error Solid-Liquid Interface Detection. Scale = $2\mu m/pixel$

In the program, the soild-liquid interface surface is calculated by finding the intensities of pixels normal to the surface. The pixel with maximum intensity gradient is then found along this normal. This procedure is repeated over the entire visible surface of the substrate (part of the substrate without the drop). A straight line is fitted to these points of maximum intensity gradients by the method of least squares. This line is approximated at the surface of the solid and the location where the drop profile intersects this line is the calculated solid-liquid interface. If the automated procedure fails to locate the solid-liquid interface, the program images_reader is run which allows the user to reposition the interface.



Figure 3.8. Error in Contact Angle Measurements with Error Solid-Liquid Interface Detection. Scale = 5μ m/pixel

CHAPTER 4. EXPERIMENTAL PROCEDURE

4.1 Experimental Setup



Figure 4.1. Schematic Diagram of experimental setup for ADSA

The contact angle measurement apparatus, shown in Figure 4.1, consists of a source of illumination, the stage to place the drops and a microscope coupled to CCD camera. Köhler illumination is used as it provides a beam of light of equal intensity. This helps in producing drop images with a good contrast between the drop and the background. The stage consists of an X-Y translation stage (Velmex AXY2509W1) on which a labjack (Thorlabs L200) is mounted which enables X-Y-Z movement. A long distance microscope (Infinity K2/S) is coupled to a CCD camera (PULNIX TM-1325CL). The camera is connected to framegrabber (EPIX EL1DB) and the images are captured using EPIX XCAP, a software that controls the camera on IBM Intellistation Z Pro (6223-7BU) workstation.

Figure 4.2 shows the stage of the experimental apparatus with the heat enclosure installed. The top of the stage consists of a copper block which is heated by four thermo-electric heaters (Marlow Industries DT12-6-01L). The temperature is controlled by varying the voltage across the heaters. The heat enclosure consists of two glass windows through which drop images are taken. The glass is coated with Indium-Tin Oxide which is heated by passing current through it. Heating of the glass prevents condensation of water vapor at higher temperatures on the glass when the enclosure is humidified.



Figure 4.2. Image of the stage with enclosure

Figure 4.3 shows the setup that is used for the formation of advancing and receding drops on the GDL. This unit is placed inside the heat enclosure during dynamic contact angle measurements. Figure 4.3a shows the disassembled unit whereas Figure 4.3b shows the assembled unit with a GDL attached to the unit. The hypodermic needle is connected to a PTFE coated tubing. The other end of the tubing is coupled to the syringe pump.

Before the drop images are taken, a scale factor is needed to identify the dimension of the drop. For this purpose, after the magnification and the focus of the microscope is set, an optical micrometer (Larman Rulings KR 812) is placed on the stage at the focal point of the microscope and an image of the micrometer is captured. This image is used to calculate the scale factor and hence determine the dimensions of the drop.



(a) Liquid Injection Setup (Disassembled)

(b) Liquid Injection Setup (Assembled)

Figure 4.3. Setup for liquid infusion and withdrawl

4.2 Static Measurement

To measure the static contact angle, a drop of liquid is formed on the tip of the hypodermic needle attached to a screw syringe. The syringe is fastened to a stand which reduces any irregularities that are produced by manual drop deposition. The substrate is then raised till it touches the drop using the Y control of the stage. The drop is the then brought into the field of view and onto the focal point of the microscope by x-y translation of the stage and image is captured.

4.3 Dynamic Contact Angle Measurement

For measurement of advancing contact angle, syringe pump is used to inject fluid continuously at a constant rate. The GDL substrate is attached to the top of aluminum plate using Kapton tape. A small hole is punched on the GDL. The size of the piercing is kept close to the diameter of the needle used for injecting the liquid. This is done as safety precaution to prevent the fluid from seeping through the hole and beneath the GDL. A series of images is captured at constant time rate from which advancing contact angles are obtained. At the end of the sequence, the syringe pump is reversed and water is withdrawn from the drop.

4.4 Humidity Control

As the temperature increases the amount of water vapor in the air needed for saturation increases. If the air is not humidified, the water drops formed for measurements will evaporate and hence the obtained contact angle will deviate from the actual one. Humidity is increased by placing water filled containers in the heat enclosure. To check and the rate of evaporation, a very small droplet of water (approximately 2- 3μ l) is injected in the chamber at set temperature and the time required for the drop to evaporate is measured. Evaporation rate of less than 0.5μ l/min, was considered satisfactory for the experiment to be carried on.

Sessile drops are formed by injecting water through a small hole in the GDL substrate by a hypodermic needle. Teflon tubing is used to pass water from the syringe to the needle. The temperature of the enclosure is increased by increasing the voltage across the thermo-electric heaters. Once the plate, on which the GDL substrate is kept, reaches the desired temperature, the voltage is kept constant and the enclosure is kept in the same state for a period of 20-30 min. This allows the entire chamber to attain an equilibrium temperature. Around 5-6 inches of the tube is present in the heat chamber and is in contact with the heated copper plate allowing the water to attain the equilibrium temperature. This ensures the temperature of water is same as that of experimental temperature.

CHAPTER 5. RESULTS

With aim to understand the wetting characteristics of fuel cells, different GDL samples were tested under static and dynamic conditions and also at different temperatures. The GDL samples with composition are shown in Table 5.1. SEM images of the tested samples in shown in Figure 5.1. PTFE coating in the samples is seen as the webbing in between the fibers. Apart from Freudenberg which has intertwined structure, all other samples consists of carbon fibers. Pore size distribution for three samples is shown in Table 5.2.

Table 5.1. GDL samples tested

Baseline	Mitsubishi MRC 105 9% PTFE (weight) with MPL
SGL	SGL 25 BC
Freudenberg	Freudenberg H2315 with MPL
Toray	Toray TFP-H-060 7% PTFE

Table 5.2. Pore size distribution of the tested GDL samples (Nishith Parikh, MTU, unpublished data)

	SGL	Freudenberg	Toray
Average Pore Radius (μm)	8.25	15.92	13.2
Standard Deviation	8	19.5	9.75


Figure 5.1. SEM images of GDL samples tested for contact angle measurement

5.1 Asymmetry in Drop Profile

The surface of a GDL is highly rough and porous. The contact angle obtained on such a surface becomes dependent on the profile of the surface where the drop is deposited. This results in different contact angles on the left and right side of the drop. Figure 5.2 shows the image of a water drop on Toray obtained during advancing contact angle measurements. From the figure, it is seen that the contact angle at the left side of the drop is lower than the angle on the right side of the drop. During dynamic contact angle measurements, in many runs, pinning of the drop on one side occured while the movement of the contact line would take place on the other side. For such cases, only the data on the side with contact line movement is considered.

Temperature	Equatorial	θ	θ	Difference
(°C)	Radius (cm)	Left	Right	in θ
	0.109	153.8	152.7	1.1
	0.088	153.7	151.9	1.8
25	0.11	156.2	153.1	3.1
	0.100	154.0	155.8	1.8
	0.124	151.8	154.0	3.2
	0.080	153.9	152.5	1.6
	0.127	158.0	153.5	4.5
55	0.089	152.1	151.7	0.4
	0.088	154.5	153.9	0.6
	0.923	154.8	155.5	0.7
	0.086	154.2	152.8	1.1
	0.103	153.7	156.4	0.7
85	0.093	154.6	155.8	1.2
	0.096	153.1	153.7	0.6
	0.089	153.3	151.7	1.6

Table 5.3. Difference in Contact Angle for Left and Right Side of Drop.Fluid: Water, Substrate: Toray



Figure 5.2. Difference in θ between left and right side of drop

5.2 Static Contact Angle Data

The static contact angle was measured on GDLs using the technique explained in 4.2. Figure 5.3 shows the observed variation in contact angle with respect to the equatorial radius at different temperatures. The mean contact angle obtained for the four GDL samples at different temperatures is shown in Table 5.4. Extremely rough and porous surface of the GDLs results in large hysteresis. Depending upon the placement of the drop, the contact area as well as the contact line develop different configurations and causes this hysteresis. Also some of the fibers protruding from the surface create additional contact zones over the drop surface altering the drop into an asymmetric drop. In such asymmetric drops, the obtained contact angle is then dependent on the cross-section plane of which the image was taken, as along different cross-sections different profiles would be obtained. Miller et al. [1996] and Veeramasuneni et al. [1997] observed an increase in both advancing and receding contact angles for thin film PTFE coatings with increasing roughness in nanoscale regime. However, the only data that is available pertaining to the structure of GDLs is the pore size distribution and from the results, concrete conclusion cannot be drawn regarding the drop size or temperature dependence of contact angle on GDL.



Figure 5.3. Static Contact Angle on Baseline vs temperature

GDL	$25^{\circ} \mathrm{C}$	$55^{\circ} \mathrm{C}$	85° C	
Mitsubishi	154.2 ± 3	154.8 ± 3.5	154.3 ± 3.5	
SGL 25BC	151.7 ± 4	149.1 ± 4.5	150.5 ± 3	
Freudenberg	148.2 ± 4.5	147.5 ± 5	145.8 ± 4.5	
Toray T060	154.7 ± 3	153.6 ± 2.5	154.3 ± 2	

Table 5.4. Mean static contact angle on GDLs at different temperatures

5.3 Dynamic Contact Angle on GDL

Advancing and receding contact angles were measured on the samples and the results are plotted in Figure 5.5 through 5.12. Figure 5.4 shows the variation in contact angle that was observed when multiple runs were carried out on the same sample. Different runs result in a wide range of advancing contact angles for the same sample, the cause of which can be attributed to reasons explained previously in Section 5.2. On Baseline, Freudenberg and Toray, lower advancing contact angles were obtained at higher temperatures. On SGL, a similar behavior is observed for smaller drops. However at larger drop size, this change became negligible. Low contact angles observed on Baseline and Toray for small drop sizes is observed because of the contact line being pinned and the drops size being increased.



Figure 5.4. Advancing Contact Angle on Toray obtained for 3 test runs at 25° C

The receding contact angles however show a definite reduction in contact angle as the temperature is increased. As the drop volume is reduced, the contact line would move towards the needle. But beyond a certain point, it would be pinned



Figure 5.5. Advancing Contact Angle on Mitsubishi vs temperature

and the angle would keep reducing. This phenomenon was more evident at higher temperature.

