An Alternative Arrangement for Measurement of Line Tension on Solid Substrates

By

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Abstract

An improved experimental method for measuring line tension on self-assembled monolayer (SAM) surfaces has been proposed and investigated, in order to minimize the difficulties that exist with previous designs on the basis of drop shape methods. This approach employs the wetting/dewetting behaviours of liquids on a heterogeneous surface. The surface consists of patterns of hydrophilic SAM surface domain in a square and hydrophobic SAM surface surrounding the square. To prepare the above patterned surface, a precision stamping device was designed to facilitate micro-contact printing (μ CP) with elastometric stamps. This assures an accurate surface patterning, and provides an enhanced printing quality, as compared to those performed by hand. According to the modified Young's equation, a line tension magnitude can be estimated from digital image analysis of the contact line profile on the solid surface, right before liquid drop breaks out-off the inner square region. The experimental results show that the line tension values are positive and on the order of 10^{-6} to 10^{-7} J/m.

JinPy Xu.

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Table of Contents

Abstract	ii
Acknowledgements	iv
Table of Contents	v
List of Tables	viii
List of Figures	x
Nomenclature	xiv
 1. Introduction	 1
 2. Surface and Interfacial Phenomena	 4
2.1 Surface/Interfacial tension	4
2.2 Curved interface: Laplace's capillarity relation	5
2.3 Contact angles and wetting	7
2.4 Line tension and modified Young's equation	8
2.4.1 Description of line tension	8
2.4.2 Surface curves	9
2.4.3 Modified Young's equation	11
2.5 Surface thermodynamics	12
2.5.1 General equation for bulk phases	12
2.5.2 General relation of classical surface thermodynamics	13
2.5.3 Thermodynamic potentials	14
References	21

3. Measurements of Surface Tension and Line Tension	23
3.1 Surface tension measurements	23
3.2 Line tension measurements	26
3.2.1 Current measurement techniques	27
3.2.2 Problems of current measurement attempts	32
3.2.3 Measurement requirements and conditions	34
3.3 Novel technique for line tension measurement	36
References	45
4. Experimental Preparation for Line Tension Measurement	47
4.1 Control of the pressure pump	50
4.2 Control of the chemical potential	53
4.3 Solid substrate preparation with Ti and Au	58
4.4 Patterned surface preparation with SAMs	59
4.4.1 Introduction to self-assembled monolayer	60
4.4.2 Micro-contact printing	62
4.4.3 Precision stamping set-up/fixture	63
4.4.4 Producing heterogeneously patterned surface	64
References	76
5. Drop Spreading Experiments and Results	78
5.1 Selection of test liquids and experimental cleaning	79
5.2 Digital image acquisition	80
5.3 Digital image fundamentals	83
5.4 Digital image processing	86
5.5 Calibration measurements	88
5.6 Contact angle measurements	92
5.6.1 Drop profile data acquisition	92
5.6.2 Axisymmetric drop shape analysis-profile (ADSA-P) technique	94
5.7 Line tension measurements	96
References	134

6. Conclusions and Future Work	135
6.1 Conclusions	135
6.2 Future work	139
Reference	140
Appendix A: Calculation of Contact Line Velocity	141
Appendix B: Calculation of Chemical Potential Control	148
B.1 Chemical potential difference across the drop interface	149
B.2 Equilibrium of vapour in contact with liquid	150
B.3 Pressure and chemical potential variations with height	152
B.4 Comparison with the previous sessile drop arrangements in chemical potential control	152
References	167
Appendix C: Image Processing Programs (MATLAB)	168
Appendix D: ADSA-P Program (FORTRAN)	175

List of Tables

3.1	Line tension values from past different experimental arrangements. . . .	39
3.2	Results of line tensions using sessile drops on 1-octadecanethiol SAM surface.	39
4.1	Advancing and receding contact angles of water and hexadecane (HD) on SAMs, formed in ethanol solutions, obtained on four metal substrates.	68
4.2	Advancing contact angles on derivatized thiol monolayers on gold. . . .	69
4.3	Adsorption of terminally functionalized alkyl chains on gold.	69
5.1	Physical and chemical properties of measuring liquids.	101
5.2	Contact angle values of water on SAM I (hydrophilic) surface.	102
5.3	Contact angle values of water on SAM II (hydrophobic) surface.	103
5.4	Contact angle values of ethanol on SAM II (hydrophobic) surface.	104
5.5	Contact angle values of hexadecane (group #1) on SAM II (hydrophobic) surface.	105
5.6	Contact angle values of hexadecane (group #2) on SAM II (hydrophobic) surface.	106
5.7	Contact angle values of hexadecane (group #3) on SAM II (hydrophobic) surface.	107
5.8	Contact angle values of hexadecane (group #4) on SAM II (hydrophobic) surface.	108
5.9	Estimated Line tension values of water ($\gamma_v = 72.75 \text{ mJ/m}^2$).	109

5.10	Estimated line tension values of ethanol ($\gamma_v = 23.70 \text{ mJ/m}^2$).	109
5.11	Estimated line tension values of hexadecane ($\gamma_v = 27.76 \text{ mJ/m}^2$).	110
5.12	Summary of experimental results at room temperature, where the line tension values of liquids on SAM I were measured using “drop spreading experiment” and the line tension values of liquids on SAM II were measured using “sessile drop arrangement”.	110

List of Figures

2.1	(a) Density variation in liquid-vapour interfacial region, where x is the distance normal to the surface; (b) stress across the interface, where σ_N and σ_T are the normal and tangential stresses, respectively.	17
2.2	Distribution of forces on the molecules in a drop.	17
2.3	Two principal radii of curvature for a surface, where P is a surface point at the intersection point of two orthogonal curves.	18
2.4	(a) A sessile drop on an ideal solid surface; (b) profile of an axisymmetric liquid lens on a liquid support.	18
2.5	Contact angles measured through the vapour phase are: $\theta=0$ (wetting), $0<\theta<\pi$ (partial wetting), $\theta=\pi$ (non-wetting).	19
2.6	(a) Side and top views of an axisymmetric sessile drop; (b) an axisymmetric lens with the line tension effect.	19
2.7	Schematic of a surface curve frame.	20
3.1	Schematic of the ring method.	40
3.2	Meniscus profile for non-wetting liquid.	40
3.3	Shape of a pendant drop.	40
3.4	Behaviour of contact angles and the cosine of contact angles versus drop size. The slope is negative in (a) and the line tension is positive, whereas the slope is positive in (b) and the line tension is negative. ...	41
3.5	Liquid meniscus in contact with a stripwise heterogeneous wall.	41
3.6	Pendent drop in contact with second immiscible liquid.	42
3.7	Schematic of a cone-shaped capillary.	42

3.8	(a) Top view of three-phase contact lines of the liquid drop; (b) side view of the profiles of the liquid drop while expanding.	43
3.9	Photographs of square-like water drops resting on silicon wafers coated with gold.	44
4.1	Block diagram of the experimental set-up.	70
4.2	Photographs of the experimental set-up: (a) entire experimental assembly; (b) enlarged experimental surface.	71
4.3	Apparatuses for connections (Cole-Parmer Inc.): (a) barbed fitting with 1/8" ID, which was a straight connector, made of clear Polypropylene; (b) quick-disconnect hose barbs connecting 1/8" ID tubing.	71
4.4	Schematic of the molecules in a self-assembled monolayer.	72
4.5	(a) Contact angle of a distilled water drop on the C ₁₈ SAM surface produced on gold is ~106°; (b) contact angle of a distilled water drop on a gold surface is ~50°.	73
4.6	PDMS elastometric stamping fixture assembly: (a) linear precision micrometric translator; (b) reverse angle mirror mount; (c) metric tilt platform; (d) gold surface to be patterned; (e) slide rod; (f) mounting post; (g) adjustable rack with pinion post.	74
4.7	Photographs of PDMS stamp (a) with the stamp holder (b) and 65 μm step (c) on stamp with RUBY calibration ball (d) (radius of 500 μm).	75
5.1	Schematic of focal length in the case of a simple lens.	111
5.2	Relations between focal length and image size.	111
5.3	Depth of field when different focal length lenses are used at the same f-stop settings.	112
5.4	Change in depth of field corresponding to f-numbers at the same focus settings.	112
5.5	Relations of f-numbers, image brightness, aperture, and depth of field.	112

5.6	Waterfall-like 3D grey-level profiles (b) of the upper corner of the original image (a).	113
5.7	Schematic of RGB model.	114
5.8	RGB model color cube.	114
5.9	Grey-level profiles (c) of the original image (a) versus the smoothed image (b) at the location illustrated by two short lines in images (a) and (b). Plot (c) indicates an edge in the image had a 5-6 pixel smooth transition zone.	115
5.10	(a) 3×3 image region, and Sobel operator masks: (b) column differential gradient edge operator and (c) row differential gradient edge operator.	116
5.11	Top view of grid distortion targets.	116
5.12	Histogram of the image of the calibration object with one peak around 25 and the other one around 253. Intensities range from 0 to $2^8-1=255$	117
5.13	(a) Original image of RUBY calibration ball; (b) processed image with threshold of 139-20; (c) processed image with threshold of 139; (d) processed image with threshold of 139+20.	117
5.14	Procedure for obtaining the profile of a water drop resting on SAM II (hydrophobic surface): (a) original drop image; (b) image of the drop section above the substrate surface; (c) filtered and detected drop profile.	118
5.15	(a) Side view of a water drop resting on SAM I (hydrophilic surface) produced on glass coated with gold; (b) drop advancing profiles in physical space.	119
5.16	(a) Side view of a water drop resting on SAM II (hydrophobic surface) produced on glass coated with gold; (b) drop advancing profiles in physical space.	120
5.17	(a) Side view of an ethanol drop resting on SAM II (hydrophobic surface) produced on glass coated with gold; (b) drop advancing profiles in physical space.	121

5.18	(a) Side view of a hexadecane drop resting on SAM II (hydrophobic surface) produced on glass coated with gold; (b) drop advancing profiles in physical space.	122
5.19	Dependence of the contact angle on the drop size for water on SAM I produced on glass coated with gold.	123
5.20	Dependence of the contact angle on the drop size for water on SAM II produced on glass coated with gold.	124
5.21	Dependence of the contact angle on the drop size for ethanol on SAM II produced on glass coated with gold.	125
5.22	Dependence of the contact angle on the drop size for hexadecane on SAM II produced on glass coated with gold.	126
5.23	Dependence of the contact angle on the drop size for water on SAM I produced on <i>Si</i> wafer coated with gold.	127
5.24	Dependence of the contact angle on the drop size for water on SAM II produced on <i>Si</i> wafer coated with gold.	128
5.25	Dependence of the contact angle on the drop size for ethanol on SAM II produced on <i>Si</i> wafer coated with gold.	129
5.26	Dependence of the contact angle on the drop size for hexadecane on SAM II produced on <i>Si</i> wafer coated with gold.	130
5.27	Top views of an ethanol drop growing and breaking out of the inner, SAM I, zone (photographs in alphabetical sequence denote increasing times).	131
5.28	Contact line profile of one corner of an ethanol drop with two straight edge sides and the curved line at the corner before the drop broke-out of the inner square region (SAM I).	132
5.29	Contact line profile of one corner of an ethanol drop with the 95% confidence interval on the two straight sides and a best-fit circle on the curved contact line at the corner.	133

Nomenclature

a_1, a_2	: width of the two strips of the heterogeneous wall; [m]
a, b	: intercept and slope of the best-fit line
$\bar{b}$	: binomial curvature vector of a space curve
c	: capillary constant; [m ⁻²]
f	: Darcy friction factor; [unitless]
$f(x, y)$	: function of the image's pixel coordinates x and y
g	: gravitational acceleration, 9.80665 [m/s ²] or 32.174 [ft/s ²]
$g(x, y)$	: processed image from $f(x, y)$
h	: height of the meniscus above the flat liquid surface where the capillary tube is placed in liquid; [m]
h_f	: friction head loss; [m]
$i(x, y)$	: illumination components
l	: perimeter of the plate; [m]
l_p	: actual length of each size of a pixel; [m]
Δl	: uncertainty of each pixel length; [m]
n	: number of the points selected for the estimation of the best-fit line
$\bar{n}$	: normal curvature vector of a space curve
$r(x, y)$	: reflection components
s	: arc length; [m]
t	: student t-distribution probability
$\vec{t}$	: unit tangent vector to a surface curve
$\bar{x}$	: mean value of x_i

$\hat{y}_i$	: vertical ordinate on the best-fit line corresponding to x_i
z_{max}	: vertical distance between the substrate surface and the drop apex; [m]
Δz	: vertical distance between the adjustable stands (8) and (10) in Fig. 4.1; [m]
D	: inner diameter of given tubing; [m]
F	: Helmholtz free energy; [J]
$\bar{F}$	: surface curve frame vector (see Fig. 2.7)
$\bar{F}'$	: surface curve frame rate
G	: Gibbs free energy; [J]
$I_0(X)$	: modified Bessel function of the first kind of the order zero
$I_1(X)$	: modified Bessel function of the first kind of the order one
J_{lv}	: mean curvature of a surface; [m ⁻¹]
L	: length of given tubing; [m]
M_i^b	: total mass of component i in a bulk phase; [kg]
M_i^s	: extrapolated mass for the surface system; [kg]
N_p	: number of pixels included in the object
$\bar{N}$	: unit normal vector to a surface curve (see Fig. 2.7)
P	: bulk pressure; [J/m ³]
P_k	: partial pressure of the liquid vapour in the vapour phase; [J/m ³]
P_l	: liquid drop pressure; [J/m ³]
P_N	: solid surface stress component in the normal direction; [J/m ³]
P_{sat}	: saturated liquid pressure in vapour phase; [J/m ³]
P_v	: total vapour pressure around the drop from all components; [J/m ³]
ΔP	: pressure difference across an interface; [J/m ³]
ΔP_o	: pressure difference at the origin of an axisymmetric system (considered as the apex of a sessile drop or the top of the drop); [J/m ³]
Q	: volume flow rate passing through the tubing; [m ³ /s]
R	: local radius of the drop's contact line on the solid substrate; [m]
R_1	: maximum principal radius of a curved surface; [m]
R_2	: minimum principal radius of a curved surface; [m]
R_{best}	: radius of the best-fit circle; [m]

Re	: Reynolds number; [unitless]
R_g	: universal gas constant, 8.314 [J/mol·K] or 1545 [ft·lbf/lbmol·°R]
$\Delta R/\Delta t$	: velocity of the contact line of a sessile drop during spreading; [m/s]
S	: spreading parameter; [J/m ²]
$S(X^2)$	: corrected sum of squares
S^b	: bulk phase entropy; [J/K]
S^s	: entropy for the surface phase; [J/K]
SSD	: residual sum of squares
T	: temperature; [K]
$\bar{T}$	: intersection of a tangent plane and a normal plane (see Fig. 2.7)
(U^a+U^b)	: energy of the bulk hypothetical system constructed to be uniform right-up to the surface division separating the two bulk phase; [J]
U^b	: internal energy of a thermodynamic bulk system; [J]
U_{total}^b	: total energy of the system; [J]
U^s	: surface energy for the surface system; [J]
dU^b	: change in the internal energy; [J]
V	: bulk volume; [m ³]
$\bar{V}$	: mean velocity of the flow; [m/s]
W	: weight of the drop; [N]
W_{total}	: sum of the weight of the ring and the force to pull the ring out-off the surface caused by surface tension; [N]
ΔW	: change in the weight of the plate after contacting the liquid; [N]

Greek symbols

α	: tail area of the student t-distribution
γ_{lv}	: liquid-vapour surface tension; [J/m ²]
γ_{sl}	: solid-liquid surface tension; [J/m ²]
γ_{sv}	: solid-vapour surface tension; [J/m ²]

θ_1	: contact angle between the liquid A-vapour interface and the liquid B-liquid A interface; [degree]
θ_2	: contact angle between the liquid A-vapour interface and the liquid B-vapour interface; [degree]
θ_∞	: contact angle corresponding to an infinitely large drop; [degree]
$\theta_{\kappa 1}$	: angle between the liquid A-liquid B interface and the $\bar{\kappa}$ direction; [degree]
$\theta_{\kappa 2}$	: angle between the liquid B-vapour interface and the $\bar{\kappa}$ direction; [degree]
$\theta_{I[1]}, \theta_{I[2]}$	: corresponding contact angles that the liquid forms on an infinitely wide strip of either material [1] or [2]; [degree]
θ_C	: Cassie contact angle; [degree]
$\theta_{I\infty}$	: contact angle of a large drop on Surface I; [degree]
$\theta_{II\infty}$	: contact angle of a large drop on Surface II; [degree]
κ	: plane curvature of a curve; [m ⁻¹]
κ_{gs}	: geodesic curvature of the contact line; [m ⁻¹]
κ_n	: normal curvature; [m ⁻¹]
μ	: dynamic viscosity of a given liquid; [Ns/m ²]
μ_0	: chemical potential at unit pressure (set as 1 atm); [J/kg]
μ_i	: chemical potential of component i ; [J/kg]
μ_l	: chemical potential of the drop's liquid phase; [J/kg]
μ_v	: vapour chemical potential around the drop; [J/kg]
ν	: kinematic viscosity; [m ² /s]
$\Delta\rho$	: density difference between two bulk phases; [kg/m ³]
σ	: line tension; [J/m or N]
σ_N	: stress normal to the surface; [N/m ²]
σ_T	: stress tangent to the surface; [N/m ²]
τ	: torsion of a contact line curve; [radians/m]
τ_g	: geodesic torsion of a contact line curve; [radians/m]
ϕ	: relative humidity; [unitless]
ω^b	: free energy density of a bulk phase; [J/m ³]
ω^l	: free energy density of a line phase; [J/m ³]

- ω^s : free energy density of a surface phase; [J/m³]
 Φ : rotated angle; [degree]
 Ω : grand canonical potential; [J]

Chapter 1

Introduction

Line tension effects have been noted in drop wise condensation/nucleation, wetting/spreading of liquids on solids, cell adhesion and micro-fluidic applications. Line tension is defined in complete analogy with accepted thermodynamic definitions of pressure and surface tension. In other words, surface tension is the two-dimensional analogue of bulk pressure, while line tension is its one-dimensional analogue. The concepts of surface tension and line tension are explained in Chapter 2. Since surface tension and line tension are related to each other in the general scope of surface thermodynamics, the fundamentals of surface thermodynamics are also briefly introduced in Chapter 2.

Despite being a well-defined thermodynamic quantity, there are still significant discrepancies in both the magnitude and the sign of line tension among the reported measurements in the open literature. The existing experimental arrangements for line tension estimations are mostly based on either the modified Young's equation or the Neumann triangle relation. Unfortunately, these experimental attempts all suffered from different kinds of difficulties or inaccuracy in measuring the line tension, as will be discussed in Chapter 3. Thus, an alternative arrangement for line tension measurement on a patterned surface has been developed in this thesis. This experimental arrangement

was named as “drop spreading method”. In this method, the estimation of line tension is based on the measurements of three-phase contact line shape, in order to minimize the difficulties and problems existing in previous other experimental arrangements.

To implement line tension measurement with the proposed new experimental method, an experimental set-up has been designed, and is introduced in detail in Chapter 4. The schematic of the entire experimental assemble is presented in this chapter. One of the most important components of this experimental setup is a solid substrate, which was coated with gold. On the gold surface, there was a patterned surface of SAMs with two wettabilities, i.e., a square inlay with low-contact angle SAM that is surrounded by another SAM surface with high-contact angle. The substrate preparation was carried out using a precision stamping fixture developed for accurate surface patterning, based on the micro-contact printing technique. Another important component of this experimental setup is a hydrostatic pump. It controls the growth of the sessile drop on the substrate, by controlling the flow rate of the measuring liquid coming onto the substrate. The entire experimental set-up was designed and improved to reduce the liquid evaporation and minimize chemical potential effects during the measurements.

Chapter 5 focuses on the experimental procedure for line tension estimation, using the new experimental method, i.e., drop spreading method. First, the contact angles of liquid drops on the two SAM surfaces should be measured. These liquid drops were digitized by a CCD camera. In each experiment, the images were calibrated using an accurate calibration object with known dimensions. The drop profile data was obtained by processing the images using MATLAB® Image Processing Toolbox (MathWorks Inc.). Then the contact angles were calculated based on the drop profile, using the

Axisymmetric Drop Shape Analysis-Profile (ADSA-P) program. Likewise, the image of contact line profile at the corner of the inner square was acquired just before the drop broke. The contact line profile was processed to calculate the curvature of the corner curve. Line tension values were estimated based on the contact angles of two SAM surfaces and the radius of the contact line profile, using the modified Young's equation. The experimental results showed that the line tension values were positive and of the order from 10^{-6} to 10^{-7} J/m.

Finally, the line tension measurement results are summarized and discussed in the Chapter 6. The sensitivity of the experimental results to the measurement error is emphasized. Conclusions are presented to stress the advantages and critical factors of this experimental arrangement. Some recommendations for future work are given at the end of this thesis.

Chapter 2

Surface and Interfacial Phenomena

An interface is the boundary between two phases. Since interfaces are very thin, they are often regarded as equivalent to geometric surfaces, and their thickness are neglected for this study. The property of a surface or interface is affected by changes in either one of the two phases adjacent to the interface (Adamson, 1990).

2.1 Surface/Interfacial tension

The changes in density and stress across a surface give it particular properties. The lateral stress or excess free energy across the surface is called surface/interfacial tension. The main effect of surface tension is that a system acts to minimize its interfacial area, e.g., a small drop of one fluid in another is spherical when the gravitational effects can be neglected.

Consider the interface between a pure liquid and its vapour as an example. This interface is not strictly discontinuous, in the sense that the density does not change sharply, but it changes continuously when averaged over a small time interval (refer to Figure 2.1a). This interface thickness is only a few molecular diameters (Miller and Neogi, 1985). An exception occurs for liquids near their liquid-vapour critical points. As

shown in Figure 2.1b, the stress tangent to the surface σ_T is much greater than normal to the surface σ_N , in the normal direction $\sigma_N = -P$ is the thermostatic pressure.

Surface tension of a fluid interface can be viewed in two different ways. From a thermodynamic point of view, it is excess free energy per unit area caused by the surface, or defined as the work required to increase the surface area. The molecules are tied to each other due to the Van der Waals force. Energy must be supplied to separate them. The energy per molecule is thus greater in the interfacial region than in the bulk. This energy is also called the surface energy, expressed in units of J/m^2 . Surface energy is not always equivalent to the surface tension. In the case of liquids, surface energy and surface tension are identical; but, as shown by Gibbs in 1876, the surface tension of a solid can greatly differ from its surface energy. From a mechanical point of view, the molecule near the surface undergoes anisotropic forces, which have weaker forces in a direction perpendicular to the surface than those parallel to it, as shown in Figure 2.2. It could be the reason of $\sigma_T > \sigma_N$ as presented in Figure 2.1b. Thus, surface tension is also defined as a tensile force per unit length parallel to the interface, denoted by γ and expressed in units of N/m . Accordingly, surface tension is the two-dimensional counterpart of the three-dimensional bulk pressure.

2.2 Curved interface: Laplace's capillarity relation

One special property of a curved interface is the pressure discontinuity across it, e.g., a liquid drop resting on a solid surface and surrounded by its vapour has a larger liquid phase pressure than the surrounding vapour phase. This discontinuity is called the

capillary pressure. Laplace's formula of capillarity describes the jump in the pressure across a curved interface (Daoud and Williams, 1993):

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

where γ_{lv} is the liquid-vapour surface tension, ΔP is the pressure difference across the interface, and J_{lv} is the mean curvature of the surface and it can be expressed as $(1/R_1 + 1/R_2)$, where R_1 and R_2 are the principal radii of the curved surface. They can be understood as the maximum and minimum radii of two orthogonal curves draw on the curve surface from a point on the surface (refer to Figure 2.3). Laplace's capillarity relation (Equation (2.1)) also indicates that the mechanical equilibrium between surface tension and external force causes the surface to bend and change J_{lv} (Eskinazi, 1967). If the only external force on the system is gravity, then ΔP is the sum of the pressure difference at the origin of the axisymmetric system (the apex of a drop), denoted by ΔP_o , and the hydrostatic pressure $\Delta \rho g(z - z_o)$. At the origin of an axisymmetric sessile drop, which is set at the top of the drop, $R_1 = R_2 = R_o$ and $\Delta P_o(z = z_o) = 2\gamma_{lv}/R_o$. Thus, Equation (2.1) for the sessile drop may be written as

$$\Delta P(z) = \Delta P_o + \Delta \rho g(z - z_o) = \gamma_{lv} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.2)$$

where $\Delta \rho$ is the density difference between the two bulk phases involved, g is the gravitational acceleration, and z is the vertical distance between an arbitrary point in the drop and the plane that is horizontal and tangent to the top or apex of a sessile drop and the vertical z -axis is directed parallel to the gravitational vector $\vec{g}$ (Duncan et al., 1995).

2.3 Contact angles and wetting

When two interfaces meet, the junction forms a curve known as a contact line. The angle that these two interfaces make with each other is called the contact angle. For a liquid drop resting on a rigid, homogeneous, horizontal, and smooth surface (refer to Figure 2.4a), there are three interfaces: the solid (*s*)-liquid (*l*), the liquid-vapour (*v*) and the solid-vapour, three surface tensions γ_{sl} , γ_{lv} , γ_{sv} , and an intrinsic contact angle θ . If these surface tensions can be taken as forces, then the forces balance at the contact line along the horizontal direction according to:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (2.3)$$

This is the classical Young's equation of capillarity, developed in 1805. If the solid surface is not smooth and homogenous, different expressions for the relation between contact angles and surface tensions are given by Wenzel equation for a rough surface and Cassie equation for a heterogeneous surface. If the volume is increased, the drop deforms to a lens-shape, flattened by gravity. However, the contact angle doesn't change and is independent of the gravitational effect (Daoud and Williams, 1999). If all three phases are deformable, e.g., liquid *A*, liquid *B* and the vapour phase *V*, then the Neumann's triangle construction is applicable (refer to Figure 2.4b). It can be written in the following vector form (Chen et al., 1996):

$$\vec{\gamma}_{AV} + \vec{\gamma}_{BV} + \vec{\gamma}_{AB} = 0 \quad (2.4)$$

The shape of a sessile drop resting on a solid substrate most often describes wettability that is a comprehensive problem about the interaction of liquids with solids. The contact angle is one of parameters that show the wettability. If the liquid wets the surface, called complete wetting, then the contact angle is small and may even vanish.

Partial wetting occurs when the drop does not spread completely (refer to Figure 2.5) (Binks, 2001). Zero contact angles are possible, but contact angles are always less than 180° in real (the highest observed angle, by a mercury drop on glass, has been reported to be around 148°) (Berg, 1993). Other important parameters, such as the spreading parameter and the temperature, may also decide the wetting. A quantity to characterize spreading, termed as spreading parameter S , was introduced by Marangoni in 1865 as:

$$S = \gamma_{sv} - (\gamma_{sl} + \gamma_{lv}) \quad (2.5)$$

When $S < 0$, the surface has the lower free energy and the liquid does not spread (non-wetting or partial wetting), i.e., this surface is hydrophobic. When $S \geq 0$, the wetting is complete, i.e., the surface is hydrophilic (Maugis, 2000). In some applications, it is often necessary to control wettability. As discussed later in this thesis, coating different types of self-assembled monolayers on a gold substrate was undertaken to produce wetting or non-wetting surfaces.

2.4 Line tension and modified Young's equation

Gibbs argued “Just as a surface separating two bulk media (surface tension), so it is a line separating two interfaces (line tension)”. Line tension may still be estimated using the Young's equation, even though it may not be well defined due to the overlap of part of the interfacial regions.

2.4.1 Description of line tension

Line tension is the linear force acting at the edges of surface zones where multiple, immiscible phases meet, expressed in units of N. It can be also understood as

the effect of tightening or loosening the “collar” (the contact line) that bounds the drop (Widom, 1995). Analogous to surface tension, line tension may be defined as the free energy per unit length of the multiple-phase contact line in thermodynamics, expressed in units of J/m (Duncan et al., 1995). Thus, line tension is the one-dimensional analogue of surface tension.

The determination of line tension depends on the mechanical equilibrium condition at the contact line as well. For the liquid/solid/vapour system, if the system has a constant line tension and it is restricted to moderate curvatures, then the modified Young’s Equation (2.6) can be used to incorporate the line tension into the classical as:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} - \sigma \kappa_{gs} \quad (2.6)$$

where, σ is the line tension, and κ_{gs} is the geodesic curvature of the three-phase line, i.e., the curvature of the circle in the plane of the solid phase, as illustrated in Figure 2.6a.

2.4.2 Surface curves

The modified Young’s equation, Equation (2.6), tells us that one of the important parameters needed to estimate line tension is the geodesic curvature. To understand the geodesic curvature of a line, the knowledge of surface curves is required. A surface curve frame set is as shown in Figure 2.7, where $\vec{t}, \vec{N}$ are unit tangent vector and unit normal vector to the surface curve, respectively, and $\vec{T}$ is the intersection of the tangent plane and normal plane. The surface curve frame $\vec{F}$ can be expressed in terms of the arc length s in a matrix notation as follows:

$$\bar{F}(s) = \begin{bmatrix} \bar{t}(s) \\ \bar{T}(s) \\ \bar{N}(s) \end{bmatrix} \quad (2.7)$$

As both $\bar{N}$ and $\bar{T}$ lie on the normal plane of the curve, they can be related to the curve normal $\bar{n}$ and binomial $\bar{b}$ by rotating $\bar{N}$ and $\bar{T}$ around $\bar{t}$ (refer to Figure 2.7). This rotated angle is denoted by Φ . The following relations among $\bar{N}$, $\bar{T}$, $\bar{n}$ and $\bar{b}$ exist:

$$\bar{T}(s) = \bar{n}(s) \cos \Phi(s) + \bar{b}(s) \sin \Phi(s) \quad (2.8a)$$

$$\bar{N}(s) = -\bar{n}(s) \sin \Phi(s) + \bar{b}(s) \cos \Phi(s) \quad (2.8b)$$

Equations (2.7), (2.8a) and (2.8b) can be reorganized, and put into the following matrix notation

$$\bar{F}(s) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \Phi(s) & \sin \Phi(s) \\ 0 & -\sin \Phi(s) & \cos \Phi(s) \end{bmatrix} \begin{bmatrix} \bar{t}(s) \\ \bar{n}(s) \\ \bar{b}(s) \end{bmatrix} \quad (2.9)$$

The surface curve frame rate $\bar{F}'$, i.e., the derivative of $\bar{F}$ with respect to arc-length s , analogous to a space curve frame rate proposed by Frenet-Serret relations (well known in Differential Geometry), can be calculated as follows:

$$\bar{F}'(s) = \begin{bmatrix} 0 & \kappa(s) \cos \Phi(s) & \kappa(s) \sin \Phi(s) \\ -\kappa(s) \cos \Phi(s) & 0 & \tau(s) + \Phi'(s) \\ -\kappa(s) \sin \Phi(s) & -[\tau(s) + \Phi'(s)] & 0 \end{bmatrix} \begin{bmatrix} \bar{t}(s) \\ \bar{n}(s) \\ \bar{b}(s) \end{bmatrix} \quad (2.10)$$

where κ and τ are the plane curvature and the curve torsion, and Φ' denotes $d\Phi/ds$. Here $\kappa(s) \cos \Phi(s)$ is called the geodesic curvature, and is denoted by κ_g ; $\kappa(s) \sin \Phi(s)$ is the normal curvature, and is denoted as κ_n ; $(\tau(s) + \Phi'(s))$ is called the geodesic torsion of the curve, and is denoted as τ_g . Thus, when the surface curve does not rotate, i.e., $\Phi=0$, the

geodesic curvature should be the plane curvature and there is no normal curvature (Nutbourne and Martin, 1988). In this thesis, the three-phase contact lines under study in the experiments are assumed to be circular or a portion of a circle. Thus, the geodesic curvature is equal to the reciprocal of the radius of the three-phase circle, $1/R$.

2.4.3 Modified Young's equation

For a very large drop, i.e., $R \rightarrow \infty$ and $\kappa \rightarrow 0$, the line tension term in the modified Young's Equation (2.6) becomes neglectable and can be simplified to:

$$\gamma_{lv} \cos \theta_{\infty} = \gamma_{sv} - \gamma_{sl} \quad (2.11)$$

where θ_{∞} is the contact angle corresponding to an infinitely large drop. In order to measure line tension experimentally, it is desirable to reduce the number of parameters. Combining Equations (2.11) and (2.6) gives the following equation (Neumann and Spelt, 1996; Amirfazli et al., 2003).

$$\cos \theta = \cos \theta_{\infty} - \frac{\sigma}{\gamma_{lv}} \frac{1}{R} \quad (2.12)$$

Equation (2.12) tells us that the line tension effect becomes significant only for a drop with a small size. The equation also tells that the contact angle depends on the drop size R if $\sigma \neq 0$, and that there should be a linear relationship between $\cos \theta$ and $1/R$, assuming that the liquid-vapour surface tension is constant and independent of the drop size. Likewise, the classical Neumann's triangle relation can be modified with the line tension term, which converts the triangle of forces into a quadrilateral (refer to Figure 2.6b) (Chen et al., 1996).

$$\vec{\gamma}_{AV} + \vec{\gamma}_{BV} + \vec{\gamma}_{AB} - \sigma \vec{\kappa} = 0 \quad (2.13)$$

The modified Young's equation and Neumann's equation quadrilateral have provided the basis for experimental measurements of line tension. The arrangements of experimental measurements of line tension will be introduced in Chapter 3.

2.5 Surface thermodynamics

The macroscopic thermodynamics of interfaces is sometimes called the theory of capillarity. As mentioned before, those quantities, i.e., contact angle, wettability, surface tension and line tension, can be defined from the surface thermodynamic point of view. The foundation of classical surface thermodynamics was laid by Gibbs, who created a "pure statics of the effects of temperature and heat" (Truesdell et al., 1984; Neumann and Spelt, 1996).

2.5.1 General equation for bulk phases

The fundamental study of bulk phases has been conducted to reveal the relation between the internal energy of a simple thermodynamic bulk system, U^b , and the modes of energy transfer between the system and the surroundings. The change in the internal energy, dU^b , is usually written as (Neumann and Spelt, 1996):

$$dU^b = TdS^b - PdV + \sum_i \mu_i dM_i^b \quad (2.14)$$

where T is the bulk temperature, S^b , P , V are the bulk or 3-dimensional entropy, pressure and volume, μ_i is the chemical potential of component i , and M_i^b is the total mass of component i in the bulk phase. TdS^b represents the reversible heat transfer, PdV is the

reversible mechanical work, while $\mu_i dM_i^b$ represents the reversible chemical work. Another expression of this fundamental equation is the integrated relation (Callen, 1962):

$$U^b = TS^b - PV + \sum_i \mu_i M_i^b \quad (2.15)$$

This is well known as the Euler equation. Another important relation called the Gibbs-Duhem equation, which is also often applied in thermodynamics, can be obtained by substituting Equation (2.15) into (2.14) as follows (Callen, 1962):

$$S^b dT - V dP + \sum_i M_i^b d\mu_i = 0 \quad (2.16)$$

2.5.2 General relation of classical surface thermodynamics

As mentioned earlier, due to the difference of the molecular interaction in the interfacial region, the density, the energy and the entropy in the neighbourhood of the interface will differ from those in the bulk phase. The internal energy expression of the surface is defined as the difference:

$$U^s = U_{total}^b - U^\alpha - U^\beta \quad (2.17)$$

where U^s represents the energy in the interfacial region, U_{total}^b is the total energy of the system, $(U^\alpha + U^\beta)$ represents the energy of the bulk hypothetical system constructed to be uniform right-up to the surface division separating the two bulk phase. The change of the internal energy at the interface can be expressed as

$$dU^s = T dS^s + \gamma dA + \sum_i \mu_i dM_i^s \quad (2.18)$$

where γdA represents the work done in generation a surface increment dA , U^s , S^s , M_i^s are the corresponding internal energy, the entropy and the mass for the surface system. It

should be noted that the sign of the term γdA in Equation (2.18), and the one of PdV in Equation (2.15), are opposite. The positive sign in Equation (2.18) means that growing the area of the surface increases the internal energy of the surface system, while a volume expanding consumes internal energy of the bulk system. The analogous Euler equation and the Gibbs-Duhem equation, also known as the Gibb's adsorption equation, for a surface system are respectively given by

$$U^s = TS^s + \gamma A + \sum_i \mu_i M_i^s \quad (2.19a)$$

$$S^s dT + A d\gamma + \sum_i M_i^s d\mu_i = 0 \quad (2.19b)$$

Thus, one can know from Equation (2.19b) that the surface tension varies with the temperature and chemical potential and it is the reason why in experimental measurements of surface tension, the thermal and chemical equilibrium need to be maintained.

2.5.3 Thermodynamic potentials

The relation between the various expressions of the fundamental equation is realized by means of Legendre transformations. The Legendre transformed functions are called thermodynamic potentials. These transformations permit parameters in the fundamental equations to be replaced by their corresponding intensive quantities. Therefore, the entropy, the volume, and the interfacial area may be replaced by the temperature, the pressure, and the surface tension, which are easier to control in experiments (Neumann and Spelt, 1996).

The Helmholtz potential, or Helmholtz free energy F , is the partial Legendre transform of U which replaces S with T as independent variable. The Gibbs function, or Gibbs free energy G , is the Legendre transformation of U which replaces S with T and V with P as independent variables. For a total system, those changes of free energy are expressed as (Callen, 1962):

$$dF = -SdT - PdV + \gamma dA + \sum_i \mu_i dM_i \quad (2.20a)$$

$$dG = -SdT + VdP + \gamma dA + \sum_i \mu_i dM_i \quad (2.20b)$$

The Gibbs function is not suitable for capillary systems because it requires controlling each phase pressure during an experiment, which is impossible for a small drop or bubble. Thus, the Helmholtz's function is usually used to treat capillary systems. For instance, the changes in Helmholtz's free energy can be calculated by generalizing Equation (2.20a) for a liquid/solid/vapour system, if the temperature and the individual phase volumes are constant,

$$dF = \sum_i \mu_i (dM_i^{lv} + dM_i^{sl} + dM_i^{sv}) + \sum_i \mu_i (dM_i^s + dM_i^l + dM_i^v) + \gamma_{lv} dA_{lv} + \gamma_{sl} dA_{sl} + \gamma_{sv} dA_{sv} \quad (2.21)$$

As the total mass of the system remains unchanged,

$$(dM_i^{lv} + dM_i^{sl} + dM_i^{sv}) + (dM_i^s + dM_i^l + dM_i^v) = 0 \quad (2.22)$$

and thus Equation (2.21) can be simplified to,

$$dF = \gamma_{lv} dA_{lv} + \gamma_{sl} dA_{sl} + \gamma_{sv} dA_{sv} \quad (2.23)$$

Furthermore, geometry dictates that $dA_{sl} = -dA_{sv}$. If the interface is a spherical cap, it can be proved that $dA_{lv} = \cos\theta dA_{sl}$. Combining these equations gives:

$$\frac{\partial F}{\partial A_{sl}} = \gamma_{sl} - \gamma_{sv} + \gamma_{lv} \cos \theta \quad (2.24)$$

If the total system is in a mechanical equilibrium, then the total free energy is minimized, i.e., $\partial F / \partial A_{st}$ tends to zero and Equation (2.24) reduce to the classical Young's equation (Miller and Neogi, 1985).

The thermodynamic potential that arises in the statistical mechanical theory of a single-component system is the grand canonical potential Ω . When applied to a surface, a change of Ω can be calculated using Equation (2.25). In this potential, S and M_i are replaced by T and μ_i respectively, so that T and μ_i become independent parameters of the fundamental equation for Ω . The grand canonical potential is more suitable for investigating open capillarity systems with both heat and mass transport across the interface. Two key relations for a surface system are:

$$d\Omega^s = -S^s dT + \gamma dA - \sum_i M_i^s d\mu_i \text{ or } \Omega^s = U^s - S^s T - \sum_i M_i^s \mu_i \quad (2.25)$$

According to Equation (2.25) and the Euler equation (2.19a), $\Omega^s = \gamma A$ for the surface system. The free energy for a total system can be derived in the same way and may be obtained as

$$\Omega_t = \sum_i \Omega_i^b + \sum_i \Omega_i^s + \sum_i \Omega_i^l = \sum_i \omega_i^b V_i + \sum_i \omega_i^s A_i + \sum_i \omega_i^l L_i \quad (2.26)$$

where ω^b , ω^s and ω^l are the free energy density of a bulk, a surface and a line phase, respectively. Obviously, $\omega^b = -P$, $\omega^s = \gamma$ and $\omega^l = \sigma$. Young's equation of capillarity, Neumann triangle relation and Laplace's relation of capillarity can also be derived by minimizing the grand canonical potential with free boundaries and a fixed mass constraint (Neumann and Spelt, 1996).

Figure 2.1 (a) Density variation in liquid-vapour interfacial region, where x is the distance normal to the surface; (b) stress across the interface, where σ_N and σ_T are the normal and tangential stresses, respectively (Neumann and Spelt, 1996).

Figure 2.2 Distribution of forces on the molecules in a drop.

Figure 2.3 Two principal radii of curvature for a surface, where P is a surface point at the intersection point of two orthogonal curves (Defay and Prigogine, 1966).

Figure 2.4 (a) A sessile drop on an ideal solid surface; (b) profile of an axisymmetric liquid lens on a liquid support.

Figure 2.5 Contact angles measured through the vapour phase are: $\theta=0$ (wetting), $0<\theta<\pi$ (partial wetting), $\theta=\pi$ (non-wetting).

Figure 2.6 (a) Side and top views of an axisymmetric sessile drop (Duncan et al., 1995); (b) an axisymmetric lens with the line tension effect (Chen et al., 1996).

Figure 2.7 Schematic of a surface curve frame (Nutbourne and Martin, 1988).

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Chapter 3

Measurements of Surface Tension and Line Tension

Since the surface tension and line tension cannot be measured directly, they are usually estimated through some experimental methodologies. Several often used methods for surface tension measurements will be explained below. Line tension can also be estimated by a few measurement attempts. However, there are still many arguments in both magnitude and sign of reported measurements. Thus, a novel technique for line tension measurement was developed in this thesis, in order to minimize difficulties that exist in previous attempts.