For a Cassie drop with air trapped in the pores, the hysteresis is much less as compared to a Wenzel drop (He et al. [2004] and Marmur [2004]) as the drops rests on the peaks of rough surfaces, whereas in Wenzel wetting, the drops are heavily pinned. From the results, a large difference between the advancing and receding



Figure 5.6. Receding Contact Angle on Mitsubishi vs temperature



Figure 5.7. Advancing Contact Angle on SGL vs temperature

contact angles is observed and hence Wenzel wetting occurs on GDLs. This type of wetting is also expected during the operation of fuel cell as water droplets are formed in the pores and on the GDL.

Another observation that was made during experiments was the vibration of sessile drops on hydrophobic GDLs at larger drop volumes. For a sessile drop with high contact angle, a large volume of the drop is supported on a small contact area. At



Figure 5.8. Receding Contact Angle on SGL vs temperature



Figure 5.9. Advancing Contact Angle on Freudenberg vs temperature

high drop volumes, typically 50-60 μ l and above, the drop starts to vibrate because of the small vibrations that exists in the stage. This produces a large variation in the measured contact angle at high drop volumes.

Receding contact angle at 25 °C on Mitsubishi GDL in Figure 5.6 is replotted in Figure 5.13c. A large discontinuity in contact angle is visible between the data points at A (Figure 5.13a) and B (Figure 5.13b). Smaller discontinuities are also visible



Figure 5.10. Receding Contact Angle on Freudenberg vs temperature



Figure 5.11. Advancing Contact Angle on Toray vs temperature

at points C, D and E. These jumps in contact angles occur when the contact line moves rapidly from one position to another as the drop volume is reduced. Such a variation in contact angle due to rapid contact line motion is seen on other GDLs as well. Movement of the contact line also affect the advancing contact angle and it manifests as the wavy or oscillatory trend in advancing contact angles. If the contact line is pinned or moves slowly, increase in the drop volume results in an increase in



Figure 5.12. Receding Contact Angle on Toray vs temperature



Figure 5.13. Receding Contact Angle on Mitsubishi

the contact angle. Beyond a certain value, represented by the 'peaks', the contact line moves rapidly which causes the contact angle to reduce. This phenomenon repeats resulting in the oscillatory nature of the advancing contact angles.

CHAPTER 6. CONCLUSION

6.1 Summary

A program to determine the contact angle has been developed in MATLAB[®]. The program is automated to analyze multiple images which enables the calculation of advancing and receding contact angles. The contact angles are determined by fitting an ideal sessile drop profile curve obtained from the Laplace-Young equation with the drop edge profile obtained from the drop images. The existing setup for the measurement of contact angles was modified to incorporate a heat enclosure to maintain the humidity at higher temperatures, which is necessary to prevent droplet evaporation. The new setup allows for injection and removal of water on the surface of GDL from which advancing and receding contact angles are obtained. Also, these measurements were performed at different temperatures.

Accuracy in contact measurement is dependent on the drop deposition method, drop profile acquisition method and the accuracy in determining the solid-liquid interface. For drops with contact angles less than 90° on a smooth surface, solid-liquid interface in determined with high accuracy making the results more accurate. For GDLs, the high contact angles coupled with porous and rough fibrous surface restricts the accuracy in determining the contact angles.

Pixelation of drop images induces uncertainty in the contact angle measurement. As the drop edge obtained from image processing deviates more from the actual drop profile, the uncertainty increases. Incorrect scale calculations produce no effect on the contact angle obtained from images. At high contact angles, the inability in exact solid-liquid interface detection further increases the error.

Advancing and receding and contact angles were collected for four GDL samples at three different temperatures. Contact angle hysteresis that exists on GDL samples hinders any concrete conclusion to be drawn from the experimental results for advancing measurements. Advancing Contact angles obtained from multiple runs on GDLs result in a wide range of values which are comparable to that obtained at other temperatures. A decrease in receding contact angle is observed as the temperature is increased in all samples except SGL. Static contact angles obtained on GDL are dependent on the drop deposition technique.

6.2 Recommendations

Experiments to measure contact angles on GDLs should be performed with care and precision as the hysteresis produces a large variation in results. For a better understanding of the wetting characteristics of the GDLs more experiments need to be performed. This will allow a better statistical analysis of wetting in GDLs. Also, the experiments were performed on new or unused samples. Similar experiments should be conducted on 'end-of-life' samples as it may be helpful in understanding the changes that take place in the wetting characteristics of GDLs during the life cycle.

APPENDICES

APPENDIX A. ABBREVIATIONS

θ	Contact angle
θ_a	Advancing contact angle
θ_r	Receding contact angle
$ heta_C$	Cassie-Baxter's contact angle
θ_Y	Young's contact angle
$ heta_W$	Wenzel's Contact Angle
ρ	Density
σ	Surface tension
σ_{LV}	Liquid-vapor interfacial tension
σ_{SL}	Solid-liquid interfacial tension
σ_{SV}	Solid-vapor interfacial tension
ADSA	Axisymmetric Drop Shape Analysis
b	Radius of curvature at apex
В	Non-dimensional radius of curvature at apex
Bo	Bond number
С	Capillary constant
f	Fractional Area
g	Gravitational constant
GDL	Gas Diffusion Layer
p	Perimeter
ΔP	Change in pressure
ΔP_g	Change in hydrostatic pressure
ΔP_{σ}	Change in pressure across curved interface
PEM	Proton Exchange Membrane
PTFE	Polytetrafluoroethylene
R_1	First principal radius of curvature
R_2	Second principal radius of curvature
r	Roughness factor
s	Arc Length of drop surface
S	Non-dimensional arc Length of drop surface

ΔW	Change in weight
x	Horizontal distance
X	Non-dimensional horizontal distance
z	Vertical distance
Z	Non-dimensional vertical distance

APPENDIX B. CONTACT ANGLE MEASUREMENT PROGRAMS

2.1 scale

	0 0	<pre>% This function creates sc.mat which conta the</pre>	ins the sc	ale fac	tor	for	
	0 0	% drop images. Enter the number of scales a	taken and	import	them		
	0 0	% First zoom the images and select a suital line	ble point	on the	left	most	
5	0 0	<pre>% which has uniformly varying pixel intens. the</pre>	ity. Then	select	the	top	or
	0 0	<pre>% bottom part of the same line used initia. rightmost</pre>	lly. Do th	e same	for		
	0 0	% line. Enter the scale im mm for each imag	ge				
	00	0 0 0 0					
10	2	a - input (leptor number of gapled). & En	tor the nu	mbor of		10	
	d	images	lei the nu	MDEL OI	SCa	16	
	sc	<pre>scale img = zeros(1,a);</pre>					
	pi	pix_ind_x = -7:1:7; % Piz	xels used	for spl	ine	fit	in
		X					
15	nc	nop = 30;					
	fc	for j = 1:a					
		<pre>pix_x = zeros(nop,length(pix_ind_x));</pre>					
20		pix_z = pix_x;					
		% Opens filepath of previously opened :	folder				
		<pre>oldpath=char(textread('filepath.dat','?</pre>	ks','white	space',	''))	;	
		% Lets user select full filepath of ima	age graphi	cally			
25		[filename,filepath]= uigetfile ([oldpath,	,'*.tif'],	'open f	ile:	');	

```
fid=fopen('filepath.dat','w');
      fprintf(fid, '%s', filepath);
      fclose(fid);
30
      % Saves image to 'scale_fig' from specific filepath as selected
         above
      scale_fig = imread([filepath, filename]);
      figure, imshow(scale_fig, [])
35
      x \text{ top} = \text{zeros}(1, 2);
                                        % x coordinate of top/bottom
      z_top = zeros(1,2);
                                        % z coordinate of top/bottom
      for k = 1:2
          figure, imshow(scale_fig, [])
40
          pause(7);
          if k == 1
                                               % Select scale points
              [x1, z1]=ginput(1);
          else
              [xr, zr]=ginput(1);
                                              % Select scale points
45
          end
          pause(5)
          [x_top(k) z_top(k)] = ginput(1); % Select top point for
             tilt
      end
      x_1(1:nop) = (x1-(nop/2)+1):1:(x1+nop/2);
50
      z_1(1:nop) = zl;
      x_r(1:nop) = (xr-(nop/2)+1):1:(xr+nop/2);
      z_r(1:nop) = zr;
      pixel_index_l = zeros(nop,length(pix_ind_x)); % Pixel intensity
55
         saved here
      pixel_index_r = zeros(nop,length(pix_ind_x)); % Pixel intensity
         saved here
      for k = 1:nop
          pix_x_l(k,1:length(pix_ind_x)) = round(x_l(k)) + pix_ind_x;
          pix_z_l(k,1:length(pix_ind_x)) = round(z_l(k));
60
          for m = 1:(length(pix_ind_x))
              pixel_index_l(k,m) = double(scale_fig(pix_z_l(k,m),
                 pix_x_l(k,m)));
          end
65
      end
      for k = 1:nop
          pix_x_r(k,1:length(pix_ind_x)) = round(x_r(k)) + pix_ind_x;
          pix_z_r(k,1:length(pix_ind_x)) = round(z_r(k));
```

```
for m = 1:(length(pix_ind_x))
                                         pixel_index_r(k,m) = double(scale_fig(pix_z_r(k,m),
                                                   pix_x_r(k,m)));
                              end
                   end
  75
                   tilt = atand((z_top(2)-z_top(1))/(x_top(2)-x_top(1)));
                  multiplier = (z_top(2)-z_top(1))/cosd(tilt)-(z_top(2)-z_top(1));
                  n pts = length(pix ind x);
                   x_opt_l = zeros(1, nop);
  80
                   x_opt_r = zeros(1, nop);
                   % Fits a spline curve and finds location of minimum pixel
                             intensity
                   for k = 1:nop
                             base_pts_x = linspace(pix_x_1(k,1),pix_x_1(k,end),(n_pts*100)
  85
                                       +1);
                              spline_fit_x = spline(pix_x_l(k,:),pixel_index_l(k,:),
                                       base_pts_x);
                              x_opt_l(k) = base_pts_x(find((spline_fit_x) == min())
                                       spline_fit_x),1,'first'));
                   end
  90
                   for k = 1:nop
                              base_pts_x = linspace(pix_x_r(k,1),pix_x_r(k,end),(n_pts*100)
                                       +1);
                              spline_fit_x = spline(pix_x_r(k,:),pixel_index_r(k,:),
                                       base_pts_x);
                              x_opt_r(k) = base_pts_x(find((spline_fit_x) == min(
                                       spline_fit_x),1,'first'));
                   end
 95
                   for k = 1:nop
                   pixels(k) = x_opt_r(k)-x_opt_l(k);
                   end
                                                 = input ('Enter size of scale in mm: ');
                              mm
                                      = mm/10;
100
                   CM
                   scale_all = zeros(nop, 1);
                   for k = 1:nop
                   scale_all(k) = (abs(pixels(k)/cm)) + ((abs(z_top(2)-z_top(1)))/(abs(z_top(2)-z_top(1)))) = (abs(z_top(2)-z_top(1))) = (abs(z_top(2)-z_top(2)-z_top(1))) = (abs(z_top(2)-z_top(2)-z_top(1))) = (abs(z_top(2)-z_top(2)-z_top(1))) = (abs(z_top(2)-z_top(2)-z_top(1))) = (abs(z_top(2)-z_top(2)-z_top(1))) = (abs(z_top(2)-z_top(2)-z_top(2)-z_top(1))) = (abs(z_top(2)-z_top(2)-z_top(2)-z_top(2))) = (abs(z_top(2)-z_top(2)-z_top(2)-z_top(2))) = (abs(z_top(2)-z_top(2)-z_top(2))) = (abs(z_top(2)-z_top(2)-z_top(2)-z_top(2))) = (abs(z_top(2)-z_top(2)-z_top(2)-z_top(2))) = (abs(z_top(2)-z_top(2)-z_top(2))) = (abs(z_top(2)-z_top(2)-z_top(2)-z_top(2))) = (abs(z_top(2)-z_top(2)-z_top(2))) = (abs(z_top(2)-z_top(2))) = (abs(z_top(2)-z_top(2))) = (abs(z_top(2)-z_top(2))) = (abs(z_top(2)-z_top(2))) = (abs(z_top(2)-z_top(2))) = (abs(z_to
105
                            x_l(k)-x_r(k))) *multiplier;
                   end
                   scale_img(1,j) = mean(scale_all);
       end
```