3.1 Surface tension measurements

In this section, some popular methodologies for surface tension measurement are introduced. Among all available methodologies, the capillary rise method is most often used and can be easily implemented. This method is based on the Laplace's formula of capillarity (Equation (2.1)). When a capillary is inserted into a liquid, the liquid will wet the wall and rise up due to the pressure difference across the curved interface as

explained in Section 2.2. The surface is approximately hemispherical for a small radius capillary. In this case, Laplace's Equation (2.1) reduces to

$$\Delta P = \frac{2\gamma_{lv}}{R} \quad (3.1)$$

where R is the radius of the capillary. If let h be the height of the meniscus above the flat liquid surface where the capillary tube is placed, then $\Delta P = \Delta\rho gh$, where $\Delta\rho$ represents the density difference between liquid and vapour phases. Substituting this equation into Equation (3.1), gives

$$\Delta\rho gh = \frac{2\gamma_{lv}}{R} \quad (3.2)$$

Equation (3.2) tells us that, if the height and radius can be measured, then the surface tension can be calculated. This method is considered to be one of the easiest and most accurate methods of surface tension measurement.

Another convenient experimental method for surface tension measurement is the drop weight method. This procedure requires one to form liquid drops at the end of a tube in a vapour phase, allowing them to fall into a container until enough drops have been collected, so that the weight per drop can be determined. An expression for the weight W of the drop is given by

$$W = 2\pi R\gamma_{lv} \quad (3.3)$$

Equation (3.3) can be interpreted as the maximum force to support the weight of a single drop is equal to the surface tension force times the circumference of the tube. This approach can be used for the measurement of liquid-liquid surface tension as well.

The third method, called the du Nouy ring method, evaluates the surface tension through the determination of the force required to detach a ring of wire from a liquid surface (refer to Figure 3.1). The expression is given by

$$W_{total} = W_{ring} + 4\pi R\gamma_{lv} \quad (3.4)$$

where W_{total} is the sum of the weight of the ring and the force to pull the ring out-off the surface caused by surface tension. This approach belongs to the family of detachment methods. Another example from the family of detachment methods is the well-known Wilhelmy slide method. This widely used procedure requires one to raise the liquid level gradually until it just touches a hanging plate, as illustrated in Figure 3.2. The change in the weight of the plate, ΔW , after contacting the liquid is expressed as

$$\Delta W = l\gamma_{lv} \cos \theta \quad (3.5)$$

where l is the perimeter of the plate and θ is the contact angle (Adamson, 1990).

Other methods for surface tension measurement are based on the shape of static drops. There are mainly two factors that could affect the shape of a drop. One is gravity, which is the dominating effect for a large volume drop. The other is the surface tension, which dominates on a smaller drop. In an ideal situation, when gravity is absent, the surface would be a portion of a spherical surface. In reality, the drop shape reflects a balance between the effects of gravity and surface tension (Miller and Neogi, 1985). When these two effects are comparable, the surface tension can be determined from a measurement of the drop's shape, by catching the profile of the drop using either a video or a static image. In this catalogue of methodologies, the pendant drop method (refer to Figure 3.3) and the sessile drop method (refer to Figure 2.4a) are usually adopted. The procedure is to match the entire drop profile to a best fitting theoretical curve (Laplacian

curve). Rotenberg et al. (1984) developed a technique, called Axisymmetric Drop Shape Analysis (ADSA), which has been used successfully in drop profile matching.

The results obtained by these techniques of surface tension measurements are not much different and agree well with each other. It should be noted that there is a main concern in these experiments, that is, evaporation must be prevented at the liquid-vapour interface to prevent cooling of the interface so as to change the surface tension. The above measurement techniques were all developed for measuring the liquid-vapour surface tension. Indirect techniques to measure the liquid-solid or solid-vapour surface tension are available, but are not within the scope of discussion in this study.

3.2 Line tension measurements

There are a few practical and theoretical reasons to measure line tension. First, the magnitude of line tension determines whether or not it is a relevant factor in wetting/spreading of liquids on solids, dropwise condensation in heat transfer, stabilization of emulsions, or cell adhesion to implants. If the line tension were so small, e.g., about 10^{-11} J/m, then its effect would be limited. So, it is worthwhile to measure the line tension, in order to determine whether their effects are neglectable or not. Second, models studied in theoretical calculations are often used in simplified cases and have some uncertainty. Hence, the calculation results from theoretical estimations need to be verified by those from the experimental measurements (Amirfazli et al., 2000). However, unlike surface tension, line tension is not a well-quantified property: experimental values are in the range from 10^{-11} to 10^{-5} J/m and their signs are reported to be positive and negative (refer to Table 3.1); theoretical computations show the values ranging from 10^{-11}

to 10^{-10} J/m with either a positive or a negative sign. The wide range of experimental values may be due to the application of different systems, so that the molecular structures/interactions are different in the zone where multiple phases meet (Koch, 1995). For instance, line tension values obtained from the liquid/solid/vapour system would differ from the results from liquid/liquid/vapour system.

3.2.1 Current measurement techniques

There are also a number of approaches available for evaluating line tension. Theoretically, it can be estimated using statistical mechanics, but there are numerous assumptions involved in its estimation that may not be appropriate. Significant studies have been conducted (Tarazona and Navascues, 1981; Churaev et al., 1982; Blokhuis, 1994; Indekeu, 1994; Widom, 1995), but an analysis of this work is beyond the scope of this thesis. On the experimental side, several distinct experimental arrangements have been developed to determine the line tension.

Three techniques for line tension measurements are introduced in this thesis (other measurement techniques are summarized and explained by Amirfazli and Neumann (2004)). The first one is based on the dependence of the contact angle on the drop/bubble size on a rigid surface and the modified Young's equation, the second technique is based on the contact line shape across a stripwise heterogeneous wall, and the third one is the contact line quadrilateral relation for liquid lens and thin films. For these above methods, the prerequisite assumption is that the line tension will not change over the entire size range of multiphase contact line.

3.2.1.1 Drop size dependence of contact angles

Line tension of small liquid droplets (a few mm in radius) on a rigid surface in a vapour phase can be studied by means of the modified Young's Equation (2.12). This experimental arrangement was carried out by growing a liquid drop on a smooth, homogenous and horizontal solid surface. Equation (2.12) is then applied to determine the numerical value of line tensions by measuring the drop radius R , and the contact angle θ between the sessile drop and the solid substrate (Amirfazli, 2000).

As mentioned in Section 2.4.2, for the case of an axisymmetric sessile drop, the geodesic curvature is given by $\kappa_{gs}=1/R$, where R is the radius of the three-phase contact circle on the solid surface. When performing this measurement, one can plot the data in terms of θ versus R or $\cos\theta$ versus $1/R$ as shown in Figure 3.4. The straight line represents the linear best fit to the experimental data points using a least squares algorithm. Consequently, according to Equation (2.12), the line tension σ can be estimated from the slope ($-\sigma/\gamma_{lv}$) of the best-fit line, assuming the surface tension γ_{lv} does not change during measurement. Moreover, the contact angle θ_∞ of a large drop can be estimated from the intercept of the best-fit line. Figure 3.4 shows that if a contact angle becomes larger when the drop size shrinks, the line tension is positive, i.e., since $\gamma_{lv}>0$ and if $-\sigma/\gamma_{lv}<0$, then $\sigma>0$, and vice versa. Some results from this arrangement are shown in Table 2.2, which tells us that those line tension values are positive and on the order of 10^{-6} J/m. Furthermore, the larger the solid-liquid surface tension is, the larger the line tension appears to be. Such a dependence of line tension on the solid-liquid interfacial tension can be explained in terms of the thermodynamic phase rule (Duncan et al., 1995; Neumann and Spelt, 1996).

3.2.1.2 Contact line shape across a stripwise heterogeneous wall

The ‘contact line shape across a stripwise heterogeneous wall’ method was investigated by Gaydos and Neumann (1994). It estimated line tension values by comparing contact line profiles across the stripwise heterogeneous solid wall to the various numerical contact line profiles that satisfy the Laplace equation of capillarity’s boundary conditions.

The special heterogeneous wall used in this method was planer, consisting of alternating parallel surface patches of two different wetting properties. The width of each patch was as narrow as approximately 0.5 mm. When the solid wall was placed into a liquid, the liquid-vapour contact line profile will have a periodic wave shape, due to the unique contact angle formed on each adjacent strip of homogeneous material (refer to Figure 3.5). Away from the immediate vicinity of the heterogeneous patches the surface undulations die away and the liquid surface flattens-out to a surface called the Cassie plane in the absence of gravitational affects. For this stripwise wall, the Cassie contact angle θ_C is defined as the weighted average

$$\cos \theta_C = \frac{a_1}{a_1 + a_2} \cos \theta_{l[1]} + \frac{a_2}{a_1 + a_2} \cos \theta_{l[2]} \quad (3.6)$$

where a_1 and a_2 are the width of the two strips, $\theta_{l[1]}$, $\theta_{l[2]}$ are the corresponding contact angles that the liquid forms on an infinitely wide strip of either material. For finite line tension, each contact line boundary condition, in the modified Young’s Equation form, is given by

$$\cos \theta_l = \cos \theta_{l[i]} - \frac{\sigma}{\gamma_{lv}} \kappa_{gs} \quad (3.7)$$

For this periodic arrangement of parallel strips, the magnitude of the contact line's amplitude is related to the magnitude of the line tension. A positive line tension will dampen the magnitude of the contact line amplitude, and shorten the length of the contact line and the length of the interfacial line along the junction of two stripes. For an infinite line tension, the contact line would be straightened, and θ_C would be the apparent or experimentally measured contact angle of the liquid on the wall.

Experimental contact line profiles across the stripwise wall were obtained by advancing a wetting liquid across the strip wall and then recorded digitally the contact line shape. Once these profiles (the Cassie line) were acquired, they were compared with the corresponding theoretical contact lines of changing line tension by a technique called template matching. The results from this arrangement are positive and around 10^{-6} J/m, which are in good agreement with the axisymmetric sessile drop measurements in liquid/solid/vapour system (Neumann and Spelt, 1996).

3.2.1.3 Contact line quadrilateral relation

The line tension, in a liquid/liquid/vapour system, appears explicitly in the Neumann's triangle relation at the lowest level of the thermodynamic generality. This relation can be modified and expressed in terms of a corresponding line tension. Thus, the graphical representation is a quadrilateral rather than a triangle, as shown in Figure 2.6b. The quadrilateral represents the mechanical equilibrium balance between three surface tensions and a line tension at the contact line. It is suitable for at least three typical applications: (i) a liquid lens, (ii) a pendant drop in contact with a second immiscible liquid, and (iii) a cone-shaped capillary (Chen et al, 1996).

i) **A liquid lens.**

As described in Figure 2.6b, for an axisymmetric liquid lens (e.g., oil lens floating on water), the angle θ_1 is the contact angle between the liquid A-vapour interface and the liquid B-liquid A interface; θ_2 is the contact angle between the liquid A-vapour interface and the liquid B-vapour interface; $\theta_{\kappa 1}$ is the angle between the liquid A-liquid B interface and the $\bar{\kappa}$ direction, and $\theta_{\kappa 2}$ is the angle between the liquid B-vapour interface and the $\bar{\kappa}$ direction, respectively. Net forces balancing in the $\bar{\kappa}$ direction are written as

$$\gamma_{AB} \cos \theta_{\kappa 1} + \gamma_{BV} \cos \theta_{\kappa 2} + \gamma_{AV} \cos(\theta_{\kappa 2} + \theta_2) + \sigma \kappa_{gs} = 0 \quad (3.8)$$

According to the above expression, three contact angles and three surface tensions need to be measured. If the geodesic curvature of the three-phase contact line is known, then the line tension can be calculated. But experimental procedure requires the measurement of several parameters.

ii) **A pendant drop in contact with a second immiscible liquid**

Figure 3.6 shows that an arrangement needs only two contact angles θ_2 and $\theta_{\kappa 2}$. Likewise, the line tension could be determined using Equation (3.8).

iii) **A cone-shaped capillary**

It is similar to the sessile drop arrangement for line tension measurements. The mechanical equilibrium at the contact line is (refer to Figure 3.7)

$$\gamma_{lv} \cos \theta_2 + \gamma_{sv} - \gamma_{sl} - \sigma \kappa_{gs} \cos \theta_{\kappa 1} = 0 \quad (3.9)$$

and

$$\gamma_{lv} \sin \theta_2 + \sigma \kappa_{gs} \sin \theta_{\kappa 1} - P_N = 0 \quad (3.10)$$

where P_N is the solid surface stress component in the normal direction. The same assumption works in sessile drop experiments, where a normal component of surface

stress balances the net forces in the vertical direction of a contact line. According to Equation (3.9), once the contact angles, surface tensions and the geodesic curvature are known, the line tension can be estimated. The results from the arrangement of liquid lens indicate that the line tension is positive recorded by Langmuir (1933), Harkins (1937) and Stöckelhuber et al. (1999), or negative recorded by Chen et al. (1997) and the magnitude is ranging from 10^{-11} to 10^{-5} J/m (refer to Table 3.1).

3.2.2 Problems of current measurement attempts

The above experimental arrangements have been applied in measuring line tension in recent years. With resort to these methods, researchers obtained reasonable line tension values and found that the values from a liquid/solid/vapour system are usually greater than those from a liquid/liquid/vapour system. It may be due to the property of solid surfaces used in the experiments. Thus, sessile drop arrangements and stripwise wall measurements are sensitive to the solid surface, so that an imperfect surface could cause errors in measurement. These errors will affect further calculations, because the measured contact angles cannot be correctly related to the contact line geometry.

As mentioned earlier, under experiment conditions, the thermal and chemical equilibrium state should be maintained throughout the duration of an experiment. However, for the drop size dependence of contact angles arrangement, the condition of keeping the chemical potential fixed cannot be actually achieved, because one measures contact angles by growing a drop so that the drop size is changing all the time. According to the Laplace's formula of capillarity (Equation (2.1)), when the drop size R

increases, the difference of the pressure ΔP across the interface will decrease. As the result, the chemical potential will also reduce according to the following equation derived from the Gibbs-Duhem Equation (2.16) (Kondepudi and Prigogine, 1998):

$$\Delta\mu = \mu - \mu_0 = R_g T \ln\left(\frac{P}{P_0}\right) \quad (3.11)$$

where, μ_0 is the chemical potential at unit pressure P_0 , T is the absolute temperature and R_g is the universal gas constant. Equation (3.11) tells us that the smaller sessile drops have larger liquid pressure and larger chemical potential than the larger sessile drops. Unequal chemical potentials will drive the diffusion of particles from a region of high concentration to a region of lower concentration. Evaporation of liquid from the drop's surface is one important effect of the chemical potential change with smaller drops experiencing greater mass transfer per unit area than larger drops. Accordingly, the evaporation of the liquid will have a notable effect on a small drop, so that this 'drop size dependence of contact angles' arrangement could not use sufficiently small drops to acquire accurate results. Moreover, evaporation will cool the drop and alter the surface tension and even the line tension.

The stripwise wall experiment seems to be able to avoid the variation of chemical potential. But this arrangement needs complicated numerical calculation and is not easy to analyze. Another problem with this arrangement is that two distinct line tensions might exist, i.e., one for each solid material. This could cause some errors in evaluating the two line tensions as one value, but may yield a reasonable estimate for an order of magnitude.

The contact line quadrilateral relation is good measuring line tension in a three-fluid phase system and avoids the difficulty in producing a near ideal solid surface.

However, the arrangement needs to measure too many parameters: three surface tensions, two contact angles at least and a radius. It would bring some difficulties to the measurement and cause more errors to the calculation due to the accumulation of the error from each parameter measurement. Furthermore, the liquid lens surface is still curved so that there is a pressure difference across the surface and exist the same problem as in the sessile drop arrangement.

The above discussion indicates that a better and simpler measurement technique for line tension needs to be developed, to obtain more accurate results.

3.2.3 Measurement requirements and conditions

If we assume that line tension is extremely small and sensitive to the experimental conditions, then the conditions of line tension measurement should be handled properly and carefully before any experimental design or measurement are performed. First of all, thermodynamic equilibrium needs to be maintained in the experimental system throughout the entire experiment, i.e., the temperature, the pressure, and the chemical potential should be fixed; the surface tension and line tension are remained constant and independent of the drop size. These experimental condition requirements can be easily interpreted from the Gibbs-Duhem equation for a total system, i.e.,

$$SdT + Ad\gamma - VdP + \sum_i M_i d\mu_i = 0 \quad (3.12)$$

where T is the system temperature, S , P , V and A are the system entropy, pressure, volume and surface, γ is the surface tension, μ_i is the chemical potential of component i , and M_i is the total mass of component i .

Second, a solid/liquid combination should be prepared as well as possible. The solid substrate should be smooth, chemical homogeneous, and not deformable when applied in the sessile drop method. Unfortunately, there is no ideal surface. Thus, it is important to produce solid surfaces of sufficient quality to ensure that contact angles accurately reflect the interaction between bulk, surface, and line phases as described by the modified Young equation. Aside from smoothness and homogeneity requirements, solid surfaces should be stable and chemically inert with respect to the test liquids (Amirfazli et al., 2003). Sometimes, the imperfection of solid surfaces could be easily noticed by contact-angle hysteresis. Surfaces with more than one stable contact angle are said to have contact-angle hysteresis (Berg, 1993), which can also be explained as the disparity between the advancing and receding contact angles. These angles may be defined by considering a tilted surface where the maximum contact angle at the lower end of the drop just before the drop begins to roll is called the advancing contact angle; the minimum angle at the higher end of the drop just before the drop rolls is the receding contact angle (Decker and Garoff, 1997). Causing drops to be retained on surfaces, contact-angle hysteresis phenomenon is ubiquitous in nature. Preventing this hysteresis depends largely on the surface preparation. Oliver et al., (1980) investigated this issue and found that scratches of less than 0.5 μm depth and steps of less than 0.05 μm can result in considerably reducing the effects of surface roughness on liquid spreading. Neumann (1974) demonstrated that the size of the heterogeneous patches must be held below approximately 0.1 μm to reduce the influence of surface heterogeneity.

Moreover, liquids selected for measurements need to have a high boiling point to avoid significant mass transport, i.e., the evaporation of the liquid drop. The purity of the

measured liquids is also necessary for the accuracy of the measurement of contact angles (Xia and Whitesides, 1998). They should be non-hazardous and available in laboratory operation and insensitive to laboratory illumination.

The last but not the least requirement is to maximize the geodesic curvature. Previous experiments proved that the measured values of line tensions do not depend strongly on the phase of substances, i.e., a solid or a liquid substrate, but on the three-phase contact diameter. As mentioned in Section 2.4.3, the line tension effect gets significant with the increase of geodesic curvature, i.e., the smaller a drop size is, the larger the effect of line tension.

3.3 Novel technique for line tension measurement

In order to minimize the difficulties that exist with previous designs, an improved experimental arrangement for measuring line tension has been investigated on the basis of the drop shape method in this thesis. The proposed approach employed the wetting/non-wetting behaviour of liquids on a solid surface. This particular surface is a chemically structured surface, which consists of hydrophilic and hydrophobic materials. They are formed by patterning the lower contact-angle surface material (Surface I) domain in a square (20 mm×20 mm) and the higher contact-angle surface material (Surface II) surrounding the square, as illustrated in Figure 3.8a.

An experimental set-up was designed to slowly pump a liquid drop onto the solid surface through a hole drilled on it beforehand. The drop was made to grow gradually and spread from the center of the square to the corners by a controlled flow of the liquid. Since Surface II has a non-spreading character (a higher equilibrium contact-angle), the

increment of the contact line of the drop would be restrained when it reached the edges of the inner square, i.e., the boundary of Surface I adjacent to Surface II. The portions of the contact line, which did not touch the edges, would continue extending. The liquid drop would move towards the corners so that the radii of the contact-line arcs near the corners became smaller and smaller, as shown in Figure 3.8a. Meanwhile, the contact angle of the drop on Surface I would increase from a lower angle to a higher one after the drop was confined by the heterogeneous boundary between Surface I and Surface II, i.e., the edges of the inner square. The contact angle increased, because circumscribed the liquid drop had to grow its volume upwards more than extending the periphery (refer to Figure 3.8b). The contact angle would continue advancing until eventually it hit the intrinsic contact angle of Surface II. Just before the drop broke out of the square region of Surface I and flew over Surface II, the contact line profile at the corner, i.e., the smallest contact arc, was captured by a digital camera, and then the arc radius was evaluated by processing the image data. This minimum radius of the contact line corresponded to the maximum geodesic curvature.

The modified Young's Equation (2.12) can be written for this arrangement as,

$$\cos \theta_{II\infty} = \cos \theta_{I\infty} - \frac{\sigma}{\gamma_{lv}} \frac{1}{R} \quad (3.13)$$

where $\theta_{II\infty}$ is the contact angle of a large drop on Surface II, and $\theta_{I\infty}$ represents the contact angle of a large drop on Surface I. The line tension value can be estimated from Equation (3.13) when the surface tension γ_{lv} is known and the contact line radius R is measured. Since the liquid/solid/vapour system was used in this experiment, the line tension values should be positive and on the order of 10^{-7} - 10^{-6} J/m, which would not be different from those using the same three-phase system, i.e., the sessile drop arrangement.

The entire procedure of the experiment was carried out at a fixed pressure (~ 1 atm) and at room temperature. Surfaces with low roughness and heterogeneity were used in this arrangement. Thus, neither morphological nor chemical heterogeneities would disturb the drop shape. Since the “square” liquid drop (refer to Figure 3.9), with nearly identical shape, was measured at each arrangement, the chemical potential was almost fixed (the control of the chemical potential will be discussed in Section 4.2), unlike the situation with previous sessile drop measurements. The experiment is easy to implement by simply measuring the contact line profile’s radius, and the estimation does not require many parameters. Thus, this method is much simpler than the stripwise wall arrangement and the liquid lens experiment. Furthermore, it maximizes the geodesic curvature ($\sim 10^6$ 1/m) without decreasing the drop size. The last contact line radius before the drop breaks is relatively small compared with the whole drop size, so that the influence of evaporation is minimized in the measurement. It should be noted that the advantages of this method satisfy the experimental requirements and conditions mentioned before. Therefore, it could be a better experimental arrangement for the line tension measurements. However, the proposed new experimental method in this project also needs some cautions. A few parameters must be controlled in order to obtain accurate measurements of line tensions. Among them, the geodesic curvature of the curved contact line before the drop breaks out of the inner square is the most crucial one. Its magnitude determines the order of the line tension value. The line tension is also related to the liquid-vapour surface tension as mentioned in Section 3.2.1.1 (refer to Table 3.2). The selection of material for Surface I and Surface II is determined by the contact angles to be produced.