70

save sc.mat scale_img;

% eof

2.2 needle Scale

```
clc
  clear
  close all
  no_p = 41;
                            %Max permitted value 100
5 k = 1;
  filepath = 'C:\ABCD\ABCD\'; % Enter filepath
  filename = ('needle.tif'); % Enter filename
10 needle_img_uint = imread([filepath,filename]);
  needle_img = double(needle_img_uint);
  figure, imshow(needle_img, [])
15 pause(5)
  [x, z]=ginput(4);
  %% For left side
  Z_1 = (round(z(1)):1:round(z(2)));
20 \ Z_r = (round(z(3)):1:round(z(4)));
  X_1 = round((x(1)+x(2))/2);
  X_r = round((x(3)+x(4))/2);
25 for j = 1:length(Z_1)
      pixel_ind = X_l+ ((-no_p):1:(no_p));
      for k = 1: (no_p * 2 + 1)
      pixel_data(k) = needle_img(Z_l(j),pixel_ind(k));
30
      end
      ind = find(pixel_data < 80,1,'first');</pre>
     mean_top = mean(pixel_data(1:ind));
35
      mean_bot = mean(pixel_data((ind+1):end));
      avg_int = (mean_top+mean_bot) /2;
40
      base_pts = linspace(pixel_ind(1),pixel_ind(end),(no_p*200));
      spline_fit = spline(pixel_ind, pixel_data, base_pts);
      diff_int = abs(avg_int - spline_fit);
```

```
45
      x_l(j) = base_pts(find(min(diff_int)==diff_int));
      k = k+1;
  end
50
  %% For right side
  for j = 1:length(Z_r)
55
      pixel_ind = X_r+ ((-no_p):1:(no_p));
      for k = 1: (no_{p*2+1})
      pixel_data(k) = needle_img(Z_r(j),pixel_ind(k));
      end
60
      ind = find(pixel_data < 80,1,'first');</pre>
      mean_top = mean(pixel_data(1:ind));
65
      mean_bot = mean(pixel_data((ind+1):end));
      avg_int = (mean_top+mean_bot) /2;
70
      base_pts = linspace(pixel_ind(1),pixel_ind(end),(no_p*200));
      spline_fit = spline(pixel_ind, pixel_data, base_pts);
      diff_int = abs(avg_int - spline_fit);
      x_r(j) = base_pts(find(min(diff_int)==diff_int));
75
      k = k+1;
  end
80 x_mean_l = mean(x_l);
  x_mean_r = mean(x_r);
  scale_pic = x_mean_r - x_mean_l;
85 load sc.mat
  Diamater_needle = scale_pic/scale_img
  % eof
```

2.3 Contact Angle Measurement Program

% Main program for contact angle measurement

clear close 5 **clc** %% Load scale load sc.mat % loads previously saved scale S_span=(0:.0001:3.5); % S_span is the step variable for ode45 solver 10 *%% Analysis parameters* % These parameters affect the number of points and their location on drop profile where calculations are done No ind = 21;% No of points where fit is calculated; 15 No_pt_slp = 16; % No of pts used for quadratic fit on each side $dif_slp = 3;$ % Difference in pixels for slope calcutation % difference between the end pt on the drop and cut off = 17;last pt where error is calculated %% Load properties and images 20total_imgs = input('Enter total number of images'); % Number of images total_scl = input('Enter total number of scales'); % Number of scales expt_type = input('Entrer the type of experiment: 1-Static, 2-Advancing'); % Type of Experiment 25 prefix_img = input('Enter a prefix if it exists (Press Enter if nothing exist)'); % Prefix to image number start_no_img = input('Enter Image Start Number'); % Number of 1st image range_lim = input ('Range of images: For 1-10 Enter 1 For 11-99 Enter 2 For 101-999 Enter 3 '); % The Range of images file_location = input('Enter Filepath (ex: C:\Folder\Folder\ Image_Folder\) :','s')'; % Location of images file_location = file_location'; 30 d_side = input('Enter side for More accuracy: Left = 1, Right = 2, Both = 3 : '); % The side where more accuracy is needed A = struct('scale_i',{},'folder_i',{},'file_i',{},'x_data_all_i',{},' z_data_all_i',{},'x_l_i',{},'z_l_i',{},'x_r_i',{},'z_r_i',{},' apex_x_i',{},'apex_z_i',{},'xpl_i',{},'zpl_i',{},'xpr_i',{},'zpr_i

```
',{}); % Structure for variables
                                      % Variable to store data
35 Data = zeros(total_imgs,13);
  Err_data = zeros(total_imgs,72); % Variable to store data
  for i = 1:total_imgs
      [I,A(i).folder_i,A(i).file_i] = image_input(i,expt_type,
40
         prefix_img,start_no_img,range_lim,file_location); % Images
         input here
      [BW, A(i).IC i]
                                     = image_analysis(I); % Image
         converted to Black and White
                                     = edge_detector(BW); % Boundary of
      [boundary]
      [mean_l,mean_r,A(i).xpl_i,A(i).xpr_i,A(i).zpl_i,A(i).zpr_i ] =
         plane( A(i).IC_i, boundary ); % Detects the solid-liquid
         interface
      [A(i).x_data_all_i, A(i).z_data_all_i, A(i).x_l_i, A(i).z_l_i, A(i).
         x_r_i,A(i).z_r_i,A(i).apex_x_i,A(i).apex_z_i] = profile_split(
         boundary,mean_l,mean_r); % Data points obtained
45
      close all
      display(A(i).file_i);
      if total_scl > 1
          scl = input('Enter scale number');
          A(i).scale_i = scale_img(scl);
      else
50
          A(i).scale_i = scale_img(1,1);
      end
  end
55 clear I_sobel I BW boundary
  %% Main loop
  for r = 1:total_imgs
60
      folder
                  = A(r).folder_i;
      file
                  = A(r).file_i;
      scale
                  = A(r).scale_i;
                  = A(r).IC_i;
      IC
      x_data_all = A(r).x_data_all_i;
65
      z_data_all = A(r).z_data_all_i;
      x_l
                  = A(r) \cdot x_l_i;
                  = A(r) \cdot z_l_i;
      z_l
      x_r
                  = A(r) \cdot x_r_i;
                  = A(r) \cdot z_r_i;
70
      z_r
      apex_x
                  = A(r).apex_x_i;
      apex_z
                  = A(r).apex_z_i;
      xpl i
                  = A(r).xpl_i;
```

```
zpl_i
                   = A(r).zpl_i;
      xpr_i
                   = A(r).xpr_i;
75
       zpr_i
                    = A(r).zpr_i;
       %% Indices of the points for left profile
80
       ind_l = floor(0:((length(x_l)-cut_off)/(No_ind-1)):(length(x_l)-
          cut_off));
       ind_r = floor(0:((length(x_r)-cut_off)/(No_ind-1)):(length(x_r)-
          cut_off));
       %% This finds the points where the average of slope is calculated
85
       if ind_l(2) < (No_pt_slp+2) || ind_r(2) < (No_pt_slp+2)
           No_pt_slp = min(abs((ind_1(2)-1)), abs((ind_r(2)-1)));
       end
90
       x_avg_slope_l = zeros(No_ind, (2*No_pt_slp+1));
       z_avg_slope_l = x_avg_slope_l;
      for k = 2:No_ind
95
           ind_slope = (-No_pt_slp:1:+No_pt_slp)+ind_l(k);
           x_avg_slope_l(k,:) = x_l(ind_slope);
           z_avg_slope_l(k,:) = z_l(ind_slope);
       end
100
      x_avg_slope_r = zeros(No_ind, (2*No_pt_slp+1));
       z_avg_slope_r = x_avg_slope_r;
       for k = 2:No ind
           ind_slope = (-No_pt_slp:1:+No_pt_slp)+ind_r(k);
105
           x_avg_slope_r(k,:) = x_r(ind_slope);
           z_avg_slope_r(k,:) = z_r(ind_slope);
       end
110
      %% Finds the average slope
       avg_slope_l = zeros(No_ind, 1);
       if (2*No_pt_slp+1)-(2*dif_slp) == 0
           dif_slp = dif_slp -1;
115
       elseif (2*No_pt_slp+1)-(2*dif_slp) == -1
           dif_slp = dif_slp -2;
       end
      for k = 2:No ind
120
```

49

```
slope_temp = zeros(1, ((2*No_pt_slp+1)-(2*dif_slp)));
           for j = (dif_slp+1):(2*No_pt_slp+1)-dif_slp
                                            % slope carried bet 3 pts
               slope_temp(k,j-dif_slp) = (z_avg_slope_l(k,j+dif_slp)-
                   z_avg_slope_l(k,j-dif_slp))/(x_avg_slope_l(k,j+dif_slp
                   )-x_avg_slope_l(k,j-dif_slp));
           end
           avg_slope_l(k,1) = mean(slope_temp(k,:));
125
       end
       avg_slope_r = zeros(No_ind, 1);
       for k = 2:No ind
130
           slope_temp = zeros(1, ((2*No_pt_slp+1)-(2*dif_slp)));
           for j = (dif_slp+1):(2*No_pt_slp+1)-dif_slp
                                            % slope carried bet 3 pts
               slope_temp(k,j-dif_slp) = (z_avg_slope_r(k,j+dif_slp)-
                   z_avg_slope_r(k,j-dif_slp))/(x_avg_slope_r(k,j+dif_slp))
                   )-x_avg_slope_r(k,j-dif_slp));
           end
           avg_slope_r(k,1) = mean(slope_temp(k,:));
135
       end
       %% check_l/r is used to vary the pixel direction
140
       check_l = zeros(No_ind, 1);
       for k = 1:No ind
           if avg_slope_1(k,1) ≥0 && avg_slope_1(k,1) ≤ tan(22.5*pi/180)
145
               check l(k) = 1;
           elseif avg_slope_1(k,1) > tan(22.5*pi/180) && avg_slope_1(k
              (1) \leq \tan(67.5 * pi/180)
               check_l(k) = 2;
           elseif avq_slope_1(k,1) > tan(67.5*pi/180) || avq_slope_1(k
150
              (1) \leq \tan(112.5 * pi/180)
               check_l(k) = 3;
           elseif avg_slope_1(k,1) > tan(112.5*pi/180) && avg_slope_1(k
               (1) \leq \tan(157.5 * pi/180)
               check_l(k) = 4;
155
           elseif avg slope 1(k,1) > tan(157.5*pi/180) && avg slope 1(k
              ,1) < 0
               check l(k) = 5;
           end
```

160end check_r = zeros(No_ind, 1); for k = 1:No_ind 165**if** avg_slope_r(k,1) ≥0 && avg_slope_r(k,1) ≤ **tan**(22.5***pi**/180) $check_r(k) = 1;$ 170 elseif avg_slope_r(k,1) > tan(22.5*pi/180) && avg_slope_r(k $(1) \leq \tan(67.5 * pi/180)$ $check_r(k) = 2;$ elseif avg_slope_r(k,1) > tan(67.5*pi/180) || avg_slope_r(k $(1) \leq \tan(112.5 * pi/180)$ 175 $check_r(k) = 3;$ elseif avg_slope_r(k,1) > tan(112.5*pi/180) && avg_slope_r(k $(1) \leq \tan(157.5 * pi/180)$ $check_r(k) = 4;$ elseif avg_slope_r(k,1) > tan(157.5*pi/180) && avg_slope_r(k (1) < 0180 $check_r(k) = 5;$ end end 185%% Finds the Data points on drop profile [x_sub_l, z_sub_l] = pixel_data(x_data_all, z_data_all, x_l, z_l, apex_x,apex_z,No_ind,No_pt_slp,ind_l,check_l,IC); [x_sub_r, z_sub_r] = pixel_data(x_data_all, z_data_all, x_r, z_r, apex_x, apex_z, No_ind, No_pt_slp, ind_r, check_r, IC); 190 00 x_abs_l = zeros(No_ind,1); $z_abs_l = x_abs_l;$ x_plot_l = zeros(size(x_sub_l)); 195 $z_plot_l = x_plot_l;$ x_plot_r = zeros(size(x_sub_r)); z_plot_r = x_plot_r; for k = 1:No_ind 200

[x_abs_l(k,1),z_abs_l(k,1),x_plot,z_plot] = abs_data_pts(
 x_sub_l(k,:),z_sub_l(k,:),k);

```
x_plot_l(k, :) = x_plot;
           z_plot_l(k,:) = z_plot;
       end
205
      x_abs_r = zeros(No_ind,1);
       z_abs_r = x_abs_r;
      for k = 1:No_ind
           [ x_abs_r(k,1),z_abs_r(k,1),x_plot,z_plot ] = abs_data_pts(
210
              x_sub_r(k,:),z_sub_r(k,:),k);
           x_plot_r(k, :) = x_plot;
           z_plot_r(k,:) = z_plot;
       end
215
      %% Restructuring points
      true_apex_x = x_abs_r(1);
      true_apex_z = z_abs_r(1);
220
      apex_diff_x = apex_x - true_apex_x;
      apex_diff_z = apex_z - true_apex_z;
      x_lhs = x_abs_l - true_apex_x;
       z_lhs = z_abs_l - true_apex_z;
225
      x_rhs = x_abs_r - true_apex_x;
       z_rhs = z_abs_r - true_apex_z;
      x_plot_l = x_plot_l - true_apex_x;
230
       z_plot_l = z_plot_l - true_apex_z;
      x_plot_r = x_plot_r - true_apex_x;
       z_plot_r = z_plot_r - true_apex_z;
      000
235
      xpl = xpl_i - true_apex_x;
       zpl = zpl_i - true_apex_z;
      xpr = xpr_i - true_apex_x;
      zpr = zpr_i - true_apex_z;
240
       %% clear
       clear avg_slope_1 avg_slopr_r check_1 check_r cut_1 cut_r dh_1
          dh_r
       clear height_1 height_r ind_1 ind_r ind_slopr slope_temp
       clear x_abs_l x_abs_r x_avg_slope_l x_avg_slope_r x_sub_l x_sub_r
245
      clear z_abs_l z_abs_r z_avg_slope_l z_avg_slope_r z_sub_l z_sub_r
```

%% Scaling done here

[x_left_cm, z_left_cm, x_right_cm, z_right_cm, xl_cm, xr_cm, zl_cm, 250zr_cm] = scale_data(x_lhs,z_lhs,x_rhs,z_rhs,xpl,xpr,zpl,zpr, scale); 00 p_l = polyfit(xl_cm, zl_cm, 1); 255p_r = polyfit(xr_cm, zr_cm, 1); $p_1(1) = -p_1(1);$ %% Find optimum 'b' 'c' 260if d side == 1 [b_l,c_l] = bc_optimization(-x_left_cm, z_left_cm, No_ind); [b_r,c_r] = bc_optimization_la(x_right_cm, z_right_cm, No_ind); elseif d_side == 2 265[b_l,c_l] = bc_optimization_la(-x_left_cm, z_left_cm, No_ind); [b_r,c_r] = bc_optimization(x_right_cm, z_right_cm, No_ind); else [b_l,c_l] = bc_optimization(-x_left_cm, z_left_cm, No_ind); [b_r,c_r] = bc_optimization(x_right_cm, z_right_cm, No_ind); 270end %% finds theta 275[x_ly_l, z_ly_l, theta_l, vol_l, Err_theta_l] = contact_angle(b_l, c_l ,p_l,S_span,scale); [x_ly_r,z_ly_r,theta_r,vol_r,Err_theta_r] = contact_angle(b_r,c_r ,p_r,S_span,scale); %% Finds drop volume and theta drop_volume = (vol_l+vol_r)/2; 280 [eq_radius, wet_radius, drop_height_l, drop_height_r] = drop_properties(x_ly_l, z_ly_l, x_ly_r, z_ly_r); tilt_left = atand(-p_l(1)); tilt_right = atand(p_r(1)); 88 285xl_n = -x_ly_l*scale; zl_n = z_ly_l*scale; xr_n = x_ly_r*scale; zr_n = z_ly_r*scale; 290 x_l_n = xl_n + true_apex_x; z_l_n = zl_n + true_apex_z;

```
x_r_n = xr_n + true_apex_x;
       z_r_n = zr_n + true_apex_z;
295
       00
       p_l_i = polyfit(xpl_i, zpl_i, 1);
       p_r_i = polyfit(xpr_i, zpr_i, 1);
300
       x_new_l = linspace(1, (xpl_i(end)+80), 500);
       x_new_r = linspace((xpr_i(1)-80), xpr_i(end), 500);
       z_new_l = polyval(p_l_i, x_new_l);
305
       z_new_r = polyval(p_r_i, x_new_r);
       figure
       imshow(IC);
310
       hold on
       plot (x_l_n, z_l_n, 'g', x_r_n, z_r_n, 'g');
       plot(x_new_l, z_new_l, 'c', x_new_r, z_new_r, 'c')
       imagenumber = file(1:end-4);
315
       imagefolder = [folder,'Images\',imagenumber,'_drop','.fig'];
       saveas(gcf, imagefolder)
       clear gcf
       close all
320
       %% Plots LY profile
       figure
       for k = 1:No ind
           hold on
325
           plot(x_plot_l(k,:)/scale, z_plot_l(k,:)/scale, 'r');
           plot(x_plot_r(k,:)/scale,z_plot_r(k,:)/scale,'r');
       end
       plot((-x_ly_l), z_ly_l, 'b', x_ly_r, z_ly_r, 'b')
330
       set(gca, 'YDir', 'reverse');
       axis([-.5 .5 -.5 .5]);
       axis square
       % Saves the figure
335
       imagenumber = file(1:end-4);
       imagefolder = [folder, 'Images\', imagenumber, '.fig'];
       saveas(gcf, imagefolder)
       clear gcf
       close all
340
```

```
%% Solution stored in the m file
Data(r,:) = [ eq_radius wet_radius drop_height_l
drop_height_r c_l c_r b_l b_r drop_volume tilt_left
tilt_right theta_l theta_r];
Err_data(r,:) = cat(1,Err_theta_l,Err_theta_r);
No_pt_slp = 16; % No of pts used for quadratic fit on
each side
dif_slp = 3;
end
%% Saves the result
350 datafolder = [folder,'Data\','Data'];
errfolder = [folder,'Data\','Err_data'];
strutfolder = [folder,'Data\','Struct_A'];
```

```
save(errfolder,'Err_data')
```

save(datafolder, 'Data')

```
355 save(strutfolder, 'A')
```

2.4 Functions

Here is a list of all of the functions used in the contact angle measurement program in alphabetical order.