Researchers	Experiment	Line tension σ (J/m)
Gaydos and Neumann	Sessile drop	+1 to 3×10^{-6}
Li and Neumann	Sessile drop	+1 to 6×10^{-6}
Wallace and Schürch	Sessile drop on monolayer	+1 to 2.4×10^{-8}
Langmuir	Liquid lens	$+6.5 \times 10^{-5}$
Harkins	Liquid lens	+1 to 10×10^{-11}
Chen et al.	Liquid lens	-1 to -4×10^{-6}
Stöckelhuber et al.	Liquid lens	$+5.4 \times 10^{-9}$
Torza and Mason	Emulsion bubbles	-6 to $+58 \times 10^{-9}$
Ivanov et al.	Bubbles in surfactant solution	-12 to $+3 \times 10^{-8}$
Kolarov and Zorin	Common black film	-1.7×10^{-10}
Platikanov et al.	Newton black film	-0.8 to $+1.2 \times 10^{-10}$
Churaev et al.	Thin film	-10^{-10}
de Feijter et al.	Thin film	-10^{-12}
Gaydos et al.	Stripwise wall	+0.2 to 4×10^{-6}
This study (p.110)	Sessile drop (SAM II)	+0.9 to 6×10^{-6}
This study (p.110)	Square inlay (SAM I)	+0.2 to 6×10^{-6}

Table 3.1 Line tension values from different experimental arrangements (Neumann and Spelt, 1996).

Tested liquid	Line tension σ ($\mu\text{J/m}$)	θ_{∞} (deg)	Surface tension γ_{lv} (mJ/m^2)	Surface tension γ_{sl} (mJ/m^2)
Hexadecane	0.81	45.4	27.3	0.86
Ethylcinnamate	1.23	66.3	37.2	4.77
Dibenzylamine	2.17	66.7	40.8	5.61
1-Bromonaphthalene	1.50	67.2	44.3	6.54
Ethylene glycol	2.75	82.0	47.6	12.29
Formamide	4.96	88.7	59.1	20.51
Water	4.36	110.1	72.7	41.99

Table 3.2 Results of line tensions using sessile drops on 1-octadecanethiol SAM surface (Amirfazli et al., 1998).

Figure 3.1 Schematic of the ring method (Adamson, 1990).

Figure 3.2 Meniscus profile for non-wetting liquid (Adamson, 1990).

Figure 3.3 Shape of a pendant drop.

Figure 3.4 Behaviour of contact angles and the cosine of contact angles versus drop size. The slope is negative in (a) and the line tension is positive, whereas the slope is positive in (b) and the line tension is negative (Neumann and Spelt, 1996).

Figure 3.5 Liquid meniscus in contact with a stripwise heterogeneous wall (Neumann and Spelt, 1996).

Figure 3.6 Pendent drop in contact with second immiscible liquid (Chen et al., 1996).

Figure 3.7 Schematic of a cone-shaped capillary (Chen et al., 1996).

Figure 3.8 (a) Top view of three-phase contact lines of the liquid drop; (b) side view of the profiles of the liquid drop while expanding.

Figure 3.9 Photographs of square-like water drops resting on silicon wafers coated with gold.

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Chapter 4

Experimental Preparation for Line Tension Measurement

In this thesis, an alternative arrangement has been proposed and applied to measure line tension, as explained in Section 3.3. An experimental set-up has been developed for the line tension measurement purpose. A schematic of the entire experimental set-up is presented in Figure 4.1, and pictures of the setup are displayed in Figure 4.2. This setup included some main components, such as, a specially processed substrate supported by optical flats (items 5 and 6 in Figure 4.1, items be noted by numbers only hereafter), and a container (11), which was used as a hydrostatic pump. The experiment also employed other facilities, such as a precision stamping fixture (refer to Figure 4.6). These facilities will be introduced and discussed in detail later in this chapter. An important component of this experimental setup is the substrate (5), which was coated with gold, and had a patterned surface with SAMs. The preparation of this substrate is one of the major efforts in this experiment. Before getting into details, the entire experimental setup will be introduced, starting with the container (11).

The container (11) was placed on a stand (10) (Thermo-Oriel Co.), which can be micro adjusted vertically. The container was used to pump the measuring liquid onto the

solid substrate (5) to generate a sessile drop (4) and to control the liquid flow rate. It took advantage of the hydrostatic pressure, and thus avoided the vibration generated if an electrical pump was used. Vibration was a critical factor that can affect the drop spreading. The solid substrate (5) was placed in a relatively large, deep glass vessel (3), which was 26 cm long, 13 cm wide and 21 cm high. The vessel was rested on an adjustable stand (8) (Thermo-Oriel Co.). The adjustment screws (14) (64-pitch thread with stand (8) over 4½" length) allowed the stand to tilt in two angular directions, i.e., roll and pitch, about the axes x and y , as illustrated in Figure 4.1. They can be used to control the direction of the movement of the drop contact line on the solid substrate (5).

The measuring liquid was stored in the container (11). The liquid flowed from the container to the vessel through a tubing passage (12) (Tygon precision tubing, Cole-Parmer Inc.). Both the container and the vessel were connected to the tubing with barded fittings (Cole-Parmer Inc., refer to Figure 4.3a). There was a connector (Cole-Parmer Inc., refer to Figure 4.3b) installed on the passage to link up two pieces. It gave the convenience of permitting one to disconnect the passage and drain the liquid after an experiment. The liquid flow rate can be also controlled by two tubing clamps (15) (Cole-Parmer Inc.), by simply releasing or tightening them. The connection of all these components should be tight to prevent any leaks. A digital thermometer (with a resolution of $\sim 0.05^{\circ}\text{C}$) was used to measure the temperature around the sessile drop with the thermometer probe placed inside the vessel (3). The entire set-up was placed on a heavy steel table to minimize the vibration. All materials of the apparatuses in contact with the measuring liquids were selected carefully to avoid any chemical reaction with the liquids.

The patterned solid substrate (5) was placed on the optical flat support (6). The solid substrate had a hole drilled in the middle. The measuring liquid coming into the vessel passed through this hole and formed a sessile drop on the substrate. Technically, it was not easily and practical to make the vessel gastight. Moreover, even though the sessile drop was enclosed by the vessel, it still evaporated to the atmosphere. In order to reduce the drop evaporation and minimize the chemical potential effects during measurements, a liquid bath was used. As illustrated in Figure 4.1, the same measuring liquid was added into the vessel, without covering the substrate, and was left inside for a while before each experiment. The vapour in the vessel would be slightly under-saturated with respect to the sessile drop to slow down the evaporation of the drop (Emelyanenko et al., 2004). Flat glass slides and silicon (*Si(111)*) wafers were adopted as non-deformable, smooth solid substrates. To apply these substrates to the drop spreading experiment, they were coated with *Ti* and then *Au*. On each gold substrate, a patterned surface with a low-contact-angle inlay and high-contact-angle surrounding was finally produced. An advanced stamping method (Fetahi et al, in progress), based on a micro-contact printing technique, was applied to the surface patterning.

A Nikon D100 digital camera (1) (Nikon Co.) with a high quality micro zoom lens (2) (Nikon Co.) was used to observe the drop movement and capture images of the drop profiles and the contact lines. The drop was illuminated by a compact fluorescent lamp (Osram Sylvania Inc.) from the side when measuring contact angles, or from the top when observing the movement of contact lines. The image data acquired by the digital camera were transferred to a computer for image analysis and a TV monitor for instant viewing.

4.1 Control of the pressure pump

Obviously, if the liquid surface in the container had a higher position than the sessile drop in the vessel, the liquid would have higher potential, i.e., higher hydraulic head, than the sessile drop. Thus, the liquid tended to flow from the container towards the vessel. This kind of potential could be easily obtained by simply raising the stand (10), or increasing the liquid height in the container. Assume the vertical distance between the adjustable stands (8) and (10) was Δz , the height of the measurement liquid in the container was h . The larger the value of Δz or h was, the higher the potential was, and the faster the liquid would flow towards the vessel. On the other hand, the objective of this experiment is to study the line tension of the sessile drop by observing its contact angle and contact line. This required a slow movement or growth of the sessile drop, so that the digital camera would be able to appropriately capture the images of the drop movement. If the contact line moved too fast before the drop broke out of the inner surface region (Surface I), it would be difficult for the camera to record the minimum contact line profile. Thus, some calculations were needed to figure out how fast the contact line should move and what values of Δz and h would be proper for this drop spreading experiment.

In the case of this experiment, since the pressure driving the liquid flow depended on gravity and density, the steady flow energy equation could be reduced to

$$\Delta z + \frac{\Delta P}{\rho g} = h_f \quad (4.1)$$

where ΔP is the pressure difference existing between the inlet and the outlet of the tubing, and h_f is the friction head loss and always positive (White, 2003). The well-established

Darcy-Weisbach empirical relation, Equation (4.2), is used to calculate the head loss for a pipe flow problem as

$$h_f = f \left(\frac{L}{D} \right) \frac{\bar{V}^2}{2g} \quad (4.2)$$

where L and D are the length and the inner diameter of the given tubing, respectively; and $\bar{V}$ is the mean velocity of the flow. The loss h_f is proportional to L/D and $\bar{V}^2$ with the dimensionless parameter f , called the Darcy friction factor, denoting the proportionality coefficient. The following equation is given by substituting Equation (4.1) into Equation (4.2)

$$\Delta z + \frac{\Delta P}{\rho g} = f \left(\frac{L}{D} \right) \frac{\bar{V}^2}{2g} \quad (4.3)$$

It can be rewritten as

$$\frac{(\Delta z \rho g + \Delta P)}{L} = f \cdot \frac{1}{D} \cdot \frac{\bar{V}^2 \rho}{2} \quad (4.4)$$

For Laminar flow, $f \approx 64/Re$, where Re is the primary parameter correlating the viscous behaviour of Newtonian fluids, called Reynolds number, and is expressed as:

$$Re = \frac{\rho \bar{V} D}{\mu} = \frac{\bar{V} L}{\nu} \quad (4.5)$$

where, μ is the dynamic viscosity of a given liquid, and ν is the kinematic viscosity and has a relation with μ through $\nu = \mu/\rho$. The volume flow rate Q passing through the tubing is given by $Q = \bar{V} A$, where A is the inner cross section area of the tubing and equal to $\pi D^2/4$. Substituting f into Equation (4.4) gives

$$\frac{(\Delta z \rho g + \Delta P)}{L} = \frac{128 \mu Q}{\pi D^4} \quad (4.6)$$

It should be noted that Q is also the volume increase or decrease of the sessile drop. If it is assumed in this calculation that the sessile drop is a hemisphere, then the change of the drop volume is $dV_{vol}=2\pi R^2 dR$, where R is the radius of the hemisphere-like drop. Therefore, the change of the contact line per unit time can be calculated as follows,

$$\frac{dV_{vol}}{dt} = 2\pi R^2 \frac{dR}{dt} \Rightarrow \frac{\Delta V_{vol}}{\Delta t} = Q = 2\pi R^2 \frac{\Delta R}{\Delta t} \quad (4.7)$$

Combining Equation (4.6) and (4.7), the velocity of the contact line of the sessile drop $\Delta R/\Delta t$ can be evaluated approximately by

$$\frac{\Delta R}{\Delta t} = \frac{(\Delta z \rho g + \Delta P) D^4}{256 \mu L} \cdot \frac{1}{R^2} \quad (4.8)$$

Since the sessile drop was much smaller as compared the liquid in the container, it is reasonable to assume that the liquid height h was constant throughout an entire experiment, even if some liquid flowed onto the substrate and Surface II region. Accordingly, the pressure difference ΔP is given by $\Delta P = \rho g h$, if the surface tension of the drop is neglected. Equation (4.8) could be simplified to

$$\frac{\Delta R}{\Delta t} = \frac{(\Delta z + h) g D^4}{256 \nu L} \cdot \frac{1}{R^2} \quad (4.9)$$

Assuming that both Δz and h are fixed permits one to conclude that the velocity of the contact line gets smaller as the volume, i.e., the radius, of the sessile drop increases, or the diameter of the tubing is reduced, or the viscosity of the measuring liquid increases. However, changing the diameter of the tubing, or the viscosity of the liquid, is not practical for the experiment during measurements. Thus, adjusting the position of the container or the liquid height in the container was considered as more practical to control the pumping. Based on Equation (4.9) and the actual experimental settings, some

preliminary calculations were carried out before the experiments, to find an appropriate setting for Δz and h . The calculation of the velocity of the contact line movement was performed by changing the height h of the measuring liquid or changing Δz (refer to Appendix A). The results of these calculations show that the movement of the contact line of the water drop was fastest compared with other two measuring liquid drops of larger viscosities under the same sum of h and Δz . The height of the liquid should be controlled under 10 cm, or the position difference of the two stands should be less than 10 cm, in order to maintain the velocity of the contact line in mm/s, the flow rate in ml/s, and the flow velocity in mm/s.

4.2 Control of the chemical potential

As mentioned in Section 3.2.3, maintaining thermodynamic equilibrium during experiments is one of the primary experimental conditions required for the line tension measurement, i.e., the temperature T , the pressure P and the chemical potential μ should be fixed throughout the entire measurement (refer to Equation (3.12)). Since this experiment was carried out at room temperature ($20 \pm 1^\circ\text{C}$) and at a fixed pressure (~ 1 atm) as explained before, it could be assumed that $\Delta T \approx 0$ and $\Delta P \approx 0$. However, keeping the chemical potential fixed might not be easy during the experiment, because the vessel containing the sessile drop could not be closed perfectly and drop size might change during the experiment. Therefore, decreasing chemical potential variations as much as possible was one of the main goals for the design of the experimental setup.

First, consider the relation between drop size R and chemical potential. As indicated by the Laplace equation of capillarity for an axisymmetric drop (Equation

(3.1)), the pressure difference across the surface of the drop (or the interface of the drop and the vapour) varies with the drop size. Thus, the chemical potential difference across the interface of the liquid drop and the vapour will change with the drop size, as represented by Equation (3.11), which can be rewritten for a pure component system as

$$\Delta\mu = \mu_l - \mu_v = R_g T \ln\left(\frac{P_l}{P_v}\right) \quad (4.10)$$

where, μ_l and μ_v are the chemical potential of the liquid drop phase and the chemical potential of the vapour around the drop, respectively; P_l and P_v are the liquid drop pressure and the vapour pressure around the drop, respectively, where $P_v \approx P$ (~ 1 atm, the total pressure in this measurement system). The sessile drop pressure can be estimated using Equation (2.1) with the angular inclination θ of the drop surface to the horizontal, given by

$$\Delta P = (P_l - P_v) = \gamma_{lv} \left(\frac{d\theta}{ds} + \frac{\sin \theta}{x} \right) = \frac{2\gamma_{lv}}{R} + \Delta \rho g z \quad (4.11)$$

This equation can be written in dimensionless form as Equation (4.12) using the capillary constant c , defined as $c = \Delta \rho g / \gamma_{lv}$, to scale Equation (4.11).

$$\frac{d\theta}{dS} = \frac{2}{B} + Z - \frac{\sin \theta}{X} \quad (4.12)$$

where the dimensionless physical quantities are defined as the arc length along the drop profile $S = sc^{1/2}$, the radius of drop contact line $X = xc^{1/2}$, the vertical distance $Z = zc^{1/2}$, and the drop radius $B = Rc^{1/2}$. Differentiating Equation (4.12) with respect to X , and using the approximation that $\sin \theta$ approximately equals to $\tan \theta$ at small contact angles, gives

$$\frac{dZ}{dX} = \tan \theta \approx \sin \theta \quad (4.13)$$

Substituting this equation into Equation (4.12) gives

$$\frac{d^2(\sin \theta)}{dX^2} + \frac{d(\sin \theta)}{XdX} - \frac{\sin \theta}{X^2} - \sin \theta = 0 \quad (4.14)$$

It can be shown that this differential equation has the solution (Hartland and Hartley, 1976)

$$\sin \theta \approx \frac{2}{B} I_1(X) \quad (4.15)$$

where $I_1(X)$ is a modified Bessel function of the first kind and the subscript 1 denotes this order one. Equation (4.15) can be reorganized as

$$R \approx \frac{2}{c^{1/2} \sin \theta} I_1(X) \quad (4.16)$$

Thus, the chemical potential difference across the drop interface, $\Delta\mu$, can be estimated as

$$\Delta\mu = R_g T \ln\left(\frac{P_l}{P_v}\right) = R_g T \ln\left(1 + \frac{2\gamma_{lv}}{PR}\right) \quad (4.17)$$

Provided the contact angle θ is small. In this experimental station, the contact angles θ of the sessile drops on Surface I are small ($\sim 5^\circ$ to 30°) so the drop radii, from Equation (4.16), would be extremely large. Thus, $\Delta\mu$ is so small that it could not have a significant affect on the surface tension or line tension measurements. Detailed calculations for the drop contact angle dependence of chemical potential are presented in Appendix B, which shows that $\Delta\mu$ is small and on the order of 10^{-3} - 10^{-2} J/kg.

As mentioned earlier in this chapter, a relatively deep vessel (~ 20 cm high), with the measuring liquid bath at the bottom, was used for holding the sessile drops to be measured. These drops were placed near the bottom of this vessel. The vessel with a liquid bath could be considered a type of slow diffusion system. The vapour phase concentration of the liquid, expressed in mole fraction, is x_k , i.e., the partial pressure of the liquid vapour divided by the total pressure, P_k/P , assuming that the liquid in vapour

phase formed an ideal gas. This concentration variation with the vessel height z can be expressed as (Bird et al., 1960)

$$-\ln(1 - x_k) = C_1 z + C_2 \quad (4.18)$$

where the two constants C_1 and C_2 can be determined from the boundary conditions:

$$\text{B.C. 1 (near the liquid surface in the vessel): } z = z_1, x_k = x_{k1} = \frac{P_{k1}}{P}$$

$$\text{B.C. 2 (at the top of the vessel): } z = z_2, x_k = x_{k2} = \frac{P_{k2}}{P}$$

Thus, the constants can be obtained as:

$$C_1 = \frac{\ln(1 - x_{k1}) - \ln(1 - x_{k2})}{z_2 - z_1} \quad (4.19a)$$

$$C_2 = \frac{z_1 \ln(1 - x_{k2}) - z_2 \ln(1 - x_{k1})}{z_2 - z_1} \quad (4.19b)$$

where, x_{k1} is the vapour phase concentration of the liquid right above the liquid-vapour interface, i.e., the saturated liquid pressure at the room temperature divided by the total pressure of this system, P_{sat}/P (it has been demonstrated in Appendix B that the departure of the partial pressure of the liquid vapour in contact with the liquid from the saturated pressure of liquid is very small, so it can be justified in stating $P_{k1} \approx P_{sat}$); x_{k2} is the vapour phase concentration of liquid at the top of the measurement vessel, i.e., just outside this vessel (provided that this vessel was open). Moist air (a mixture of dry air and water vapour) at the vessel's top was taken into account, and the composition of the moist air can be described in terms of the relative humidity ϕ (40%-70% in the experiments), expressed as the liquid vapour pressure in the moist air, P_ϕ , divided by the liquid saturated pressure, P_ϕ/P_{sat} (Moran and Shapiro, 1999). Thus, x_{k2} can be given by P_ϕ/P , or $\phi P_{sat}/P$ for water with x_{k2} for other measuring liquids assumed to be zero. For this

calculation, the airflow at the vessel's top was neglected. The change of the liquid vapour pressure with the vessel height can be obtained by rewriting Equation (4.18) as

$$P_k = [1 - \exp(-C_1 z - C_2)] \cdot P \quad (4.20)$$

The chemical potential with respect to the liquid in the vapour phase is (Kondepudi and Prigogine, 1998)

$$\mu_k(P, T) = \mu_k(P_0, T) + R_g T \ln\left(\frac{P_k}{P_0}\right) \quad (4.21)$$

The chemical potential $\mu_k(P_0, T)$ is a reference potential state, which is, by definition, zero at the reference pressure $P_0=1$ bar and for all temperature around $T=298.15$ K for pure substances not undergoing chemical reaction. Equation (4.21) can be rewritten as

$$\mu_k(P, T) = R_g T \ln\left(\frac{P_k}{P_0}\right) = R_g T \ln\left(x_k \cdot \frac{P}{P_0}\right) \quad (4.22)$$

In our case, $P \approx P_0$. Detailed calculations are given in Appendix B and the pressure and the chemical potential profiles are plotted in Figures B.1 and B.2. It should be noted that the closer one approaches the liquid-vapour interface at the bottom of the measurement vessel (the location of the experiments), the more likely the vapour will be saturated, the smaller the difference between pressures will be and the smaller the difference between the two chemical potentials will be. Therefore, the liquid evaporation from the drop could be controlled. In this design, the sessile drop was placed near the liquid-vapour interface and the drop was so close to this interface (due to the small contact angle) that the liquid vapour around the drop was nearly saturated, as discussed above. The height of the sessile drop could be estimated as (Hartland and Hartley, 1976)

$$Z = \int_0^X \tan \theta dX \approx \int_0^X \sin \theta dX \approx \int_0^X \frac{2}{B} I_1(X) dX \quad (4.23)$$

and simplified to

$$z = \frac{Z}{c^{1/2}} \approx \frac{I_0(X) - 1}{I_1(X)c^{1/2}} \sin \theta \quad (4.24)$$

where $I_0(X)$ is a modified Bessel function of the first kind of order zero. The drop height calculations, presented in Appendix B, indicate that the sessile drops were very low relative the vessel height and that the vapour pressures around the drops were approximately saturated.