2.4.1 abs data pts

```
function [ x_abs, z_abs, xx, pp ] = abs_data_pts(x, z, iter)
  % This function fits a quadratic curve between the points and
  % finds optimum point.
5 \text{ fit} = 2;
                              % Fit types
  n = length(x);
  if iter == 1
      xx = x(1) : ((x(end)-x(1))/(n*50)) : x(end);
10
      p = polyfit(x,z,fit);
      pp = polyval(p, xx);
      z_abs = min(pp);
      x_abs = xx(find(pp == z_abs)); %#ok<FNDSB>
15
      XX = X;
      pp = polyval(p, xx);
  else
20
      dx = diff(x);
      if any (dx \le 0)
          zz = z(1): ((z(end)-z(1))/(n-1)): z(end);
          p = polyfit(z,x,fit);
25
          pp = polyval(p,zz);
          x_abs = pp((n+1)/2);
          z_abs = zz((n+1)/2);
30
          xx = pp;
          pp = zz;
      else
          xx = x(1): ((x(end)-x(1))/(n-1)): x(end);
35
          p = polyfit(x,z,fit);
          pp = polyval(p, xx);
          x_abs = xx((n+1)/2);
          z_abs = pp((n+1)/2);
```

```
40 end
end
45
%eof
```

2.4.2 bc optimization

```
function [b_opt,c_opt] = bc_optimization(x_n,z_n,N)
  S_span=(0:.001:6); % S_span is the step variable for ode45 solver
  step_i = 0.1;
5
  000
  c = 13.45;
  [b_initial] = Initial_guess(x_n, z_n, c, N);
  Bini = b_{initial*(c^{.5})};
10
  if Bini ≤ .2005
      step_i = (Bini-0.005)/2;
  end
15 Bnew = [(Bini-2*step_i) (Bini-step_i) (Bini) (Bini+step_i) (Bini+2*
    step_i)];
  C = zeros(1, 5);
  err = zeros(1,5);
  for j = 1:length(Bnew);
  [ C(j),err(j) ] = cfinder(Bnew(j),c,x_n,z_n,N,S_span );
20
  end
  ind = find(min(abs(err))==abs(err));
25 \text{ Cnew} = \text{zeros}(1, 5);
  errnew = Cnew;
  88
30 while (step_i) >0.0001
      if ind == 1
```

```
Bnew1 = [(Bini-6*step_i) (Bini-5*step_i) (Bini-4*step_i) (
             Bini-3*step_i) (Bini-2*step_i)];
          Cnew(5) = C(1);
          errnew(5) = err(1);
35
          condn = 1;
      elseif ind == 5
          Bnew1 = [(Bini+2*step_i) (Bini+3*step_i) (Bini+4*step_i) (
              Bini+5*step_i) (Bini+6*step_i)];
40
          condn = 2;
          Cnew(1) = C(5);
          errnew(1) = err(5);
      else
          Bnew1 = [(Bnew(ind)-step_i) (Bnew(ind)-.5*step_i) (Bnew(ind))
45
               (Bnew(ind)+.5*step_i) (Bnew(ind)+step_i)];
          condn = 3;
          Cnew(1) = C(ind-1);
          Cnew(3) = C(ind);
          Cnew(5) = C(ind+1);
          errnew(1) = err(ind-1);
50
          errnew(3) = err(ind);
          errnew(5) = err(ind+1);
      end
55
      88
      if condn == 1
          for j = 1:4
              [ Cnew(j),errnew(j) ] = cfinder(Bnew1(j),c,x_n,z_n,N,
                  S_span );
          end
60
      elseif condn ==2
          for j = 2:5
               [ Cnew(j),errnew(j) ] = cfinder(Bnew1(j),c,x_n,z_n,N,
                  S_span );
          end
      elseif condn == 3
65
          for j = [2, 4]
              [ Cnew(j),errnew(j) ] = cfinder(Bnew1(j),c,x_n,z_n,N,
                  S_span );
          end
      end
70
      ind = find(min(abs(errnew)) == abs(errnew));
      if length(ind)>1
          ind = round(mean(ind));
      end
75
```

```
C = Cnew;
err = errnew;
step_i = step_i/2;
80
Bini = Bnew1(3);
Bnew = Bnew1;
end
85
c_opt = Cnew(ind);
```

```
B_opt = Bnew1(ind);
b_opt = B_opt/(c_opt^.5);
```

90 **end**

% eof

2.4.3 bc_optimization_la

```
function [b_opt,c_opt] = bc_optimization_la(x_n,z_n,N)
  % Optimization with low accuracy for faster processing
  S_span=(0:.001:6); % S_span is the step variable for ode45 solver
5 step_i = 0.1;
  00
  c = 13.45;
10 [b_initial] = Initial_guess(x_n, z_n, c, N);
  Bini = b_{initial*(c^{.5})};
  if Bini \leq .2005
15
   step_i = (Bini-0.005)/2;
  end
  Bnew = [(Bini-2*step_i) (Bini-step_i) (Bini) (Bini+step_i) (Bini+2*
     step_i)];
_{20} C = zeros(1, 5);
  err = zeros(1,5);
  for j = 1:length(Bnew);
```

```
[ C(j),err(j) ] = cfinder(Bnew(j),c,x_n,z_n,N,S_span );
25 end
  ind = find(min(abs(err)) == abs(err));
  Cnew = zeros(1,5);
30 errnew = Cnew;
  88
  while (step i) >0.005
35
      if ind == 1
          Bnew1 = [(Bini-6*step_i) (Bini-5*step_i) (Bini-4*step_i) (
             Bini-3*step_i) (Bini-2*step_i)];
          Cnew(5) = C(1);
          errnew(5) = err(1);
40
          condn = 1;
      elseif ind == 5
          Bnew1 = [(Bini+2*step_i) (Bini+3*step_i) (Bini+4*step_i) (
             Bini+5*step_i) (Bini+6*step_i)];
          condn = 2;
45
          Cnew(1) = C(5);
          errnew(1) = err(5);
      else
          Bnew1 = [(Bnew(ind)-step_i) (Bnew(ind)-.5*step_i) (Bnew(ind))
50
               (Bnew(ind)+.5*step_i) (Bnew(ind)+step_i)];
          condn = 3;
          Cnew(1) = C(ind-1);
          Cnew(3) = C(ind);
          Cnew(5) = C(ind+1);
          errnew(1) = err(ind-1);
55
          errnew(3) = err(ind);
          errnew(5) = err(ind+1);
      end
60
      88
      if condn == 1
          for j = 1:4
65
              [ Cnew(j),errnew(j) ] = cfinder(Bnew1(j),c,x_n,z_n,N,
                  S_span );
          end
      elseif condn ==2
          for i = 2:5
```

```
[ Cnew(j),errnew(j) ] = cfinder(Bnew1(j),c,x_n,z_n,N,
                                                                 S_span );
                                      end
  70
                        elseif condn == 3
                                       for j = [2, 4]
                                                      [ Cnew(j),errnew(j) ] = cfinder(Bnew1(j),c,x_n,z_n,N,
                                                                 S_span );
                                       end
                        end
  75

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        00<
                        ind = find(min(abs(errnew))==abs(errnew));
  80
                        if length(ind)>1
                                      ind = round(mean(ind));
                        end
                       C = Cnew;
  85
                        err = errnew;
                        step_i = step_i/2;
                       Bini = Bnew1(3);
                       Bnew = Bnew1;
  90
         end
          00
00
00
  95 c_opt = Cnew(ind);
         B_opt = Bnew1(ind);
         b_opt = B_opt/(c_opt^{.5});
100 end
```

% eof

5

2.4.4 cfinder

```
function [ C,err ] = cfinder(Bini,c,x_n,z_n,N,S_span )
% This function finds the optimum `c' for given B
b = Bini/(c^.5);
```

```
[S,Y] = ode45(@laplace,S_span,[0 1e-100 0],[],b,c); % may need to
      increase second input if curve does not loop
  Z=Y(:,1);
10 i=1;
  while Z(i)<Z(i+1); % finds where contact angle is 180 degrees (</pre>
      cutoff point)
      i=i+1;
  end;
15 x_ly(1:i,1)=Y(1:i,2);  % Drop height dimensionless
7 ly(1:i,1)=Y(1:i,1);  % Drop x dimension dimension
  z_ly(1:i,1)=Y(1:i,1);
                                     % Drop x dimension dimensionless
  clear S_ly S Z Y x_ly_or_c z_ly_or_c
20 응응
  iter = 1;
  c1 = 10;
  c2 = 20;
25
  x_lynew = x_ly/(c1^.5);
  z_lynew = z_ly/(c1^{.5});
  [error_profile1] = error_drop_new_w_sign(x_n, z_n, x_lynew, z_lynew, N);
  clear x_lynew z_lynew
30
  x_lynew = x_ly/(c2^{.5});
  z_lynew = z_ly/(c2^{.5});
  [error_profile2] = error_drop_new_w_sign(x_n, z_n, x_lynew, z_lynew, N);
       %#ok<NASGU>
  clear x_lynew z_lynew
35
  close all
  while iter <16
      c3 = (c1+c2)/2;
      x_lynew = x_ly/(c3^{.5});
      z_{lynew} = z_{ly}/(c3^{.5});
40
      [error_profile] = error_drop_new_w_sign(x_n, z_n, x_lynew, z_lynew, N
           );
      clear x_lynew z_lynew
      if error_profile*error_profile1<0</pre>
45
           c2 = c3;
           error_profile2 = error_profile; %#ok<NASGU>
      else
           c1 = c3;
           error_profile1 = error_profile;
      end
50
```
```
iter = iter+1;
end
C = c3;
err =abs( error_profile);
55 clear x_ly z_ly S Z Y
```