With the comparison carried out in Appendix B, the chemical variations in this experiment are much smaller than those in any other sessile drop measurements. It is further demonstrated that the chemical potential control was improved in this experimental arrangement.

4.3 Solid substrate preparation with Ti and Au

Glass microscope slides and silicon wafers (WaferNet, Inc.) were selected as solid substrates in this experiment, because of their low roughness and low heterogeneity. The microscope slides were 7.4 cm long, 5.4 cm thick and 1 cm wide and the silicon wafers have ~10 cm diameter and ~0.5 mm thick. Before coated with titanium and gold, a hole of ~6 mm diameter was drilled in the center of each piece using a 1/4" glass drill bit (RONA Inc.) with a carbide tip. Drilling on the glass slides or *Si* wafer was a delicate task and needed great care, due to their fragility. Too much pressure or too high a drill speed would cause cracking. The speed of the drilling machine was set below 1200 rpm. Heat would be generated by the friction between the bit and the glass. When drilling, the slide was supported by a soft wood board to reduce vibration. The drilling occurred

discontinuously to prevent the slide from getting so hot as to crack from thermal stresses. To drill a glass or *Si* wafer, especially for a larger hole, it was vital to have a proper drill press.

Prior to metal film deposition, the solid substrates (glass slides or silicon wafers) were washed with acetone to remove organic contaminants. Subsequently, the substrates were soaked in a solution of Hydrogen peroxide (H_2O_2) and Ammonium hydroxide (NH_4OH) with water (H_2O) base, in a proportion of 1:1:8. After ~ 20 mins, they were rinsed with distilled water for ~ 10 mins and dried out in a stream of N_2 . A ~ 1000 Å thick gold (*Au*) film was prepared by evaporation of gold ($>99.99\%$) onto the substrates, primed with a ~ 200 Å thick titanium (*Ti*) as an adhesion layer between solid substrates and the *Au* film. This layer was applied to prevent *Au* from being abraded during experiments. These metals were evaporated in either a cryopumped e-beam chamber or a thermal evaporator at a pressure of $\sim 2 \times 10^{-4}$ Torr for ~ 3 hrs. Finally, the coated substrates were wrapped in clean paper and sealed for subsequent use. Before each patterning experiment, the substrates were soaked into n-ethanol (normal ethyl alcohol, denoted by ethanol hereafter) for ~ 12 hrs, and then dried by a gas stream.

4.4 Patterned surface preparation with SAMs

Experimental studies of wetting or dewetting on a heterogeneous surface were not carried out until recently, when a number of techniques became available for patterning surfaces on solid substrates with structures having well-defined parameters (Xia et al., 2001). The particular patterned surface, as discussed in Section 3.3, needs a wetting surface inside a square and a relatively dewetting surface surrounding it. To avoid

topographic roughness, these patterns were produced using monolayers of self-assembled molecules (SAMs) with a pattern fashioned by micro-contact printing (μ CP). The low contact angle inlay (surface I or SAM I) was created by stamping an acid-thiol solution onto the gold surface, and the outside region (surface II or SAM II) was then made by immersing the stamped gold surface into another thiol solution.

4.4.1 Introduction to self-assembled monolayer

Self-assembled monolayers are organic thin films formed by the adsorption of molecules onto a surface, when an appropriate substrate, usually planar, is contacted with a solution of surfactant in an organic solvent. When approaching equilibrium coverage, the molecular order is produced by a spontaneous chemical synthesis on the surface of the substrate. SAMs exhibit uniform and stable behaviour, and so the SAM surfaces are relatively homogeneous and smooth (Ulman, 1996). Typical advancing and receding contact angle data for SAMs produced on metal substrates are listed in Table 4.1, which show the hysteresis on SAM surfaces is relatively low.

A self-assembling molecule consists of three parts, as shown in Figure 4.4. The first part is the head group that chemisorbs on the substrate surface. The strong molecular-substrate interaction results in head group pinning on the surface through a chemical bond. The bond can be a covalent $Si-O$ bond; an ionic $-CO_2^-Ag^+$ bond, or an $Au-S$ bond (as in alkanethiols on gold), which was the case for the SAM used in this experiment. The second part is the alkyl chain or derivatized alkyl group, and the forces associated with its interchain structure arise from van der Waals and electrostatic interactions. The third part is the surface or terminal group, which can be a $-CH_3$, $-CF_3$

or $-COOH$ group (Ulman, 1994). With different terminal functional groups, the surface properties of an organic film are different. This terminal group allows for the construction of interfaces with defined structures and properties without a fundamental change in surface structures (smoothness and homogeneity). For example, a $-CH_3$ terminated film represents a non-polar surface, i.e. a hydrophobic surface, while a $-COOH$ terminated film shows a more polar surface, i.e. a hydrophilic surface (Schreiber, 2000). Contact angle measurement is one preliminary method to observe the SAM film wettability. Table 4.2 shows the wettability of the SAM surfaces with different terminal functional group. Figure 4.5 shows the wettability difference between a bare gold substrate and a SAM surface produced by 1-Octadecanethiol (C_{18}). The gold surface has a low contact angle, $\sim 50^\circ$ for a distilled water drop, while the alkanethiol SAM is a non-wetting surface with a contact angle greater than 90° . This indicates the low surface energy due to the hydrophobic character of the methyl terminal groups.

The most intensively studied class of monolayers are the films made of organosulfur compounds on metal surfaces. These SAMs have several advantages, including its well-defined order and relative inertness of the substrate, which makes it an ideal substrate for surface chemistry studies. Among these SAMs produced on metal surfaces, alkanethiolates on evaporated thin films of gold are the best-characterized system of SAMs (John et al., 1995). This is because gold is not easy to oxidize, the SAMs can easily bond to the gold surface. Moreover, gold and sulfur bond strongly, which results in relatively stable monolayer surfaces. Table 4.3 shows that the sulfur forms a strong interaction with the gold substrate and promotes the formation of a close-packed, ordered monolayer. These films are formed spontaneously by immersing the

metal substrate into dilute solutions (in the mM concentration range) of a thiol-containing compound. The long chain thiols ($C \geq 8$) usually form a more close-packed, crystalline assembly with fully extended alkyl chains than the short chain thiols (Schreiber, 2000).

4.4.2 Micro-contact printing

There exist various techniques for patterning SAMs onto a surface with feature dimensions ranging from tens of nanometres to hundreds of micrometers. Micro-contact printing (μ CP) with an elastomeric stamp is one of them and offers a powerful technique to create chemical or biological patterns on substrates. It is a soft lithographic technique developed by Whitesides et al. of Harvard University. μ CP is based on the pattern transfer from an elastomeric stamp to a solid substrate by simply contacting the two surfaces. Typically, the stamp is formed by curing polydimethylsiloxane (PDMS) on a patterned master. By inking thiols, inorganic catalysts, or biomolecules, the pattern can be replicated from the stamp to the surfaces of metals (*Au*, *Ag* or *Cu*), glass or polymers (Chen et al., 2000). Micro-contact printing has been widely adopted in the past few years, because it is simple and fast approach for creating a highly ordered monolayer. Moreover, it is flexible, inexpensive, and does not require clean-lab facility once the patterned master has been created. However, success requires that the entire area of the substrate touch the stamp at the same time, when doing the experiment. To prepare the patterned surface in this experiment, a precision stamping device (Fetahi et al, in progress) has been used to facilitate μ CP with elastometric stamps. This device used a fixture to ensure an accurate parallel surface patterning and considerably reduced blur effects, which was a major problem when operated by hands.

4.4.3 Precision stamping set-up/fixture

Fetahi's precision stamping device could provide a uniform pressure on the entire stamping surface to pattern the SAM, and it reduced the shear force effects. This stamping set-up consisted of three major components (refer to Figure 4.6), which included (a) a linear precision micrometric translator (Thermo-Oriel Co.), (b) a reverse angle mirror mount (Edmund Optics Co.), and (c) a metric tilt platform (Edmund Optics Co.).

The most important component in this fixture was the precision micrometric translator. The role of the translator was to provide very accurate vertical stamping translation, and to track its displacements micro-metrically. The LCD display on the translator facilitated setting and reading the stamping position digitally. The micrometric translator was mounted on a slide rod (e), which slid on a mounting post (f). The reverse angle mirror mount was attached to the precision translator, and was used to carry a stamp holder. It had two stainless steel fine adjustment (64-pitch) screws, which allowed precise tilting of the stamp in two rotation directions about axes x and y in the horizontal plane. The gold surface to be patterned (d) was placed on the metric tilt platform mounted on an adjustable rack with a pinion post (g). It can orient the substrate in two directions about the x and y axes. The tilting can be controlled in μm , in a similar manner as a reverse angle mirror mount.

The stamp was made of Polydimethylsiloxane (PDMS) elastomer. It was moulded to a 20 mm×20 mm square with a $\sim 65\ \mu\text{m}$ height, as shown in Figure 4.7. The corner radii of the PDMS stamp should be as small as technologically possible, in favour of the geodesic curvature measurement. Moreover, the roughness of the stamp surface

should be less than 0.5 μm in order to transfer SAM uniformly in the region of contact. To ensure that the entire stamp surface contact the solid substrate at the same time, the flatness of the stamp step should not be greater than 5 μm over its surface area.

PDMS was moulded on a patterned master generated on a photo-mask by a technique, called photolithography, under the clean-room operation. The patterned master was made by spin coating two layers of SU-8 negative Photo-Resist (PR) on a thin silicon wafer, followed by exposing a square pattern on the PR layer with a high intensity ultraviolet (UV) light. Developer solution was used to remove the unexposed PR part. Finally, the patterned wafer was baked to improve the adhesion of the PR left on the master. The temperature and the time for baking should be controlled. Otherwise they could destroy the PR and generate tiny flaws at the corners of the square, which could affect the moulding and accuracy of the PDMS stamp. Using the patterned master as the mould base and a special stamp holder as the mould, the PDMS gel was poured onto the master and then spread slowly, so that the relief surface of the master was replicated onto the stamp. After removing the air bubbles trapped in the PDMS gel using a weak vacuum (25-30" mercury) chamber for a period of 45-60 mins, it was cured in a laboratory oven for 4 hrs at 65°C. The stamp holder with the PDMS stamp was fixed onto the reverse angle mirror mount before the contact printing.

4.4.4 Producing heterogeneously patterned surface

The derivation of the modified Young's Equation (2.6) tells us that the solid surface should be smooth, homogeneous and rigid, otherwise the surface causes other effects besides the surface tension. The SAM surfaces should be carefully prepared to

meet this requirement. Gold was chosen as the surface to make SAM, because contact printing of alkanethiolates on gold was currently the simplest and most reliable process. In this way we could pattern highly ordered SAMs with relatively low densities of defects and high edge resolutions. SAMs of long-chain alkanethiols on gold substrate can produce a well-packed monolayer surface as discussed before, on which the measured contact angle hystereses of liquids were relatively small. Therefore, they were selected to create the patterned surface used in this experiment.

By choosing alkanethiols with appropriate chain lengths, the hydrophobic and hydrophilic SAMs can be made to have approximately the same molecular height (Xia et al., 2001). The vertical influence between the molecules at the interface, where the two SAMs meet, can be neglected. The 16-Mercaptohexadecanoic acid ($\text{COOH}(\text{CH}_2)_{15}\text{SH}$) (90%), denoted by C_{16} , and the 1-Octadecanethiol ($\text{CH}_3(\text{CH}_2)_{17}\text{SH}$) (98%), denoted by C_{18} , (Sigma-Aldrich Canada Ltd.) were adopted to produce the SAMs. According to the contact angles of the liquids generated on these two SAMs (refer to Tables 4.1 and 4.2), a SAM of C_{16} was used as the hydrophilic SAM I inside the square, and the C_{18} SAM as the hydrophobic SAM II surrounding this square. This gave a combined surface required for the drop spreading experiment. To form SAM surfaces, it was typical to make 1.0 mM solutions of the two alkanethiols at room temperature for stamping and immersing the gold surfaces. Those solutions were prepared from 0.05731 g of C_{18} with 200 ml ethanol (100% purity) in a 250 ml beaker, and 0.02885 g of C_{16} with 100 ml ethanol in another beaker. These beakers were beforehand soaked in the solution of Hydrogen peroxide (H_2O_2) (30%) and Sulphuric Acid (H_2SO_4) in a proportion of 1:3 for ~24 hrs. After that, they were rinsed with doubly distilled water, filled up with ethanol (95%) and

stored in a desiccator until making the alkanethiol solutions. This cleaning procedure was used elsewhere to remove major organic contaminants on all glassware. In order to avoid the oxidation of the thiols in all solutions, they were prepared fresh ~24 hrs prior to use.

The PDMS stamp also needed to be cleaned, to remove the particles sticking on its surface. After sonicated, the stamp was soaked in ethanol (95%) for a few hours. Then, it was dipped into the C_{16} solution for ~15 secs. When the stamp was taken out of the solution, usually a few droplets would adhere irregularly on the stamp's surface instead of a liquid film, because of the low surface energy of the PDMS plane. The relative big droplets can be blown away by a gas stream. Those small droplets adhering to the PDMS could cause the C_{16} solution to spread across the surfaces when the stamp touched the gold substrate. As a result it was necessary to wait ~10-15 mins for these small droplets to evaporation prior to PDMS-Au contact. However, the stamp should not be too dry to be used for the printing. Otherwise, there was not enough solution to transfer thiols onto the gold surface. Microscopically, the state of the solution on the stamp is hard to measure (Delamarche, 1998).

The formation of alkanethiolates SAMs during the contact printing was a fast process, occurred and stabilized in only a few microseconds once thiol solution contacts the Au substrate. However, in this experiment, the time for contact printing was relatively long due to the large area (20 mm $\times$ 20 mm) of contact surface being used. This contact time should be controlled (usually within 30 mins), because a too long reaction time would increase the probability of molecular diffusion towards the outside of the desired pattern and result in unclear edges or corners of contact areas (Libioulle et al.,

1999; Chen et al., 2000). This blurred patterned surface was particularly undesirable in this experiment. The contact printing between the stamp surface and the substrate surface was performed, after the two surfaces were calibrated to be parallel on the precision fixture through a microscope. The calibration had to be carried out before each experiment to ensure that the two surfaces were parallel. The elastic modulus of the stamp and the adhesive forces between the PDMS and the gold surface usually ensured good contact during the printing, so no extra pressure was applied to the stamp upon contact with the gold substrate. The SAMs of C_{16} was then formed on the gold-coated substrate, on which the thiol group covalently bonded with the gold leaving carboxylic acid groups ($-COOH$) exposed to the air. The ambient temperature was fixed at $\sim 20^{\circ}\text{C}$ throughout the experiment. When removing the stamp from the gold substrates, shear forces that might blur the pattern should be avoided.

After stamping, the patterned gold surface was immersed into the solution of C_{18} for a few minutes. The bare regions of the gold, unprotected by the SAM of C_{16} , would be further derivatized with C_{18} , which had a different head group ($-CH_3$). As a result, a solid surface patterned with different wettabilities was obtained. This patterned surface still had a golden colour, though two SAMs had been produced on it. SAMs could not be seen by naked eyes, because molecular layers were so thin and the solutions with low concentrations were adopted in this experiment. The patterning quality could not be evaluated until the drop spreading experiment was carried out on it.

Metal	Adsorbate	H ₂ O	HD
		θ_a, θ_r (deg)	θ_a, θ_r (deg)
Cu/Cu(II)	CH ₃ (CH ₂) ₁₆ CONHOH	114, 101	49, 41
	CH ₃ (CH ₂) ₁₆ COOH	111, 82	46, 38
	CH ₃ (CH ₂) ₁₇ PO ₃ H ₂	112, 76	29, 0
	CH ₃ (CH ₂) ₁₇ SH	117, 93	62, 28
	HO(CH ₂) ₁₅ CONHOH	27, 12	22, 0
Ag/Ag(II)	CH ₃ (CH ₂) ₁₆ CONHOH	113, 102	51, 44
	CH ₃ (CH ₂) ₁₆ COOH	81, 61	21, 0
	CH ₃ (CH ₂) ₁₇ PO ₃ H ₂	82, 60	0, 0
	CH ₃ (CH ₂) ₁₇ SH	113, 102	49, 43
	HO(CH ₂) ₁₅ CONHOH	68, 39	0, 0
Ti/Ti(IV)	CH ₃ (CH ₂) ₁₆ CONHOH	110, 85	45, 29
	CH ₃ (CH ₂) ₁₆ COOH	50, 15	0, 0
	CH ₃ (CH ₂) ₁₇ PO ₃ H ₂	110, 95	41, 36
	HO(CH ₂) ₁₅ CONHOH	77, 51	0, 0
Au	CH ₃ (CH ₂) ₁₆ CONHOH	84, 63	0, 0
	CH ₃ (CH ₂) ₁₇ SH	115, 103	49, 39

Table 4.1 Advancing and receding contact angles of water and hexadecane (HD) on SAMs, formed in ethanol solutions, obtained on four metal substrates (John et al., 1995).

RSH	H ₂ O	HD
	θ_a (deg)	θ_a (deg)
HS(CH ₂) ₂ (CF ₂) ₅ CF ₃	118	71
HS(CH ₂) ₂₁ CH ₃	112	47
HS(CH ₂) ₁₇ CH=CH ₂	107	39
HS(CH ₂) ₁₁ Br	83	0
HS(CH ₂) ₁₁ Cl	83	0
HS(CH ₂) ₁₁ OCH ₃	74	35
HS(CH ₂) ₁₀ CO ₂ CH ₃	67	28
HS(CH ₂) ₈ CN	64	0
HS(CH ₂) ₁₁ OH	0	0
HS(CH ₂) ₁₅ CO ₂ H	0	0

Table 4.2 Advancing contact angles on derivatized thiol monolayers on gold (Bain et al., 1989).

Adsorbate	H ₂ O	HD
	θ_a (deg)	θ_a (deg)
CH ₃ (CH ₂) ₁₇ NH ₂	90	12
CH ₃ (CH ₂) ₁₆ OH	95	33
CH ₃ (CH ₂) ₁₆ CO ₂ H	92	38
CH ₃ (CH ₂) ₁₆ CONH ₂	74	18
CH ₃ (CH ₂) ₁₆ CN	69	0
CH ₃ (CH ₂) ₂₁ Br	84	31
CH ₃ (CH ₂) ₁₄ CO ₂ Et	82	28
CH ₃ (CH ₂) ₂₂ NC	102	28
CH ₃ (CH ₂) ₁₅ SH	112	47
CH ₃ (CH ₂) ₁₅ OCS ₂ Na	108	45

Table 4.3 Adsorption of terminally functionalized alkyl chains on gold (Bain et al., 1989).

1. Nikon D100 digital camera	2. Micro zoom lens	3. Glass vessel
4. Sessile drop	5. Gold substrate with patterned surface	6. Optical flat support
7. Measuring liquid	8. Adjustable stand	9. Measuring liquid
10. Adjustable stand	11. Small container	12. Tygon tubing
13. Quick-disconnect hose	14. Set screw	15. Tubing clamp
15. Tubing clamp		

Figure 4.1 Block diagram of the experimental set-up.

Figure 4.2 Photographs of the experimental set-up: (a) entire experimental assembly; (b) enlarged experimental surface.

Figure 4.3 Apparatuses for connections (Cole-Parmer Inc.): (a) barbed fitting with 1/8" ID, which was a straight connector, made of clear Polypropylene; (b) quick-disconnect hose barbs connecting 1/8" ID tubing.

Figure 4.4 Schematic of the molecules in a self-assembled monolayer.

Figure 4.5 (a) Contact angle of a distilled water drop on the C₁₈ SAM surface produced on gold is ~106°; (b) contact angle of a distilled water drop on a gold surface is ~50°.

Figure 4.6 PDMS elastometric stamping fixture assembly: (a) linear precision micrometric translator; (b) reverse angle mirror mount; (c) metric tilt platform; (d) gold surface to be patterned; (e) slide rod; (f) mounting post; (g) adjustable rack with pinion post (Fetahi et al., in progress).

Figure 4.7 Photographs of PDMS stamp (a) with the stamp holder (b) and 65 μm step (c) on stamp with RUBY calibration ball (d) (radius of 500 μm) (Fetahi et al., in progress).

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Chapter 5

Drop Spreading Experiments and Results

As the continuity to Chapter 4, which introduces the experimental setup and preparation, this chapter explains the experimental procedure, data analysis and results. The experimental operations had the following sequence. First, three measuring liquids were selected with appropriate properties meeting the experimental requirements. The experimental apparatuses contacting the measuring liquids were cleaned properly before each experiment, due to the sensitivity of line tension to the ambient environment. Then the contact angles of the measuring liquid drops on two SAM surfaces (refer to Section 4.3) were measured for the line tension estimation. The contact angle measurement was conducted on the basis of digital images of the sessile drops. Each image was calibrated using an accurate calibration object with known dimensions. The data of the drop profiles were obtained by processing their digital images and then analyzed, by the Axisymmetric Drop Shape Analysis-Profile (ADSA-P) program, to get the contact angle values. Likewise, the contact line profiles of liquid drops, at the corners of the inner square (SAM I) patterned on the solid substrates, were acquired by the digital camera. The radii of the contact line profiles were estimated through a nonlinear fitting technique. Finally, the line tension values were calculated using the modified Young's equation,

with the contact angles for the two SAM surfaces and the radius of the contact line profile.

5.1 Selection of test liquids and experimental cleaning

Three different test liquids have been used in this experiment. They were distilled water, ethanol (Commercial Alcohols Inc.), and n-hexadecane (normal hexadecane, denoted by hexadecane hereafter) (Aldrich Chemical Co.). Their physical and chemical properties are given in Table 5.1. Water was adopted in this experiment because it is commonly available and non-toxic, and there are several previous attempts at line tension values of water. The thiol solutions used in this experiment had ethanol (100% purity) as their solvent, as discussed in Chapter 4. Thus, ethanol was chosen to be one of the test liquids. Hexadecane has a high boiling point and minimizes evaporation during an experiment, which is one of the experimental requirements as explained in Section 3.3. Furthermore, it is an oil-like liquid with a larger viscosity than water and ethanol, and can spread slowly, so that it was easier to observe and capture its last contact line position before it broke out of the SAM I inner square region. These three liquids were relatively inert to the SAM surfaces, and usually available and safe in the laboratory.

All apparatuses contacting the test liquids were cleaned with a 99.9% germ kill detergent and distilled water, to remove major organic contaminants. All glassware was cleaned in the solution of H_2O_2 and H_2SO_4 (mentioned in Section 4.4.4) to get rid of the soap solution, and then dried by air. The tubing, the barbed fittings and the quick-disconnect hose bards were soaked in the corresponding test liquid for approximately 24 hrs. Three individual sets of apparatuses were used for each type of test liquid and the

fresh test liquids were applied in each experiment run, so as to ensure the purity of the measuring liquid. The patterned solid substrates were pre-soaked in the corresponding test liquid for at least 12 hrs before each experiment. One of the reasons for the pre-soaking was to ensure that surface contaminations would be reduced as much as possible, because surface contaminations were apt to increase the contact angle hysteresis. Another reason to pre-soak apparatuses contact surfaces was to minimize the chemical effects, such as surface adsorption during an experiment, in order to maintain an approximate equilibrium state between the sessile drop and the solid surface. The solid substrates were then pulled out of the soaking liquids at an angle to remove excess visible fluid and set up in the measuring glass vessel. The cleaned glass vessel was rinsed with the corresponding test liquid before every experiment, to give the sessile drop a similar vapour environment. The bottom of the vessel was covered with a liquid bath of ~ 0.5 cm height, and was left overnight to produce a relatively saturated vapour with respect to the sessile drop, also mentioned in Chapter 4.

5.2 Digital image acquisition

A charge-coupled device (CCD) camera (Nikon Co.) with a high quality micro zoom lens having CPU contacts was used to acquire digital images in the experiments. This camera was a D100 single-lens reflex (SLR) digital camera, and the lens was the Nikon AF Zoom Micro-Nikkor ED 70-180 mm f/4.5-5.6D lens (Nikon Co.), by which macro photography can be achieved to a maximum of 0.75 times (a 1:1.32 reproduction ratio with maximum 180 mm focal length). An optional No. 6T close-up lens mounted on the end was used for macro photography up to 1:1 (maximum for 180 mm focal

length). The camera was set to produce images in a size of 3008×2000 pixels with 256 (2^8) grey levels. As shown in Figure 4.2, the camera was supported by a tripod (Manfrotto[®]), which can adjust the camera with 4-degrees of freedoms (rotations about x , y , z axes and translation at z -axis).

Digital image acquisition was one of the key steps in this experiment. The accuracy of line tension measurement relied on the quality of the acquired digital image. Thus, a good knowledge of a digital camera operation was indispensable.

The most basic concept of focusing is the focal length of a lens. As shown in Figure 5.1, in the case of a simple lens, the focal length was defined as the distance between the lens and a focused image of an object at infinity. The stronger the light-bending power of the lens, the shorter its focal length. The image of an object will be small in size, when focused by a lens with a short focal length (refer to Figure 5.2). There is an aperture behind the lens on the camera. This aperture adjusts the range of object distances, in which the objects can be focused sharply at one setting. This range is called the “depth of field”. The longer the focal length is, the less the depth of field it gives, when the same f -numbers are used (refer to Figure 5.3). The f -numbers or f -stop settings are known as a series of relative aperture settings. They are typically noted as $f/5.6$, 8, 11, 16, etc. on the control panel of a camera. The f -number equals the lens focal length divided by the effective aperture diameter. Therefore, the bigger the aperture is, the lower the f -number is, and the shorter the depth of field is, when the same focal length is used (refer to Figure 5.4). The f -numbers are related to the image brightness. As long as the same f -number is set, the image brightness usually remains constant

(Langford, 2000). A simple diagram is shown in Figure 5.5, for a better illustration of the functions and the relations of the above main settings in a camera.

The 180 mm focal length (the longest lens setting available in the camera) was used in this experiment, in order that the object could be recorded as an image that is as big as possible and with as much detail as possible. Another purpose was to make the actual image size with a small pixel size, so as to increase the resolution of the image, usually measured in pixels per inch (ppi). Moreover, small f-numbers (e.g., $f/4.5$ or $f/5.6$) were chosen to increase the image brightness. However, a long focal length and a small f-number setting lead to a short depth of field, as explained before. One problem with such a setting was that it made the camera difficult to focus on the entire object, if some parts of the object were not at the same distance from the lens, i.e., the focusing plane of the camera. Of particular interest in this measurement situation was that the profile of one side of a non-exactly axisymmetric drop could not be sharply focused, if the other side of this drop was not in the focused plane of the camera. The result would be that one side of the drop was clear, while the other side was somewhat blurred.

The “good” images suitable for this experiment were taken with “Manual focus mode” by adjusting manually using the lens-focusing ring, although the camera has auto focus modes. The manual focus mode can allow the digital camera to focus on specific positions and to take pictures when the camera is unable to focus using autofocus (AF). The camera used an exposure mode in this experiment, called “Auto multi program”. Under this exposure mode, the camera automatically adjusted its shutter speed according to the aperture for optimal exposure under the particular situation in an experiment.

As mentioned in Chapter 4, liquid drops were illuminated by a compact fluorescent lamp. The digital camera can mimic the light reflection according to this color of the light source by setting “White balance” to the “Fluorescent” option. The position of the illumination was another important factor to be considered. An appropriate illumination position could make the object more distinct from its background and the edges in the image sharper. As the result, it can make the image processing easier with the high contrast.

5.3 Digital image fundamentals

A camera produces an image by recording the light received from an object. A digital image consists of lots of elements, called pixels. The position of each pixel on the image can be indexed by its coordinate (x, y) . From the optical point of view, each pixel on the image has a certain brightness, which is also called the intensity or grey level. This brightness can be considered as a function of the pixel's coordinate, say $f(x, y)$. The entire digital image can also be regarded as a matrix, whose row and column indices correspond to the coordinates of the pixel. The matrix element value is the grey level of this pixel.

Based on the fact that an image is formed by the light from an object, $f(x, y)$ may be characterized by the illumination and reflection components, denoted by $i(x, y)$ and $r(x, y)$, respectively. Thus, $f(x, y)$ can be expressed as a compound function

$$f(x, y) = i(x, y)r(x, y) \quad (5.1)$$

where, $0 < i(x, y) < \infty$ and $0 < r(x, y) < 1$. The grey level of an image, l , is within the range $L_{\min} \leq l \leq L_{\max}$, where $L_{\min} = i_{\min}r_{\min}$ and $L_{\max} = i_{\max}r_{\max}$. The interval between

L_{min} and L_{max} is called the grey scale. This scale usually shifts in the interval of 0 and L ($L=255$ in this experiment), where $l=0$ corresponds to the black colour, while $l=L$ is considered as the white colour in the scale. All other values (colours) vary continuously from 0 (black) and L (white).

For image analysis on a computer, an image needs to be digitized in both space (image size) and amplitude (grey level). A digital image approximates a continuous image $f(x, y)$ with equally sized pixels (for the D100 they are $6.8 \mu\text{m}$ squares) in an $N \times M$ array. The values of N , M and the grey level l are usually set to be integer powers of two, i.e., $N=2^n$, $M=2^m$, and $l=2^k$. Thus, the computer memory in bits, denoted as b , which is required to store a digital image, is calculated as

$$b = N \times M \times k \quad (5.2)$$

For example, an image with 256×256 pixels and 128 grey levels needs 458,752 bits of computer memory for storage. Even though a digital image with 1024×1024 pixels and 256 grey levels might be indistinguishable from one with 512×512 pixels and 256 grey levels by vision, the former needs much more computer memory for storage than the latter. Thus, image compression, i.e., a proper decrease of the image size, is usually applied to save an image in memory.

The Joint Photographic Experts Group (JPEG) format is a popular image compression technique. A JPEG image, denoted by *.jpg*, is automatically decompressed when being opened. The advantage of saving JPEG data is that the file size is smaller and the file can be accepted by most image processing software, including Adobe Photoshop, MATLAB and MAPLE, or even sent directly to a printer. However, there is a quality loss, and the amount of loss depends on how much compression is used.

Lightly compressed JPEG files can save a significant amount of space and lose very little information, and vice versa. A TIFF image (saved as *.tif* file) is another popular image file, which retains the full quality of the image data. They can be compressed or uncompressed, but no information is lost. Unfortunately, the TIFF format is large and bulky. Furthermore, recording a TIFF image is a relative slow process when taking pictures. Unlike JPEG and TIFF, a RAW image (called NEF data in the Nikon camera) is not an abbreviated data but a raw, unprocessed data. It contains the original image information as it comes off the digital sensor in the camera. Therefore, its absence of processing makes it possible to quickly record the photo to the memory card (faster than a TIFF image and comparable to a JPEG image storage rate). However, it cannot yet be read directly by the standard retouching software (Atkins, 2004). Thus, in this experiment, image files were either compressed lightly and saved in “JPEG Fine” format at a 1:4 compression ratio, or saved in “TIFF-RGB” format.

An image is a specification of a 3D coordinate system, which is composed of the intensity as z -axis and the point position as x and y values (refer to Figure 5.6). The most often used colour image model is the RGB (red, green, blue) model, which has been widely adopted by consumer colour monitors, cameras and camcorders. In the RGB model, each colour is represented by mixing the primary visible spectrum of red, green, and blue in various proportions and intensities (refer to Figure 5.7). This model can be expressed by a Cartesian coordinate system. Where the colours overlap, they create the cyan, magenta, yellow, and white colours at four corners of this model cube, and the blue, black, red, and green colours at four other corners, as shown in Figure 5.8. In this model,

the grey scale varies from the black to the white colour along the diagonal of the cube, and colours are the points on or inside this cube (Gonzalez, 1992).

5.4 Digital image processing

There exist a number of methods that can be used for different purposes in image processing and analysis. The approaches used in this thesis fall into two major categories: image enhancement and image segmentation. They are both based on a mask processing or filtering technique. A mask, also called a filter, is defined as a small subimage used in local processing of an image pixel by pixel. Basically, a mask covers a small 2-D array on a digital image, e.g., 3×3 or 5×5 mask, and operates in a fashion of multiplying two matrices together: one from the local image and one from the mask.

When analyzing a digital image in this experiment, the very first step was to reduce the noise level of the digital image. An algorithm, known as median filtering with a 3×3 mask, was used in this experiment. It filtered noise without losing image sharpness. The image data on the edge, i.e., the contact line of a sessile drop, had key information for this experiment. The median filter algorithm is similar to the lowpass filtering, which is also called the average filtering and not used in this experiment because it slightly burrs the image when filtering the noise. The median filter algorithm determines the grey level of each output pixel as the median value of the grey levels of the neighbourhood pixels. For example, if a 3×3 image region had the grey level values:

$$\begin{bmatrix} 10 & 20 & 20 \\ 20 & 15 & 20 \\ 20 & 25 & 100 \end{bmatrix}$$

Then the median value would be the 5th $((3 \times 3)/2 = 4.5 < 5)$ largest value after sorting, i.e., the value of 20 from [10, 15, 20, 20, 20, 20, 20, 25, 100]. This value is assigned to the pixel in the centre of the 3×3 image. Thus, median filtering forces pixel points with distinct intensities to be more like their neighbours, which eliminates intensity spikes (Gonzalez, 1992). Figure 5.9 was a typical image of a calibration square ($1 \text{ mm} \times 1 \text{ mm}$) that was used to estimate the pixel size on the image. After median filtering, the numerical values of the grey levels across a straight segment of the square's edge smoothed out and the noise level was reduced.

The second step in the image analysis of this experiment was to obtain the data along the drop profile and the contact line. This required a specific image analysis technique, called edge detection. Edge detection techniques are the most common approaches in image segmentations for detecting meaningful discontinuities in grey level. Figure 4.6 shows that a typical sessile drop had dark regions and was distinct from the background on the image. Edge detection techniques take advantage of this kind of distinction. The algorithm used in most edge-detection techniques computes a local derivative of the grey level. The first derivative of an image $f(x, y)$ at any point (x, y) in the image is obtained by using the magnitude of the gradient at that point, which could be approximated with absolute values:

$$\nabla f \approx |G_x| + |G_y| = \left| \frac{\partial f}{\partial x} \right| + \left| \frac{\partial f}{\partial y} \right| \quad (5.3)$$

The Sobel operator is a first derivative operator and it was applied in this experiment to detect the edges. The operator provides both a differencing and a smoothing effect. Since derivative operations enhance the noise, the smoothing effect is an attractive

feature of the Sobel operator. The derivative calculation based on the Sobel operator masks, defined as shown in Figure 5.10, is carried out by

$$G_x = (z_7 + 2z_8 + z_9) - (z_1 + 2z_2 + z_3) \quad (5.4a)$$

$$G_y = (z_3 + 2z_6 + z_9) - (z_1 + 2z_4 + z_7) \quad (5.4b)$$

The center of the small image region is then replaced by the gradient calculated with Equation (5.3) and (5.4). To get the next value, the masks are moved to the next image region and the procedure is repeated to the whole image (Gonzalez, 1992). Before performing edge detection using the Sobel operator, the image was processed with the Median filtering technique in this experiment. The filtering was necessary, because high frequency noise might be mistakenly detected as being related to the required edge points of the contact line.

Currently, there are commercial software packages for special image processing, which can handle the tasks of noise filtering and edge detection. The MATLAB Image Processing Toolbox (MathWorks Inc.) is one of these software packages. It gives some specific functions for general operations of image processing and analysis. Median filtering for noise reduction and the Sobel operator for edge detection can be implemented directly by calling the corresponding functions in the MATLAB Image Processing Toolbox.

5.5 Calibration measurements

For any experimental measurement, it was necessary and important to know the actual sizes of the contact line and the sessile drop. Thus, the actual size represented by a pixel on an image should be known. For this reason, some calibration measurements

were required in every experiment. The calibration was carried out using some special objects, whose sizes were precise and known. A RUBY calibration ball (refer to Figure 4.7d) of 1.5 ± 0.00254 mm diameter (Edmund Industrial Optics) was used to calibrate the drop profile images, because the camera is sensitive to red and the ball has the same size from any view. A grid distortion target (Edmund Industrial Optics) was used for the calibration of the contact line profile images. This slide has many regularly displayed dots of 12.5, 25 and 50 mm diameters with ± 0.0025 mm accuracy tolerance, as shown in Figure 5.11.

The calibration ball or slide was digitized using the CCD camera by placing it on the focusing plane, where the sessile drop profile or the contact line profile was in focus. Since the calibration objects were basically dots with dark colours, they were placed against a light background under proper illumination, so that the image of the objects and the background had grey levels grouped into two dominant modes (dark and light), and a sharp, distinct demarcation between object and background was possible. Thus, a plot of the pixel numbers versus the intensity, called a histogram of a digital image, of a calibration object was usually a bimodal plot, as shown in Figure 5.12. As discussed before, the illumination plays a crucial role to bring out the object from its background on an image. Poor illumination might result in a large overlap between the two peaks on the histogram, so that the objects and the background could not be easily separated. Figure 5.13a was over-exposed with the light peak pushed up against the right-hand boundary. This means that the background light was so bright that the dark red calibration ball would appear slightly smaller.

A simple way to extract the object from the background was to set a threshold T on the histogram. Any point with an intensity $f(x, y) \leq T$ was classified as belonging to the object; otherwise, the point was regarded as a background point. The processed image $g(x, y)$ was binary (just two intensities) and defined as (Gonzalez, 1992)

$$g(x, y) = \begin{cases} 255 & f(x, y) > T \\ 0 & f(x, y) \leq T \end{cases} \quad (5.5)$$

Thus, after processing with a threshold, a black and white image of the original one was generated. The selection of a threshold value was important, because it determined how many pixels were assigned to the object. Generally, the average of the intensities (grey levels) of the two peaks, I_{peak1} and I_{peak2} , on the histogram, was taken as an approximate threshold value, i.e.,

$$T = \frac{1}{2}(I_{peak1} + I_{peak2}) \quad (5.6)$$

For example, a threshold value of 139 (approximate midway point between peaks of Figure 5.12) was used on the digital image in Figure 5.13a to replace the intensities of the light pixels greater than the threshold with the value 255, and those of the dark pixels less than the threshold with 0. The black and white image was then obtained, as shown in Figure 5.13c. In this experiment, the thresholding was carried out using the “Threshold” function in the Photoshop software (Adobe®). This software is a powerful tool for image processing, easy to use, and it has a high processing speed, even with big image files.

Since the diameter D of the calibration object (the ball or the dot) was given, the image area A covered by the object can be calculated as $\pi D^2 / 4$. As each camera pixel was a tiny square, the area of each pixel associated with the object could be obtained by dividing the object area by the number of the pixels, N_p , included in the calibration

object. Thus, the actual length of each side of a pixel l_p in the calibration object image can be calculated as,

$$l_p = \sqrt{\frac{\pi D^2}{4N_p}} \quad (5.7)$$

However, since the selection of the threshold value and the claimed dimension of the calibration object had some uncertainties, it was necessary to estimate the calibration error. As mentioned before, the object had a tolerance on radius, denoted by ΔR . Thus, the estimated calibration object area with a tolerance was equal to

$$A_{object} = A \pm \Delta A \approx \pi R^2 \pm \frac{\pi}{2} [(R + \Delta R)^2 - (R - \Delta R)^2] \quad (5.8)$$

As indicated in Figure 5.12, the threshold selection had an estimation error of $\pm \Delta T$. The number of pixels included in the object would change, if the threshold value varied within the error bound of $[T - \Delta T, T + \Delta T]$. If we let the number of object pixels under the threshold of $T + \Delta T$ be denoted as N_{p+} , and the number of object pixels under $T - \Delta T$ be N_{p-} ($N_{p+} > N_{p-}$), then the upper and the lower bounds of each pixel length can be given by

$$l_p^{upper} = \sqrt{\frac{A + \Delta A}{N_{p-}}} = l_p + \Delta l \quad (5.9a)$$

$$l_p^{lower} = \sqrt{\frac{A - \Delta A}{N_{p+}}} = l_p - \Delta l \quad (5.9b)$$

where $\pm \Delta l$ was the uncertainty of each pixel length. In this experiment, the error bounds of threshold were chosen as ± 20 intensity levels. Figure 5.13 shows that there was little difference, when an image of the calibration ball was processed with threshold values of 119, 139 or 159 (intensities), respectively. There was no special reason to use the error bounds of ± 20 intensities, but, if the variation of the threshold value, ΔT , was too big, the

number of object pixels would have some fluctuation, which could cause unreasonably large numerical errors. However, for the images in this research study, no significant changes occurred with threshold bands of ± 10 or ± 30 intensity levels.

5.6 Contact angle measurements

According to the modified Young's Equation (3.13), the contact angles of large drops on SAM I and SAM II surfaces should be measured in order to estimate the line tension. As mentioned in Section 5.1, three liquids were used as the measuring liquids. The contact angle measurements were carried out with each measuring liquid on a substrate of either SAM I material (produced by 16-Mercaptohexadecanoic acid) or SAM II material (produced by 1-Octadecanethiol), without a patterned surface. The drop profile data were obtained using the method of "drop size dependence of contact angles" in this experiment. The data were processed with the computer program "Axisymmetric Drop Shape Analysis-Profile (ADSA-P)" to estimate the contact angles.

5.6.1 Drop profile data acquisition

After cleaning the solid substrate with either SAM I or II film, the substrate was connected to the Tygon tubing, using a barbed fitting. Before each measurement, the solid surface was levelled using a "calibrated mounted circular level" (10 mins per 0.1" sensitivity) (Edmund Industrial Optics), by adjusting the setscrews of the adjustable stand, which supported the large glass vessel. A sessile drop was then pumped onto the substrate surface by adjusting the position of the reservoir container, if the liquid height in the container was fixed, as described in Section 4.1. The drop was illuminated from

the behind, and photographed by the digital camera from the front. The radius of the drop was increased from ~3 mm to ~12 mm gradually. The smallest radius was decided by the size of the small hole drilled on the solid substrate. The upper limit of the radius was set as ~12 mm, because the contact angle did not appear to change much beyond this radius. As discussed in Chapter 2, the line tension effect could be neglected for a large drop. The rate of drop growing was controlled in mm/s, and was slow enough so that the advancing contact angle could be regarded as in equilibrium. Since it has been proved that there was no significant difference between the static and the low-rate advancing contact angles, the dynamic contact angle could be used in this measurement. The longest focal length (180 mm) of the lens was used in the experiment to ensure that the drop covered a large portion of the viewing field. The f-number was selected as small as possible, to give a bright picture and a sharp drop profile. Each image produced by different setting of the camera was calibrated by the RUBY calibration ball.