% eof

2.4.5 cfinder la

```
function [ C,err ] = cfinder_la(Bini,c,x_n,z_n,N,S_span )
  %UNTITLED2 Summary of this function goes here
  % Detailed explanation goes here
5 b = Bini/(c^.5);
  [S,Y] = ode45(@laplace,S_span,[0 1e-100 0],[],b,c); % may need to
      increase second input if curve does not loop
10 Z=Y(:,1);
  i=1;
  while Z(i)<Z(i+1); % finds where contact angle is 180 degrees (cutoff
      point)
      i=i+1;
15 end;
  x_ly(1:i,1)=Y(1:i,2);%/(c^.5); % Drop height dimensionless
z_ly(1:i,1)=Y(1:i,1);%/(c^.5); % Drop x dimension
     dimensionless
20
  clear S_ly S Z Y x_ly_or_c z_ly_or_c
25 응응
 iter = 1;
```

```
c1 = 10;
c2 = 19;
```

```
30
 x_lynew = x_ly/(c1^{.5});
  z_lynew = z_ly/(c1^{.5});
  [error_profile1] = error_drop_new_w_sign(x_n,z_n,x_lynew,z_lynew,N);
  clear x_lynew z_lynew
35
  x_lynew = x_ly/(c2^{.5});
  z_lynew = z_ly/(c2^{.5});
  [error_profile2] = error_drop_new_w_sign(x_n, z_n, x_lynew, z_lynew, N);
       %#ok<NASGU>
40 clear x_lynew z_lynew
  close all
  while iter \leq 9
      c3 = (c1+c2)/2;
45
      x_lynew = x_ly/(c3^{.5});
      z_{lynew} = z_{ly}/(c3^{.5});
      [error_profile] = error_drop_new_w_sign(x_n, z_n, x_lynew, z_lynew, N
           );
      clear x_lynew z_lynew
      if error_profile*error_profile1<0</pre>
50
          c2 = c3;
          error_profile2 = error_profile; %#ok<NASGU>
      else
          c1 = c3;
          error_profile1 = error_profile;
55
      end
      00
                atr(iter) = error_profile;
      iter = iter+1;
60 end
  C = C3;
  err =abs( error_profile);
  % close all
65 clear x_ly z_ly S Z Y
```

70

end

2.4.6 contact angle

```
function [x_ly_profile, z_ly_profile, theta, drop_vol, Err_t] =
     contact_angle(b,c,p,S_span,scale )
  % This function finds the final contact angle
  [S,Y] = ode45(@laplace,S_span,[0 1e-100 0],[],b,c); % may need to
     increase second input if curve does not loop
5 Z = Y(:, 1);
  i = 1;
  while Z(i) <Z(i+1); % finds where contact angle is 180 degrees (cutoff
     point)
     i = i+1;
10 end
 x_ly = zeros(i, 1);
  z_{ly} = zeros(i, 1);
dimensionless
  j = 1;
20 while (z_1y(j) \le (p(1) * x_1y(j) + p(2))) \& i \le (i-10);
      j = j+1;
  end
  ind end = j;
25 x_ly_profile = x_ly(1:ind_end);
  z_ly_profile = z_ly(1:ind_end);
  angle = Y(ind_end,3)*180/pi; % Angle
30 theta = angle;
  drop_vol = volume(z_ly, x_ly, z_ly_profile(end));
  drop_height = z_ly_profile(end);
35
  00
  Err_t = zeros(1,51);
                         % Error matrix for interface correction
  for j = -25:1:25
     Err_t(1,j) = Y(find(z_ly < drop_height+j/scale,1,'last'));</pre>
40 end
```

```
% eof
```

2.4.7 drop_properties

```
function [ eq_rad,wet_rad,drop_ht_l,drop_ht_r] = drop_properties( x_l
    ,z_l,x_r,z_r)
% Finds physical drop properties
eq_rad = (max(abs(x_l)) + max(abs(x_r)))/2;
s wet_rad = (abs(x_l(end) + abs(x_r(end))))/2;
drop_ht_l = z_l(end);
drop_ht_r = z_r(end);
10 end
```

% eof

2.4.8 edge detector

```
function [flip_bound]=edge_detector(Black_White)
% This function converts the image into grayscale
% from Russell Stacy (2009)

5 boundary_full = bwtraceboundary(Black_White, [1,1],'S'); % Find total
        boundary of image

bound1 = boundary_full(find(boundary_full(:,2)==(length(Black_White
        (1,:))-1), 1, 'last'):length(boundary_full(:,1))-max(
        boundary_full(:,1)),1); % trim the full boundary of column one to
        eliminate the image edge

bound2 = boundary_full(find(boundary_full(:,2)==(length(Black_White
        (1,:))-1), 1, 'last'):length(boundary_full(:,2)==(length(Black_White
        (1,:))-1), 1, 'last'):length(boundary_full(:,2)==(length(Black_White
        (1,:))-1), 1, 'last'):length(boundary_full(:,1))-max(
        boundary_full(:,1)),2); % trim the full boundary of column two to
        eliminate the image edge
10
```

```
bound = [bound2,bound1]; % Recombine the two colums to form a
vector of values [x,y]
flip_bound = flipud(bound); % The "bound" vector is in reverse order
of data points from right to left. flipud() flips the vectors to
follow data points from left to right
```

15

% eof

2.4.9 error

```
function [error_profile] = error_drop(x_cm, z_cm, x_ly, z_ly, N )
  % Finds the error in the drop profile
  nop = 200;
                                 %Number fo points for fit
5 \text{ N_ly} = \text{length}(x_ly);
  distance1 = zeros(N_ly, 1);
  distance2 = zeros(nop,1);
  distance_min = zeros(N,1);
  distance_min_sign = zeros(N,1);
10
  000
  weigh = 1; % sqrt(1:1:N);
  for j = 2:N
15
      for k = 1:N_ly
          distance1(k,1) = sqrt( (x_cm(j)-x_ly(k))^2 + (z_cm(j)-z_ly(k))
              )^2);
      end
      ind_z = find(min(distance1) == distance1);
20
      if ind_z == N_ly;
          ind_z = ind_z - 2;
      end
25
      ind = (ind_z-2):1:(ind_z+2);
      p = polyfit(x_ly(ind), z_ly(ind), 2);
      x_cut = linspace(x_ly(ind(1)), x_ly(ind(end)), nop);
      z_cut = polyval(p, x_cut);
30
      for k = 1:nop
```

% eof

2.4.10 exact data

```
function [ x,z ] = exact_data(x_fit,z_fit,check,pixel_index)
  % Based on input value of check, this function gives exact profile
     data;
  n_pts = length(x_fit);
5
  if check == 1 || check == 5
      base_pts_z = linspace(z_fit(1), z_fit(end), (n_pts*100)+1);
      spline_fit_z = spline(z_fit, pixel_index, base_pts_z);
10
      median_up_z = median(pixel_index(1:5));
      median_dn_z = median(pixel_index((end-5):end));
      intensity_z = (median_up_z+median_dn_z)/2;
      dif_z = abs (intensity_z-spline_fit_z);
15
      x = mean(x_fit);
      z = base_pts_z(find(dif_z == min(dif_z),1,'first'));
```

```
20 elseif check == 2 || check == 4
      base_pts_x = linspace(x_fit(1), x_fit(end), (n_pts*100)+1);
      base_pts_z = linspace(z_fit(1), z_fit(end), (n_pts*100)+1);
      spline_fit_x = spline(x_fit,pixel_index,base_pts_x);
25
      median_up_x = median(pixel_index(1:5));
      median_dn_x = median(pixel_index((end-5):end));
      intensity_x = (median_up_x+median_dn_x)/2;
30
      dif_x = abs(intensity_x-spline_fit_x);
      x = base_pts_x(find(dif_x == min(dif_x),1,'first'));
      z = base_pts_z(find(dif_x == min(dif_x),1,'first'));
35
  elseif check == 3
      base_pts_x = linspace(x_fit(1), x_fit(end), (n_pts*100)+1);
      spline_fit_x = spline(x_fit,pixel_index,base_pts_x);
40
      median_up_x = median(pixel_index(1:5));
      median_dn_x = median(pixel_index((end-5):end));
      intensity_x = (median_up_x+median_dn_x)/2;
      dif_x = abs(intensity_x-spline_fit_x);
45
      x = base_pts_x(find(dif_x == min(dif_x),1,'first'));
      z = mean(z_fit);
50 end
```

5

end

% eof

2.4.11 image analysis

```
function [Black_White,Trimmed_image]=image_analysis(Cropped_Image)
% This function produces the black and white image
co=10; % co is cutoff for top and bottom and left and right of image
```

```
thresh=0.85;
```

```
BW1=im2bw(Cropped_Image,thresh); % thresh is the threshold of the
image for converting to black and white.
```

10 Trimmed_image=Cropped_Image(co:length(Cropped_Image(:,1))-co,co: length(Cropped_Image(1,:))-co); Black_White=BW1(co:length(BW1(:,1))-co,co:length(BW1(1,:))-co);

end

15 % eof

2.4.12 image_input

```
function [Drop_Image, filepath, filename] = image_input(im_no, ex_type,
     prefix_img,start_no,range_lim,filepath)
  % This function reads the images
  image no = start no+im no-1;  % Image number
5 image_names = num2str(image_no); % Image number in string
  if ex_type == 2
                               % Adds 0s if required
      if range_lim == 3
          if image_no <10</pre>
              image_names = ['0','0',image_names];
10
          elseif image_no <100 && image_no <100
              image_names = ['0', image_names];
          end
      elseif range_lim == 2
          if image_no <10</pre>
15
              image_names = ['0', image_names];
          end
      end
  end
20
  filename = [prefix_img,image_names,'.tif']; % Image name
  Drop_Image = imread([filepath, filename]); % Image read
  end
25
  % eof
```

2.4.13 initial guess

```
function [b_initial] = Initial_guess(x_n, z_n, c, N)
  % Initial guess. Extracted from Russell Stacy (2009)
  S_span = 0:.002:5;
_{5} up = N-5;
  88
  iter = 1;
  b1=3;
10 b2=.01;
  bb=[b1 b2];
              % range of b values to use
  for j=1:2;
15
      b=bb(j);
                          % set b as individual values of b
      [S,Y] = ode45(@laplace,S_span,[0 1e-100 0],[],b,c);
      Z=Y(:,1);
20
      i=1;
      while Z(i) <Z(i+1);
         i=i+1;
      end;
      x_ly(1:i,j)=Y(1:i,2)/(c^.5);
25
      z_1y(1:i,j) = Y(1:i,1) / (c^{.5});
  end;
30 %% Error
  [d1, z1]=min(abs(z_n(N-up)-z_ly(:,1))); % find indice of laplace data
     that closely matches raw data
  error_b1=x_n(N-up)-x_ly(z1,1);
                                         % finds relative horizontal
     error of end of trim data
35 [d2,z2]=min(abs(z_n(N-up)-z_ly(:,2))); % find indice of laplace data
     that closely matches raw data
                                        % finds relative horizontal
  error_b2=x_n(N-up)-x_ly(z2,2);
     error of end of trim data
  if error_b1*error_b2>0 && error_b1<0;</pre>
      fprintf('choose smaller b2 value');
40 elseif error_b1*error_b2>0 && error_b1>0;
      fprintf('choose larger b1 value');
```

return

end;

```
45 error_b=min(abs([error_b1 error_b2]));
 %% Minimization
 c_change=.1;
50 b = (b1+b2)/2;
 b3=b;
 while (iter≤20);
     clear x_ly z_ly S_ly Phi_ly Z
55
     [S,Y] = ode45(@laplace,S_span,[0 1e-100 0],[],b3,c); % may need
         to increase span of S if curve does not loop
     Z=Y(:,1); % the first column of Y is the Z data. Needs to be
        defined to find cutoff point below.
     i=1;
     while Z(i) <Z(i+1); % finds where contact angle is 180 degrees (</pre>
60
         cutoff point)
         i=i+1;
     end;
     % Output Variables
65
     dimensionless
      z_ly_1(1:i) = Y(1:i, 1) / (c^.5);
                                           % Drop width
        dimensionless
      [d3,z3]=min(abs(z_n(N-up)-z_ly_1)); % find indice of laplace data
          that closely matches raw data
                                    % finds relative horizontal
     error_b3=x_n(N-up)-x_ly_1(z3);
70
         error of end of trim data
     if error_b3*error_b1>0;
         b1=b3;
         error_b1=error_b3;
         error_b=error_b1;
75
     else
         b2=b3;
         error_b2=error_b3;
         error b=error b2;
     end;
80
     b=b3;
     b3=(b1+b2)/2;
     iter = iter+1;
```

85 end;

b_initial = b3;

end

2.4.14 laplace

```
%Derek Fultz and Russ Stacy
  87-24-07
  00
  * LAPLACE defines the ordinary differential equations to be solved.
5 % z=drop height
  % x=distance from axis to drop interface
  % phi=contact angle
  % 1/b=radius of curvature at apex
  % s=arc length
10 🔗
  % NON-DIMENSIONALIZE Z, X, S, B USING C^(1/2)
  % B=b*c^(1/2)
  % X = x * c^{(1/2)}
  % Z=z*c^(1/2)
15 % S=s * c^ (1/2)
  00
  % No need to define X,Z,S for equations
  00
  % KEY OF VARIABLE DEFINITIONS FOR SYSTEM
20 % Z=y(1); Z'=dy(1); Z' is with respect to S
  % X=y(2); X'=dy(2); X' is with respect to S
  % phi=y(3); phi'=dy(3); phi' is with respect to S
  00
  % Z'=sin(phi)
25 % X'=cos(phi)
  % phi'=2/B+Z-(sin(phi)/X)
  function [dy]=laplace(s,y,m,n)
  dy = zeros(3,1); % a column vector
30
                  % non-dimensionalized curvature at apex
  B=m*n^.5;
  dy(1) = sin(y(3));
  dy(2) = cos(y(3));
35 \text{ dy}(3) = (2/B) + y(1) - (sin(y(3))/y(2));
```

```
% eof
```

2.4.15 plane

```
function [mean_left,mean_right,x_plane_left,x_plane_right,
     z_plane_left,z_plane_right ] = plane( I,boundary )
  % This function finds the Solid-Liquid Interface
  ini_z = boundary(:,2);
5
  z_left_temp = ini_z(1:10); % 10 pixels from left edge of
     image
  z_right_temp = ini_z(end-10:end); % 10 pixels from left edge of
     image
  plane_left_ini = round(mean(z_left_temp)); % Mean of left plane
10 plane_right_ini = round (mean (z_right_temp)); % Mean of right plane
  apex_z_ind = (find(boundary(:,2) == min(boundary(:,2)),1,'first'));
  x_left = boundary(1:apex_z_ind, 1);
15 z_left = boundary(1:apex_z_ind,2);
  x_right = boundary((apex_z_ind+1):end, 1);
  z_right = boundary((apex_z_ind+1):end,2);
20 cutoff_x_l = x_left(find(z_left == (plane_left_ini - 20),1,'last'));
  cutoff_x_r = x_right(find(z_right == (plane_right_ini - 20),1,'first'
     ));
  z_left_int = I((plane_left_ini-18):(plane_left_ini+18),1:cutoff_x_l)
     ;
  z_right_int = I((plane_right_ini-18):(plane_right_ini+18),cutoff_x_r:
     end);
25
  z_left_img = double(z_left_int);
  z_right_img = double(z_right_int);
  00
30
  for j = 1:length(z_left_img(1,:))
      for i = 1: (length(z_left_img(:, 1))-4)
```

```
dz\_left(i,j) = (z\_left\_img(i,j)-8*z\_left\_img(i+1,j)+8*
              z_left_img(i+3,j)-z_left_img(i+4,j))/12;
      end
35 end
  for j = 1:length(z_right_img(1,:))
      for i = 1: (length(z_right_img(:, 1))-4)
          dz_right(i,j) = (z_right_img(i,j)-8*z_right_img(i+1,j)+8*
              z_right_img(i+3,j)-z_right_img(i+4,j))/12;
40
      end
  end
  00
00
00
45 for j = 1:length(z_left_img(1,:))
      plane_left(j) = round(mean(find(abs(dz_left(:,j))) == max(abs(
         dz_left(:,j))) )));
  end
  for j = 1:length(z_right_img(1,:))
50
      plane_right(j) = round(mean(find(abs(dz_right(:,j)) == max(abs(
         dz_right(:,j))) )));
  end
  88
55 z_plane_left = plane_left + plane_left_ini-17;
  z_plane_right = plane_right + plane_right_ini-17;
  00
00
00
60 I1 = I;
  for j = 1:length(z_left_img(1,:));
      I1(round(z_plane_left(j)),j)=255;
  end
65 for j = 1:length(z_right_img(1,:));
      k = cutoff_x_r + j -1;
      I1 (round(z_plane_right(j)), k) = 226;
  end
ro mean_left = round(mean(z_plane_left));
  mean_right = round(mean(z_plane_right));
  000
75 p_l = polyfit(1:length(z_plane_left), z_plane_left, 1);
  p_r = polyfit(cutoff_x_r:length(I(1,:)), z_plane_right, 1);
```

```
%%
%%
x_plane_left = 1:length(z_plane_left);
x_plane_right = cutoff_x_r:length(I(1,:));
end
```

```
85 % eof
```

2.4.16 pixel_data

```
function [ x_sub,z_sub ] = pixel_data(x_all,z_all,x_pts,z_pts,apex_x,
     apex_z, N, N_op, ind, check_xy, crop_im )
  % This function gives the sub-pixel data for N_op points
  x_mat = zeros(N, (2*N_op+1));
                                                % here 21 pts of x are
     stored (-10:10) for N points
5 z_mat = x_mat;
  x sub = x mat;
                                                % here exact 21 pts of
    x are stored (-10:10) for N points
  z_sub = z_mat;
10 응응
  for j = 1:N
      if j == 1
          apex_indice = round((find(z_all == 0,1,'first')+find(z_all ==
              0,1,'last'))/2);
          ind_pts = (-N_op:1:N_op) + apex_indice;
15
          x_mat(1,:) = x_all(ind_pts);
          z_mat(1,:) = z_all(ind_pts);
      else
      ind_pts = (-N_op:1:N_op) + ind(j);
      x_mat(j,:) = x_pts(ind_pts);
20
      z_mat(j,:) = z_pts(ind_pts);
      end
  end
25 x_mat = x_mat+apex_x;
                                             % apex added to make
     compatible with image
  z_mat = z_mat+apex_z;
```

```
pix_ind = 15;
                                             % no of points taken in
     image for spline fit
  pixel_index = zeros(1, (pix_ind)); % stores pixel data
30
  for j = 1:N
      check = check_xy(j);
      if check == 1
          pix_ind_z = -7:1:7;
          for k = 1: (2*N_op+1)
35
              pix_x(1,1:(pix_ind)) = x_mat(j,k);
              pix_z = z_mat(j,k) + pix_ind_z;
              for m = 1:(pix_ind)
                  pixel_index(1,m) = double(crop_im(pix_z(m),pix_x(m)))
                      ;
40
              end
               [x_sub(j,k),z_sub(j,k)] = exact_data(pix_x,pix_z,check,
                  pixel_index);
          end
      elseif check == 2
45
          pix_ind_x = -7:1:7;
          pix_ind_z = 7:-1:-7;
          for k = 1: (2*N_op+1)
50
              pix_x = x_mat(j,k) + pix_ind_x;
              pix_z = z_mat(j,k) + pix_ind_z;
              for m = 1:(pix_ind)
                  pixel_index(1,m) = double(crop_im(pix_z(m),pix_x(m)))
55
                      ;
              end
               [x_sub(j,k),z_sub(j,k)] = exact_data(pix_x,pix_z,check,
                  pixel_index);
          end
60
      elseif check == 3
          pix_ind_x = -7:1:7;
          for k = 1: (2*N_op+1)
65
              pix_x(1,1:length(pix_ind_x)) = x_mat(j,k) + pix_ind_x;
              pix_z(1,1:length(pix_ind_x)) = z_mat(j,k);
              for m = 1:(pix_ind)
70
```

```
pixel_index(1,m) = double(crop_im(pix_z(m),pix_x(m)))
                       ;
               end
               [x_sub(j,k),z_sub(j,k)] = exact_data(pix_x,pix_z,check,
                  pixel_index);
           end
75
       elseif check == 4
           pix_ind_x = -7:1:7;
           pix_ind_z = -7:1:7;
80
           for k = 1: (2*N_op+1)
               pix_x(1,1:length(pix_ind_x)) = x_mat(j,k) + pix_ind_x;
               pix_z(1,1:length(pix_ind_z)) = z_mat(j,k) + pix_ind_z;
85
               for m = 1:(pix_ind)
                   pixel_index(1,m) = double(crop_im(pix_z(m),pix_x(m)))
                       ;
               end
               [x_sub(j,k),z_sub(j,k)] = exact_data(pix_x,pix_z,check,
90
                  pixel_index);
           end
      elseif check == 5
           pix_ind_z = -7:1:7;
95
           for k = 1: (2*N_op+1)
               pix_x(1,1:length(pix_ind_z)) = x_mat(j,k);
               pix_z(1,1:length(pix_ind_z)) = z_mat(j,k) + pix_ind_z;
100
               for m = 1:(pix_ind)
                   pixel_index(1,m) = double(crop_im(pix_z(m),pix_x(m)))
                       ;
               end
105
               [x_sub(j,k),z_sub(j,k)] = exact_data(pix_x,pix_z,check,
                  pixel_index);
           end
       end
110
  end
  end
```