A series of images of the sessile drops were acquired immediately after the drop's deposition. The time interval for acquiring images was set to vary with the advancing of the liquid drop, because the larger the drop radius was, the slower the drop growth would be, as indicated in the calculations in Appendix A. Thus, a short interval was adopted at the beginning, and then slightly longer intervals after. All measurements were performed at room temperature. The procedure was repeated with different measuring liquids on the two SAM surfaces, respectively.

The CCD camera acquired the drop images in RGB mode. Before these images were processed by MATLAB, they were converted to the Greyscale mode in the Photoshop software. This mode used up to 256 shades of grey. Every pixel of a

greyscale image had a brightness value ranging from 0 to 255. To change a RGB image to a high-quality greyscale image, Photoshop discarded the colour information in the original image. The grey levels of the converted pixels represented the luminosity of the original pixels (Photoshop, 2002). After a few pictures of liquid drops were obtained, the images of drop sections above the substrate surface were extracted and converted to greyscale mode using Photoshop. The image data was then processed by MATLAB for noise reduction using the Median filter and for the drop's edge (the drop profile or side view in the image) detection using the Sobel operator. This procedure is illustrated in Figure 5.14. The MATLAB programs for image processing and analysis are presented in Appendix C. To analyze the data of the drop profile, the coordinates of the points along the profile were obtained using MATLAB. Each point represented a pixel. Since an image of ~6M pixels was taken in each measurement and the radius of the drops ranged from 3 mm to 12 mm, one to two thousand data points could be obtained for a drop profile. They were finally passed on to the program ADSA-P to calculate the contact angles, etc.

5.6.2 Axisymmetric drop shape analysis-profile (ADSA-P) technique

The ADSA-P technique has been mentioned in Section 3.1, where it is used to determine the surface tension of a pendant drop using a similar algorithm. This technique can also estimate the contact angle, the drop volume, the drop surface area, and the drop radius. The required input data for the ADSA-P program are the density difference across the liquid-vapour interface, $\Delta\rho$, the number of the points along the axisymmetric drop profile, the gravitational acceleration g , and the vertical distance between the

substrate surface and the drop apex, z_{max} . This technique eliminates the subjective error that exists in goniometric measurements and provides accurate estimation of the contact angles from the drop profiles (Neumann and Spelt, 1996). The ADSA-P program is developed according to the axisymmetric Laplace equation of capillarity with only the gravity effect, Equation (2.2). ADSA-P uses a least-squares curve fitting method, which fits the theoretical profile (usually the Laplace curve) to an experimental drop profile, to determine the contact angle between the drop profile and the substrate surface. This ADSA-P program has two versions currently, in C and FORTRAN languages. The FORTRAN version was used in this thesis (refer to Appendix D).

The ADSA-P program needs the coordinates of profile points in physical space. When a digital image was analyzed using the MATLAB program, the coordinates of the profile points were obtained in terms of pixel locations on the image. MS Excel was used to translate the coordinates in pixels to the physical coordinates, based on the results from the calibration measurement. The drop profiles of the three measuring liquids were plotted in Figures 5.15 through 5.18. The contact angle values of these liquid drops were listed in Tables 5.2 through 5.8. Ethanol and hexadecane wetted the SAM I surface completely, i.e., they had essentially a zero contact angle on the SAM I surface.

It can be noted that the contact angle varied as the drop size changed. That was due to the line tension effects, as mentioned before. According to the Young's Equation (2.12), these liquid/solid/vapour systems all have positive line tensions due to the negative slope of their best-fit lines, shown from Figure 5.19 to 5.26, as explained in Section 3.2.1.1. The contact angle measurements performed in this experiment were identical to the sessile drop method for line tension measurement. The line tension

values could be calculated using Equation (2.12). However, as discussed in Chapter 3, the sessile drop method could not achieve the stable chemical equilibrium throughout the experiment and may create errors in line tension estimations. To avoid this limitation and minimize the error due to experimental conditions, the improved experimental arrangement, “drop spreading method”, was developed in this thesis for line tension measurement.

5.7 Line tension measurements

Section 5.6 introduced the measurement of some of the key experimental parameters, i.e., the contact angles of liquid drops on each type of SAM surface. Another important parameter for estimating the line tension was the curvature of the contact line profile just before the drop broke out of the inner square region. The same experimental set-up as before was used, except that the camera position was changed to photograph the contact lines of drops from the top of the sessile drop. Before each measurement, the apparatuses were cleaned in the same way, as described in Section 5.1. There were two major differences between the curvature and the contact angle measurement. In the experiment of the curvature measurement, the patterned substrate surface with two SAMs was used and the substrate surface was tilted slightly towards one of the corners, instead of being levelled. Since it was difficult to handle the movement of contact lines at all four corners simultaneously and it was desirable to maximize the image size to resolve the corner as much as possible, only one corner was observed during each measurement. A slight surface incline was used to make the contact line of the drop approach one corner earlier than the other three. The camera was focused on this preferred corner

region and the drop's contact line shape was captured in a sequence of images. When the contact line of the drop was close to the corner, the pumping was controlled carefully and adjusted according to the movement of the contact line, in order to capture the minimum contact line arc just before drop break-out. Stagnancy or retraction of the drop contact line should be prevented. The camera recorded the progress of the contact line as it approached the corner with a certain time interval, typically 10-30 secs. The time interval was shortened as the contact line got closer to the corner of the inner square (SAM I). Usually, the drop broke out of the inner square from the sides of the square, i.e., the interfacial line of the two SAMs, rather than from the corner. This appears to occur because the line force holding the drop at a straight line was much smaller than the one holding a curved line with a small radius at the corner. It could be explained by the term $\sigma\kappa_{gs}$ in Equation (2.6). For a straight line, $R \rightarrow \infty$, i.e., $\kappa_{gs} \rightarrow 0$, the line tension effect would be infinitesimal small. This breaking procedure is displayed in Figure 5.27 with the top views of ethanol drops. The bright regions along the periphery of the square were illuminated by light reflection in the liquid. The drop spreading experiment should be done within a short time (as short as a few minutes) to reduce the influence of evaporation. The experiments were performed at room temperature and the vibration should be minimized during the measurements.

The small image with the curve profile at the corner was extracted from the picture, and converted from RGB mode to Greyscale mode. The data was then read into the MATLAB program for image processing and analysis. The image data was first filtered to reduce the noise and then the contact line profile, which included two straight

sides and a curve at the corner, was detected. Figure 5.28 shows the contact line profile with the coordinates of the points on the profile.

In order to determine which points should belong to the corner curve, the 95% confidence interval was performed on the two straight side profiles. Consider the best-fit line of a set of data points (x_i, y_i) on a straight side profile, based on the least-squares linear regression:

$$\hat{y}_i = a + bx_i \quad (5.10)$$

where $\hat{y}_i$ values were the vertical ordinate on the best-fit line corresponding to x_i , a and b were the intercept and the slope of the best-fit line, respectively. The 95% confidence interval for the vertical ordinate, Y_i , can be also expressed as a linear function of the horizontal ordinate x_i .

$$Y_i = A + Bx_i \quad (5.11)$$

The 95% confidence interval for the intercept A can be determined as

$$a \pm t_{n-2; \frac{\alpha}{2}} \sqrt{\left(\frac{1}{n} + \frac{\bar{x}^2}{S(X^2)}\right) s_{ey}^2} \quad (5.12)$$

where t denoted the student t-distribution probability, n was the number of the points selected for the estimation of the best-fit line, α was the tail area of the t-distribution profile and was equal to (1-95%) in this calculation, $\bar{x}$ was the mean value of x_i , and $S(X^2)$ was the corrected sum of squares, expressed as

$$S(X^2) = \sum (x_i - \bar{x})^2 = \sum (x_i^2 - n\bar{x}^2) \quad (5.13)$$

The term s_{ey}^2 in Equation (5.12) was estimated as $s_{ey}^2 = SSD/(n-2)$, where SSD was the so-called residual sum of squares, and can be calculated as

$$SSD = \sum (y_i - \hat{y}_i)^2 = \sum y_i^2 - n\bar{y}^2 - b(\sum x_i y_i - n\bar{x} \cdot \bar{y}) \quad (5.14)$$

Similarly, the 95% confidence interval for the slop B can be calculated as

$$b \pm t_{n-2; \frac{\alpha}{2}} \sqrt{\left(\frac{1}{S(X^2)}\right) s_{ey}^2} \quad (5.15)$$

Finally, the 95% confidence interval for the vertical ordinate value, Y_o , at x_o was given by

$$\hat{y}_o \pm t_{n-2; \frac{\alpha}{2}} \sqrt{\left(\frac{1}{n} + \frac{(x_o - \bar{x})^2}{S(X^2)}\right) s_{ey}^2} \quad (5.16)$$

where $\hat{y}_o$ was the vertical ordinate value on the best-fit line corresponding to x_o (Guttman, 1982). The above calculations, including the best linear fit can be easily implemented using the functions in MATLAB Statistic Toolbox (refer to Appendix C).

After calculating the 95% confidence interval on both side profiles of the contact line (i.e., the straight positions of the contact line), the data points assigned to the corner curve could be extracted from the entire contact line profile as those points not belonging to the straight lines. A nonlinear least squares fitting was then employed on the remaining corner points to find a circle, which fitted the corner curve, and the radius of this best-fit circle. The distance l_i between an arbitrary point (x_i, y_i) on the corner curve and the center of the best-fit circle (x_c, y_c) could be expressed as

$$l_i = \sqrt{(x_i - x_c)^2 + (y_i - y_c)^2} \quad (5.17)$$

Assuming the best-fit circle had a radius R_{best} , this nonlinear regression problem was simply to minimize the following objective function,

$$F_{obj} = \sum_i^n l_i^2 = \sum_i^n (R_{best} - \sqrt{(x_i - x_c)^2 + (y_i - y_c)^2})^2 \quad (5.18)$$

When F_{obj} was minimized, the corresponding parameters x_c , y_c and R_{best} would give a best-fit circle to the contact line data points at the corner. This estimation was done by

another MATLAB program, called “Nonlinear least squares fit on a curve”, and it is included in Appendix C. Figure 5.29 shows the contact line profile of the ethanol drop with 95% confidence interval on the two straight sides and a best-fit circle on the curved contact line at the corner.

The geodesic curvature was calculated as the reciprocal of the radius, $1/R_{best}$. Surface tensions of these measuring liquids were given so that the line tension values of the different test liquids on the patterned gold surface can be obtained using Equation (3.13) and are listed from Table 5.9 to 5.12. These experimental results show that the line tension values for this liquid/solid/vapour system were positive and on the order of 10^{-6} to 10^{-7} J/m. They were in reasonably good agreement with the results obtained by other researchers using the sessile drop arrangement.

Name	Formula	Purity (%)	bp (°C/1atm)	M.W. (g/mol)	Density* (g/cm ³)	Surface tension* (mJ/m ²)	Viscosity* (Ns/m ²)
Water	H ₂ O	≤99 [†]	100	18.02	0.998	72.75	10.02×10 ⁻⁴
Ethanol	C ₂ H ₅ OH	≤99	78	46.07	0.790	23.70	12.0×10 ⁻⁴
Hexadecane	C ₁₆ H ₃₄	99	287	226.45	0.773	27.76	30.32×10 ⁻⁴

Table 5.1 Physical and chemical properties of measuring liquids (Raznjevič, 1976; Dean, 1999; Lide, 2002; Sigma-Aldrich Co.). * Values at room temperature (20±1°C).

† Using a Barnstead model A56285 still with still pre-treatment cartridge D0832 (for deionising).

Drop number	Contact angle θ (deg)	Radius R (cm)	$\cos\theta$	1/radius 1/R (1/cm)
Substrate	Glass			
1	55.30	0.4230	0.5697	2.3641
2	55.00	0.4890	0.5740	2.0450
3	55.20	0.5050	0.5711	1.9802
4	55.50	0.5670	0.5668	1.7637
5	54.34	0.7268	0.5834	1.3759
6	54.80	0.8545	0.5768	1.1703
7	54.37	0.9405	0.5829	1.0633
8	54.90	1.0186	0.5754	0.9817
9	54.40	1.1000	0.5825	0.9091
Contact angle $\bar{\theta} \pm \Delta\theta$ (deg)		54.87±0.33		
Correlation coefficient		-0.73		
Contact angle $\theta_{J\infty}$ (deg)		53.94		
Estimated line tension (μJ/m)		6.08		
Substrate	Si wafer			
1	15.37	0.5747	0.9643	1.7400
2	14.76	0.7455	0.9670	1.3414
3	14.44	0.8150	0.9684	1.2270
4	13.70	0.8889	0.9716	1.1250
5	13.81	0.9532	0.9711	1.0491
6	13.66	0.9651	0.9717	1.0362
7	13.59	1.0337	0.9720	0.9674
8	13.63	1.1991	0.9719	0.8340
9	13.85	1.2198	0.9710	0.8198
Contact angle $\bar{\theta} \pm \Delta\theta$ (deg)		14.09±0.48		
Correlation coefficient		-0.92		
Contact angle $\theta_{J\infty}$ (deg)		11.54		
Estimated line tension (μJ/m)		6.39		

Table 5.2 Contact angle values of water on SAM I (hydrophilic) surface.

Drop number	Contact angle θ (deg)	Radius R (cm)	$\cos\theta$	1/radius 1/R (1/cm)
Substrate	Glass			
1	108.40	0.3277	-0.3147	3.0516
2	108.28	0.3322	-0.3128	3.0102
3	108.19	0.3723	-0.3113	2.6860
4	108.03	0.4034	-0.3086	2.4789
5	107.94	0.4382	-0.3071	2.2821
6	107.88	0.4639	-0.3061	2.1556
7	107.83	0.4900	-0.3053	2.0408
8	107.81	0.5193	-0.3050	1.9257
9	107.78	0.5405	-0.3045	1.8501
Contact angle $\bar{\theta} \pm \Delta\theta$ (deg)		108.02±0.17		
Correlation coefficient		-0.99		
Contact angle $\theta_{I\infty}$ (deg)		106.78		
Estimated line tension (μJ/m)		5.96		
Substrate	Si wafer			
1	106.62	0.9863	-0.2851	1.0139
2	106.50	1.1205	-0.2831	0.8925
3	106.60	0.8405	-0.2848	1.1898
4	106.58	1.1024	-0.2844	0.9071
5	106.31	1.1417	-0.2799	0.8759
6	106.30	1.0868	-0.2798	0.9201
7	106.48	1.1843	-0.2828	0.8444
8	106.47	1.2090	-0.2826	0.8271
9	106.35	1.1618	-0.2806	0.8607
Contact angle $\bar{\theta} \pm \Delta\theta$ (deg)		106.47±0.09		
Correlation coefficient		-0.55		
Contact angle $\theta_{I\infty}$ (deg)		105.87		
Estimated line tension (μJ/m)		7.20		

Table 5.3 Contact angle values of water on SAM II (hydrophobic) surface.

Drop number	Contact angle θ (deg)	Radius R (cm)	$\cos\theta$	1/radius 1/R (1/cm)
Substrate	Glass			
1	35.08	0.3574	0.8185	2.7980
2	35.07	0.4054	0.8186	2.4667
3	34.94	0.4270	0.8200	2.3419
4	34.89	0.4768	0.8204	2.0973
5	34.73	0.5053	0.8221	1.9790
6	34.61	0.5428	0.8232	1.8423
7	34.63	0.6286	0.8230	1.5908
8	34.50	0.6500	0.8243	1.5385
9	34.77	0.7010	0.8216	1.4265
Contact angle $\bar{\theta} \pm \Delta\theta$ (deg)		34.80±0.16		
Correlation coefficient		-0.87		
Contact angle $\theta_{l\infty}$ (deg)		34.00		
Estimated line tension (μJ/m)		0.91		
Substrate	Si wafer			
1	33.54	0.8197	0.8337	1.2200
2	33.46	0.8581	0.8344	1.1654
3	33.44	0.9364	0.8346	1.0679
4	33.47	1.0614	0.8343	0.9422
5	33.43	1.1148	0.8347	0.8970
6	33.40	1.1552	0.8350	0.8657
7	33.38	1.1809	0.8352	0.8468
8	33.35	1.2091	0.8355	0.8271
9	33.32	1.2210	0.8358	0.8190
Contact angle $\bar{\theta} \pm \Delta\theta$ (deg)		33.42±0.05		
Correlation coefficient		-0.86		
Contact angle $\theta_{l\infty}$ (deg)		33.04		
Estimated line tension (μJ/m)		0.85		

Table 5.4 Contact angle values of ethanol on SAM II (hydrophobic) surface.

Drop number	Contact angle θ (deg)	Radius R (cm)	$\cos\theta$	1/radius 1/R (1/cm)
Substrate	Glass			
1	30.99	0.4230	0.8574	2.3641
2	30.91	0.4252	0.8581	2.3518
3	30.85	0.4352	0.8587	2.2978
4	30.66	0.4404	0.8603	2.2707
5	30.74	0.4746	0.8596	2.1070
6	30.75	0.4921	0.8595	2.0321
7	30.71	0.5273	0.8599	1.8965
8	30.64	0.5310	0.8605	1.8832
9	30.72	0.5487	0.8598	1.8225
Contact angle $\bar{\theta} \pm \Delta\theta$ (deg)		30.77±0.09		
Correlation coefficient		-0.72		
Contact angle $\theta_{l\infty}$ (deg)		29.92		
Estimated line tension (μJ/m)		0.97		
Substrate	Si wafer			
1	25.23	0.8349	0.9047	1.1977
2	25.76	0.9302	0.9007	1.0750
3	25.72	0.9980	0.9010	1.0020
4	25.13	1.0249	0.9054	0.9757
5	25.10	1.0572	0.9057	0.9459
6	25.69	1.1056	0.9013	0.9045
7	25.56	1.1361	0.9022	0.8802
8	25.20	1.1870	0.9049	0.8425
9	25.12	1.1880	0.9055	0.8418
Contact angle $\bar{\theta} \pm \Delta\theta$ (deg)		25.39±0.22		
Correlation coefficient		-0.16		
Contact angle $\theta_{l\infty}$ (deg)		25.00		
Estimated line tension (μJ/m)		0.81		

Table 5.5 Contact angle values of hexadecane (group #1) on SAM II (hydrophobic) surface.

Drop number	Contact angle θ (deg)	Radius R (cm)	$\cos\theta$	1/radius 1/R (1/cm)
Substrate	Glass			
1	31.27	0.4811	0.8549	2.0786
2	31.08	0.4966	0.8566	2.0137
3	31.14	0.5501	0.8560	1.8179
4	31.18	0.6074	0.8557	1.6464
5	31.11	0.6370	0.8563	1.5699
6	30.99	0.6525	0.8574	1.5326
7	30.96	0.6825	0.8577	1.4652
8	30.91	0.7111	0.8581	1.4063
9	30.98	0.7300	0.8575	1.3699
Contact angle $\bar{\theta} \pm \Delta\theta$ (deg)		31.07±0.09		
Correlation coefficient		-0.79		
Contact angle $\theta_{I\infty}$ (deg)		30.46		
Line tension σ (μJ/m)		0.89		
Substrate	Si wafer			
9	26.01	0.7403	0.8988	1.3508
8	26.03	0.7949	0.8987	1.2580
7	26.00	0.8525	0.8989	1.1730
6	25.91	0.8685	0.8996	1.1514
5	25.98	0.9020	0.8990	1.1086
4	25.96	0.9152	0.8992	1.0927
3	25.89	0.9336	0.8997	1.0711
2	25.87	0.9510	0.8999	1.0515
1	25.85	0.9733	0.9000	1.0274
Contact angle $\bar{\theta} \pm \Delta\theta$ (deg)		25.94±0.05		
Correlation coefficient		-0.80		
Contact angle $\theta_{I\infty}$ (deg)		25.35		
Line tension σ (μJ/m)		1.08		

Table 5.6 Contact angle values of hexadecane (group #2) on SAM II (hydrophobic) surface.

Drop number	Contact angle θ (deg)	Radius R (cm)	$\cos\theta$	1/radius 1/R (1/cm)
Substrate	Glass			
1	30.07	0.4395	0.8655	2.2753
2	30.14	0.5272	0.8649	1.8968
3	30.87	0.5895	0.8585	1.6964
4	30.04	0.6056	0.8658	1.6513
5	29.93	0.6536	0.8668	1.5300
6	29.88	0.6833	0.8672	1.4635
7	29.76	0.7122	0.8682	1.4041
8	29.71	0.7451	0.8687	1.3421
9	29.78	0.7601	0.8681	1.3156
Contact angle $\bar{\theta} \pm \Delta\theta$ (deg)		30.02±0.27		
Correlation coefficient		-0.67		
Contact angle $\theta_{H\infty}$ (deg)		29.20		
Line tension σ (μJ/m)		0.81		
Substrate	Si wafer			
1	26.85	0.5354	0.8923	1.8678
2	26.81	0.6251	0.8926	1.5997
3	26.73	0.7111	0.8932	1.4063
4	26.43	0.7521	0.8956	1.3296
5	26.48	0.8143	0.8952	1.2280
6	26.58	0.8754	0.8944	1.1423
7	26.62	0.9568	0.8941	1.0452
8	26.67	0.9504	0.8937	1.0522
9	26.37	0.9896	0.8960	1.0105
Contact angle $\bar{\theta} \pm \Delta\theta$ (deg)		26.62±0.13		
Correlation coefficient		-0.70		
Contact angle $\theta_{H\infty}$ (deg)		26.07		
Line tension σ (μJ/m)		0.89		

Table 5.7 Contact angle values of hexadecane (group #3) on SAM II (hydrophobic) surface.