115 %eof

2.4.17 profile split

```
function [x_data_all,z_data_all,x_l,z_l,x_r,z_r,apex_x,apex_z] =
     profile_split( boundary, mean_l, mean_r)
  00
  apex_z = min(boundary(:,2));
                                                                   00
     Gives z position of apex
  apex_x = boundary(round(mean(find(boundary(:,2) == apex_z))),1); %
    Gives x position of apex
5
  x_data_all = boundary(:,1) - apex_x; % all x data
  z_data_all = boundary(:,2) - apex_z; % all z data
  apex_ind = round((find(z_data_all == 0,1,'first')+find(z_data_all ==
     0,1,'last'))/2);
10
  z = z data all(1:apex ind);
  z_right = z_data_all((apex_ind+1):end);
  z_cut_l = find(z_left == ((mean_l-20)-apex_z),1,'last');
15 z_cut_r = find(z_right == ((mean_r-20)-apex_z),1,'first')+apex_ind;
  x_data = x_data_all(z_cut_l:z_cut_r);
  z_data = z_data_all(z_cut_l:z_cut_r);
20 apex_ind_n = round((find(z_data == 0,1,'first')+find(z_data == 0,1,'
     last'))/2);
  x_l = x_data(apex_ind_n:-1:1); % Note apex is the start and the
    end point
  z_1 = z_data(apex_ind_n:-1:1);
25 x_r = x_data(apex_ind_n:end);
  z_r = z_data(apex_ind_n:end);
  end
```

2.4.18 scale data

% eof

2.4.19 volume

2.5 images reader

%% This program load the 'xxx_drop.fig' files to check for error

```
clear
  clc
5
  mult = 1;
  image_no = 1; % Start image no
end_no = 100; % End image no
10 \ k = 0;
  j = 1;
  step_size = 1;
15 filepath = 'C:\ABCD\ABCD\Images\';
  Image = image_no;
  while image_no < end_no</pre>
20
       image_names = num2str(image_no);
       if image_no <10</pre>
           image_names = ['0', '0', image_names];
       elseif image_no <100 && image_no <100
25
           image_names = ['0', image_names];
       end
       filename = ['A', image_names, '_drop', '.fig'];
30
       open([filepath,filename]);
           l = input('');
           if isempty(1)
                Correction(j,1) = 0;
35
           else
                Correction(j, 1) = 1;
           end
           r = input('');
40
           if isempty(r)
                Correction(j, 2) = 0;
           else
                Correction(j, 2) = r;
```

```
end
45
      close gcf
      if step_size == 1
      j = j+1;
      image_no = image_no+mult*step_size;
50
      elseif step_size == 2
          Correction(j+1,:) = Correction(j,:);
          j = j + 2;
          image_no = image_no+mult*step_size;
55
      elseif step_size == 3
          Correction(j+1,:) = Correction(j,:);
          Correction(j+2,:) = Correction(j,:);
          j = j+3;
          image_no = image_no+mult*step_size;
      elseif step_size == 4
60
          Correction(j+1,:) = Correction(j,:);
          Correction(j+2,:) = Correction(j,:);
          Correction(j+3,:) = Correction(j,:);
          j = j + 4;
          image_no = image_no+mult*step_size;
65
      end
      Image(j) = image_no;
  end
70
  save('C:\ABCD\Data\Correction.mat', 'Correction')
```

% eof

2.6 Data modifier

```
% Loads and does all the modifications
  clc
  clear
5 filepath = 'C:\ABCD\ABCD\';
  mid1 = 26;
  mid2 = 77;
10 응응
  Data_file = [filepath, 'Data\', 'Data.mat'];
  Corr_file = [filepath, 'Data\', 'Correction.mat'];
  Err_file = [filepath, 'Data\', 'Err_data.mat'];
15 D1 = load(Data_file);
  C1 = load(Corr_file);
  E1 = load(Err_file);
  Vol = D1.Data(:,9,1);
20 Error_Data = E1.Err_data(:,:,1);
  88
  Theta_l = D1.Data(:,12,1);
25 Theta_r = D1.Data(:,13,1);
  plot (Vol, Theta_l, 'ro', Vol, Theta_r, 'bo')
  legend('Left', 'Right')
30 Corr_l_1 = C1.Correction(:,1,1);
  Corr_r_1 = C1.Correction(:, 2, 1);
  88
35 if length(Theta_l) ≠ length(Corr_l_1)
      fprintf('Dimensions of Corr1 mismatch')
      Corr_l_1 = C1.Correction(1:length(Theta_1),1,1);
      Corr_r_1 = C1.Correction(1:length(Theta_r),2,1);
  end
40
  00
  Correction_l = Corr_l_1;
  Correction_r = Corr_r_1;
```

```
45
 000
  for j = 1:length(Vol)
      if Correction_r(j) == 0
         Theta_r_mod(j,1) = Theta_r(j);
50
      elseif round(Correction_r(j)) ≠ Correction_r(j)
          adder = (Correction_r(j)-floor(Correction_r(j)))*(Error_Data(
             j, (mid2+ceil(Correction_r(j))))-Error_Data(j,(mid2+floor(
             Correction_r(j))));
          Theta_r_mod(j,1) = Error_Data(j,(mid2+floor(Correction_r(j)))
             )+adder;
55
      else
         Theta_r_mod(j,1) = Error_Data(j,(mid2+Correction_r(j)));
      end
60
      if Correction_l(j) == 0
          Theta_l_mod(j,1) = Theta_l(j);
      65
         adder = (Correction_1(j)-floor(Correction_1(j)))*(Error_Data(
             j, (mid1+ceil(Correction_1(j))))-Error_Data(j, (mid1+floor(
             Correction_l(j))));
          Theta_l_mod(j,1) = Error_Data(j,(midl+floor(Correction_l(j)))
             )+adder;
      else
70
         Theta_l_mod(j,1) = Error_Data(j,(mid1+Correction_l(j)));
      end
 end
75
 Final_Data = cat(2,Vol,Theta_1,Theta_r,Theta_1_mod,Theta_r_mod);
  save([filepath, 'Final_data.mat'], 'Final_Data')
80
  88
  figure
 plot (Vol, Theta_l_mod, 'ro', Vol, Theta_r_mod, 'bo')
85 % eof
```

REFERENCES

- James Larminie and Andrew Dicks. *Fuel Cells Systems Explained*. John Wiley & Sons Ltd., 2003.
- Jeffrey S. Allen. An analytical solution for determination of small contact angles from sessile drops of arbitrary size. Journal of Colloid and Interface Science, 261(2):481 – 489, 2003. ISSN 0021-9797.
- A.F. Stalder, G. Kulik, D. Sage, L. Barbieri, and P. Hoffmann. A snake-based approach to accurate determination of both contact points and contact angles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 286(1-3):92 103, 2006. ISSN 0927-7757.
- F. Bashforth and J.C. Adams. An Attempt to Test the Theories of Capillary Action by Comparing the theoretical and Measured Forms of Drops of Fluid-Liquid. Cambride University Press, London, 1883.
- Stanley Hartland and Richard W. Hartley. Axisymmetric Fluid-Liquid Interfaces. Elsevier, 1976.
- P. Cheng, D. Li, L. Boruvka, Y. Rotenberg, and A.W. Neumann. Automation of axisymmetric drop shape analysis for measurements of interfacial tensions and contact angles. *Colloids and Surfaces*, 43(2):151 – 167, 1990. ISSN 0166-6622. Selected Papers from a Symposium on Recent Progress in Interfacial Tensiometry, held at the Third Chemical Congress of North America.
- Robert N. Wenzel. Resistance of solid surfaces to wetting by water. Industrial & Engineering Chemistry, 28(8):988–994, August 1936. ISSN 0019-7866.
- A. B. D. Cassie and S. Baxter. Wettability of porous surfaces. Trans. Faraday Soc., 40:546–551, 1944. ISSN 0014-7672.
- Jaroslaw Drelich and Jan D. Miller. Modification of the cassie equation. *Langmuir*, 9(2):619–621, February 1993. ISSN 0743-7463.

- Russell Stacey. Contact angle measurement technique for rough surfaces. Master's thesis, Michigan Technological University, 2009.
- A. W. Neumann and Jan K. Spelt, editors. Applied Science Thermodynamics. Marcel Dekker, Inc., 1996.
- J. D. Miller, S. Veeramasuneni, J. Drelich, M. R. Yalamanchili, and G. Yamauchi. Effect of roughness as determined by atomic force microscopy on the wetting properties of ptfe thin films. *Polym Eng Sci*, 36(14):1849–1855, 1996. ISSN 1548-2634.
- S. Veeramasuneni, J. Drelich, J. D. Miller, and G. Yamauchi. Hydrophobicity of ionplated ptfe coatings. *Progress in Organic Coatings*, 31(3):265 – 270, 1997. ISSN 0300-9440.
- Bo He, Junghoon Lee, and Neelesh A. Patankar. Contact angle hysteresis on rough hydrophobic surfaces. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 248(1-3):101 104, 2004. ISSN 0927-7757.
- Abraham Marmur. The lotus effect: Superhydrophobicity and metastability. Langmuir, 20(9):3517–3519, April 2004. ISSN 0743-7463.