Drop number	Contact angle θ (deg)	Radius R (cm)	$\cos\theta$	1/radius 1/R (1/cm)
Substrate	Glass			
1	30.16	0.3606	0.8648	2.7732
2	30.08	0.4419	0.8655	2.2630
3	29.87	0.5664	0.8673	1.7655
4	30.05	0.6168	0.8657	1.6213
5	29.97	0.6373	0.8664	1.5691
6	29.40	0.6614	0.8713	1.5119
7	29.66	0.6927	0.8691	1.4436
8	29.77	0.7115	0.8682	1.4055
9	29.80	0.7309	0.8679	1.3682
Contact angle $\bar{\theta} \pm \Delta\theta$ (deg)		29.86±0.18		
Correlation coefficient		-0.67		
Contact angle $\theta_{l\infty}$ (deg)		29.25		
Line tension σ (μJ/m)		0.81		
Substrate	Si wafer			
1	25.75	0.7315	0.9008	1.3671
2	25.81	0.7521	0.9003	1.3296
3	25.79	0.7744	0.9005	1.2913
4	25.77	0.7914	0.9006	1.2636
5	25.62	0.8349	0.9018	1.1977
6	25.78	0.8784	0.9006	1.1384
7	25.66	0.9227	0.9015	1.0838
8	25.67	0.9551	0.9014	1.0470
9	25.60	0.9989	0.9019	1.0011
Contact angle $\bar{\theta} \pm \Delta\theta$ (deg)		25.72±0.06		
Correlation coefficient		-0.74		
Contact angle $\theta_{l\infty}$ (deg)		25.17		
Line tension σ (μJ/m)		0.94		

Table 5.8 Contact angle values of hexadecane (group #4) on SAM II (hydrophobic) surface.

Substrate	Run	Pixel size l_p (μm)	Radius R (μm)	Line tension σ ($\mu\text{J}/\text{m}$)
Glass	1	10.99 ± 0.06	88.02 ± 0.48	5.62 ± 0.03
	2	10.99 ± 0.06	104.73 ± 0.57	6.68 ± 0.04
	3	10.99 ± 0.06	90.73 ± 0.50	5.79 ± 0.03
	4	10.99 ± 0.06	118.93 ± 0.65	7.59 ± 0.04
	5	10.99 ± 0.06	92.17 ± 0.50	5.88 ± 0.03
	6	10.99 ± 0.06	96.90 ± 0.53	6.18 ± 0.04
Si wafer	1	10.91 ± 0.18	274.70 ± 4.53	$< 25.04 \pm 0.42$
	2	10.91 ± 0.18	229.05 ± 3.78	$< 20.88 \pm 0.35$
	3	10.91 ± 0.18	275.45 ± 4.55	$< 25.11 \pm 0.42$
	4	10.75 ± 0.32	180.26 ± 5.37	$< 16.43 \pm 0.49$
	5	10.75 ± 0.32	257.63 ± 7.67	$< 23.49 \pm 0.70$
	6	10.75 ± 0.32	288.00 ± 8.57	$< 26.26 \pm 0.78$

Table 5.9 Estimated Line tension values of water ($\gamma_v = 72.75 \text{ mJ}/\text{m}^2$).

Substrate	Run	Pixel size l_p (μm)	Radius R (μm)	Line tension σ ($\mu\text{J}/\text{m}$)
Glass	1	10.87 ± 0.25	64.17 ± 1.48	0.26 ± 0.006
	2	10.87 ± 0.25	152.64 ± 3.51	0.62 ± 0.014
	3	10.87 ± 0.25	71.80 ± 1.78	0.29 ± 0.007
	4	12.12 ± 0.32	72.72 ± 1.92	0.29 ± 0.007
	5	12.12 ± 0.32	115.50 ± 3.05	0.47 ± 0.012
	6	12.12 ± 0.32	81.42 ± 2.15	0.33 ± 0.008
Si wafer	1	14.22 ± 0.10	100.69 ± 0.71	0.39 ± 0.003
	2	14.22 ± 0.10	98.66 ± 0.69	0.38 ± 0.002
	3	14.22 ± 0.10	109.79 ± 0.77	0.42 ± 0.003
	4	12.87 ± 0.20	93.04 ± 1.44	0.36 ± 0.005
	5	12.87 ± 0.20	85.52 ± 1.33	0.33 ± 0.005
	6	12.87 ± 0.20	92.99 ± 1.44	0.36 ± 0.005

Table 5.10 Estimated line tension values of ethanol ($\gamma_v = 23.70 \text{ mJ}/\text{m}^2$).

Substrate	Run	Pixel size l_p (μm)	Radius R (μm)	Line tension σ ($\mu\text{J}/\text{m}$)
Glass	1	8.37 ± 0.10	53.91 ± 0.64	0.20 ± 0.02
	2	8.37 ± 0.10	48.68 ± 0.58	0.18 ± 0.01
	3	8.37 ± 0.10	54.94 ± 0.66	0.20 ± 0.01
	4	8.37 ± 0.10	54.75 ± 0.65	0.20 ± 0.01
	5	8.37 ± 0.10	64.68 ± 0.78	0.24 ± 0.02
	6	8.37 ± 0.10	68.44 ± 0.82	0.25 ± 0.02
Si wafer	1	8.00 ± 0.43	89.94 ± 4.83	0.24 ± 0.03
	2	8.00 ± 0.43	92.06 ± 4.95	0.25 ± 0.03
	3	8.00 ± 0.43	102.25 ± 5.50	0.27 ± 0.04
	4	8.02 ± 0.14	106.18 ± 1.86	0.28 ± 0.02
	5	8.02 ± 0.14	90.94 ± 1.58	0.24 ± 0.02
	6	8.02 ± 0.14	125.41 ± 2.19	0.34 ± 0.03

Table 5.11 Estimated line tension values of hexadecane ($\gamma_v = 27.76 \text{ mJ}/\text{m}^2$).

Liquid	Substrate	Contact angles (deg)		Surface tension γ_{lv} (mJ/m^2)	Line tension on SAM I σ ($\mu\text{J}/\text{m}$)	Line tension on SAM II σ ($\mu\text{J}/\text{m}$)
		θ_{100}	θ_{1100}			
Water	Glass	53.94	106.78	72.75	6.29 ± 0.77	5.96
	Si wafer	11.54	105.87	72.75	$<22.87 \pm 3.84$	7.20
Ethanol	Glass	0	34.00	23.70	0.38 ± 0.15	0.91
	Si wafer	0	33.04	23.70	0.37 ± 0.03	0.85
Hexadecane	Glass	0	29.71 ± 0.95	27.76	0.21 ± 0.03	0.87 ± 0.12
	Si wafer	0	25.40 ± 0.75	27.76	0.27 ± 0.04	0.93 ± 0.18

Table 5.12 Summary of experimental results at room temperature, where the line tension values of liquids on SAM I were measured using “drop spreading experiment” and the line tension values of liquids on SAM II were measured using “sessile drop arrangement”.

Figure 5.1 Schematic of focal length in the case of a simple lens (Langford, 2000).

Figure 5.2 Relations between focal length and image size (Langford, 2000).

Figure 5.3 Depth of field when different focal length lenses are used at the same f-stop settings (Langford, 2000).

Figure 5.4 Change in depth of field corresponding to f-numbers at the same focus settings (Langford, 2000).

Figure 5.5 Relations of f-numbers, image brightness, aperture, and depth of field.

Figure 5.6 Waterfall-like 3D grey-level profiles (b) of the upper corner of the original image (a).

Figure 5.7 Schematic of RGB model (Photoshop, 2002).

Figure 5.8 RGB model color cube (Gonzalez, 1992).

Figure 5.9 Grey-level profiles (c) of the original image (a) versus the smoothed image (b) at the location illustrated by two short lines in images (a) and (b). Plot (c) indicates an edge in the image had a 5-6 pixel smooth transition zone.

Figure 5.10 (a) 3×3 image region, and Sobel operator masks: (b) column differential gradient edge operator and (c) row differential gradient edge operator (Gonzalez, 1992).

Figure 5.11 Top view of grid distortion targets (Edmund Industrial Optics).

Figure 5.12 Histogram of the image of the calibration object with one peak around 25 and the other one around 253. Intensities range from 0 to $2^8-1=255$.

Figure 5.13 (a) Original image of RUBY calibration ball; (b) processed image with threshold of 139-20; (c) processed image with threshold of 139; (d) processed image with threshold of 139+20.

Figure 5.14 Procedure for obtaining the profile of a water drop resting on SAM II (hydrophobic surface): (a) original drop image; (b) image of the drop section above the substrate surface; (c) filtered and detected drop profile.

Figure 5.15 (a) Side view of a water drop resting on SAM I (hydrophilic surface) produced on glass coated with gold; (b) drop advancing profiles in physical space.

Figure 5.16 (a) Side view of a water drop resting on SAM II (hydrophobic surface) produced on glass coated with gold; (b) drop advancing profiles in physical space.

Figure 5.17 (a) Side view of an ethanol drop resting on SAM II (hydrophobic surface) produced on glass coated with gold; (b) drop advancing profiles in physical space.

Figure 5.18 (a) Side view of a hexadecane drop resting on SAM II (hydrophobic surface) produced on glass coated with gold; (b) drop advancing profiles in physical space.

Figure 5.19 Dependence of the contact angle on the drop size for water on SAM I produced on glass coated with gold.

Figure 5.20 Dependence of the contact angle on the drop size for water on SAM II produced on glass coated with gold.

Figure 5.21 Dependence of the contact angle on the drop size for ethanol on SAM II produced on glass coated with gold.

Figure 5.22 Dependence of the contact angle on the drop size for hexadecane on SAM II produced on glass coated with gold.

Figure 5.23 Dependence of the contact angle on the drop size for water on SAM I produced on *Si* wafer coated with gold.

Figure 5.24 Dependence of the contact angle on the drop size for water on SAM II produced on *Si* wafer coated with gold.

Figure 5.25 Dependence of the contact angle on the drop size for ethanol on SAM II produced on *Si* wafer coated with gold.

Figure 5.26 Dependence of the contact angle on the drop size for hexadecane on SAM II produced on *Si* wafer coated with gold.

Figure 5.27 Top views of an ethanol drop growing and breaking out of the inner, SAM I, zone (photographs in alphabetical sequence denote increasing times).

Figure 5.28 Contact line profile of one corner of an ethanol drop with two straight edge sides and the curved line at the corner before the drop broke-out of the inner square region (SAM I).

Figure 5.29 Contact line profile of one corner of an ethanol drop with the 95% confidence interval on the two straight sides and a best-fit circle on the curved contact line at the corner.

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Chapter 6

Conclusions and Future Work

6.1 Conclusions

This thesis proposed a new experimental arrangement for the measurement of line tension. This experimental work performed a sequence of line tension measurements at room temperature ($20\pm 1^\circ\text{C}$) and at a fixed pressure (~ 1 atm) using a design with improved chemical potential control, as discussed in Chapter 4. This experiment was easy to implement, by simply acquiring and analyzing the contact angles and the contact line profile of a sessile drop. The intrinsic contact angles of the two materials forming the patterned surface were estimated using the ADSA-P program, as explained in Chapter 5. A CCD digital camera was used to record the drop and the contact line profiles. The profile data were obtained by processing and analyzing the digital images, using the MATLAB Image Processing Toolbox.

The experimental arrangement reduced chemical potential variations by using nearly identical drop shapes in all measurements, which could not be achieved in the “sessile drop method”. Moreover, the use of a large, deep container and a liquid bath provided an environment for the liquid drops, which achieved an approximate equilibrium state among the liquid, the substrate and the surrounding vapour phases.

This method maximized the geodesic curvature without reducing the drop volume. Thus, the evaporation did not have a significant influence in this experiment.

The results of this experiment can be summarized as follows.

- i) As presented in Table 5.5, experimental measurement showed that the contact angle values and the line tension values of hexadecane on SAM II surfaces (1-Octadecanethiol SAM surfaces) were closed to those measured using other sessile drop arrangements (refer to Table 3.2). Thus, it can be concluded that 1-Octadecanethiol SAM surfaces used in this experiment were similar to those used in other experiments. This indicated that the metal and SAM coatings were reasonable.
- ii) The line tension results of ethanol on SAM II surfaces were similar to those of hexadecane on SAM II (refer to Table 5.4 and 5.5). This may occur because the surface tensions and contact angles of ethanol were closed to those of hexadecane. It should be noted that the thiol solutions used for producing SAM surfaces in this experiment had ethanol as their solvent.
- iii) There were some uncertainties in some contact angle and line tension values of water on SAM I surfaces (16-Mercaptohexadecanoic acid SAM surface) produced on *Si* wafer coated with gold, as shown in Table 5.2, 5.9 and 5.12. In order to verify/clarify these uncertainties, more experiments are suggested to measure the line tensions of water on the SAM I surface using *Si* wafer as the substrate.
- iv) Since the corner of the inner square region (SAM I) was relatively sharp, it would be argued that there could be a two-SAM mixed surface at the corner of the inner square. This can be interpreted from statistics point of view. If the line tension

values of measuring liquids on SAM I and SAM II satisfied the mean difference inequality (6.1) (Guttman et al, 1982), it can be concluded that the two groups of line tension values differed from each other significantly at 100 α % level of significance (α is equal to (1-95%)) as mentioned in Section 5.7), i.e., they were the line tension values of liquids on SAM I surfaces and on SAM II surfaces, respectively.

$$\left| \frac{\bar{x}_1 - \bar{x}_2}{s_w \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \right| > t_{n_1+n_2-2, \alpha/2} \quad (6.1)$$

where

$$s_w = \sqrt{\frac{(n_1-1)s_1^2 + (n_2-1)s_2^2}{n_1+n_2-2}} \quad (6.2)$$

where $n_1, \bar{x}_1, s_1^2$ and $n_2, \bar{x}_2, s_2^2$ were the sizes, means and standard deviations of the two groups of line tension values. Taking hexadecane as an example gave that $n_1=4$ (the number of line tension values measured on SAM II surfaces as shown from Table 5.5 to 5.8) and $n_2=6$ (the number of line tension values measured on SAM I surfaces as shown in Table 5.11). After substituted the means and standard deviations corresponding to these line tension values, the left term of the inequality (6.1) was equal to 19.773 for the glass substrate and 13.653 for the *Si* wafer substrate. It was obvious that the above values were both greater than $t_{n_1+n_2-2, \alpha/2}$, which is $t_{8;0.025}=2.306$. This indicated that the two groups of line tension values agreed with inequality (6.1). Hence, the SAM surface at the corner of the inner square was not likely to be a mixed SAM surface, and the values

shown from Table 5.9 to 5.11 were the line tensions of the measuring liquids on just the SAM I surfaces.

- v) The line tension values of the three measuring liquids, measured on the SAM I surface using the drop spreading method, were positive and had magnitudes of the order of 10^{-6} to 10^{-7} J/m, as shown in Table 5.9 to 5.11. The line tension value of water on the SAM I surface on glass substrate ($\sigma_{SAM I - g}^{water}$) equalled 6.29 μ J/m, which was superficially consistent with those results obtained using the sessile drop method (refer to Table 5.2). The line tension value of ethanol on the SAM I surface on glass substrate ($\sigma_{SAM I - g}^{ethanol}$) equalled 0.38 μ J/m, and on *Si* wafer substrate ($\sigma_{SAM I - Si}^{ethanol}$) it equalled 0.37 μ J/m. The line tension value of hexadecane on the SAM I surface on glass substrate ($\sigma_{SAM I - g}^{hex.}$) equalled 0.21 μ J/m, and on *Si* wafer substrate ($\sigma_{SAM I - Si}^{hex.}$) equalled 0.27 μ J/m, respectively. As no results have been published in the open literature for the line tensions of ethanol and hexadecane on 16-Mercaptohexadecanoic acid SAM surfaces, no direct comparisons could be made with published literature. However, it is interesting to note that the magnitudes of the line tension values were relatively large at 10^{-6} to 10^{-7} J/m.
- vi) The line tensions of ethanol and hexadecane on the SAM I surfaces were smaller than those of water drops, which may be due to the smaller surface tensions and contact angles of the ethanol and hexadecane drops. However, the radius of contact line, just before the drop broke-out off the inner square of SAM I, was limited by the sharpness of the corner of the square region produced by the micro-contact printing. Therefore, the actual radii of the contact line profiles of the measuring liquid drops should be less than or equal to these measured radii. The

actual line tensions of the measuring liquids in the three-phase system would also be less than or equal to those values estimated with the measured radii. It has been demonstrated that the sharpness of the patterned surface was a crucial factor for this line tension measurement.

6.2 Future work

There are at least the following three things can be considered for the future effort to improve this experiment.

- i) As mentioned before, the minimum radius of the contact line profile, just before the drop broke out-off the inner square, was limited by the sharpness of the patterned SAM I square in this experiment. Thus, high-quality patterned surfaces should be prepared in order to have accurate estimations of line tension.
- ii) The optical equipment could be improved by connecting a CCD camera to a microscope if one wished to improve the drop detail in the vicinity of the corner. Improved detail, perhaps by an order-of-magnitude, would permit more precise measurements of the line tension.
- iii) The use of alternative thiols for patterning the inner and outer regions should be investigated and changed to the system's temperature considered. In the latter case, it may be possible to experimentally obtain a curve for the line tension as a function of temperature, i.e., $\sigma=\sigma(T)$, in analogy with the surface tension dependence $\gamma=\gamma(T)$ that shows surface tension decreasing with increasing temperature.

Reference:

Guttman, I., Wilks, S. S., and Hunter, J. S., *Introductory Engineering Statistics*, Wiley, New York, **1982**

Appendix A:

Calculation of Contact Line Velocity

Equation (4.9) tells that adjusting the position of the container Δz , or the liquid height in the container h , has an equivalent effect to control the contact line velocity. Thus, the term $(\Delta z + h)$ can be expressed as one variable H , and then Equation (4.9) is rewritten as

$$\frac{\Delta R}{\Delta t} = \frac{gHD^4}{256\nu L} \cdot \frac{1}{R^2} = \frac{\rho gHD^4}{256\mu L} \cdot \frac{1}{R^2} \quad (\text{A.1})$$

Where, R is the radius of a hemisphere-like drop; L and D are the length and the inner diameter of a given tubing, respectively; μ is the absolute viscosity of a given liquid, and ν is the kinematic viscosity and has a relation with μ as $\nu = \mu/\rho$. The setup in this experiment used tubing with an inner diameter of 3.2($\frac{1}{8}$ ") mm and a length of 450 mm. The properties of three measuring liquids at room temperature are given in Table 5.1. Therefore, the velocity of the drop contact line varying with H and the drop radius R could be calculated as shown from Table A.1 to A.3, assuming the surface tensions of the drops could be neglected.

When the surface tension of a drop is taken into account, Equation (A.1) should be modified, to include a surface tension term. According to the Laplace's capillarity relation (Equation (2.1)), the pressure difference ΔP across the hemisphere-like drop interface could be expressed as Equation (3.1). Thus, Equation (A.1) considering the surface tension effect is given by

$$\frac{\Delta R}{\Delta t} = \frac{\rho gHD^4}{256\mu L} \cdot \frac{1}{R^2} - \frac{\gamma_{lv}}{128\mu L} \cdot \frac{1}{R^3} \quad (\text{A.2})$$

As indicated by Table A.4 and Figure A.1, the smaller the H value is and the smaller the drop radius is, the more notable the influence of the surface tension would be.

R(mm)	R ² (mm ²)	$\Delta R/\Delta t$ (mm/s)									
		H=10(mm)	H=20	H=30	H=40	H=50	H=60	H=70	H=80	H=90	H=100
2	4	22.23	44.47	66.70	88.94	111.17	133.40	155.64	177.87	200.11	222.34
3	9	9.88	19.76	29.65	39.53	49.41	59.29	69.17	79.05	88.94	98.82
4	16	5.56	11.12	16.68	22.23	27.79	33.35	38.91	44.47	50.03	55.59
5	25	3.56	7.11	10.67	14.23	17.79	21.34	24.90	28.46	32.02	35.57
6	36	2.47	4.94	7.41	9.88	12.35	14.82	17.29	19.76	22.23	24.70
7	49	1.82	3.63	5.45	7.26	9.08	10.89	12.71	14.52	16.34	18.15
8	64	1.39	2.78	4.17	5.56	6.95	8.34	9.73	11.12	12.51	13.90
9	81	1.10	2.20	3.29	4.39	5.49	6.59	7.69	8.78	9.88	10.98
10	100	0.89	1.78	2.67	3.56	4.45	5.34	6.23	7.11	8.00	8.89
11	121	0.74	1.47	2.21	2.94	3.68	4.41	5.15	5.88	6.62	7.35
12	144	0.62	1.24	1.85	2.47	3.09	3.71	4.32	4.94	5.56	6.18
Flow velocity $\bar{V}$ (mm/s)		69.48	138.96	208.44	277.93	347.41	416.89	486.37	555.85	625.33	694.82
Flow rate Q (ml/s)		0.56	1.12	1.68	2.24	2.79	3.35	3.91	4.47	5.03	5.59

Table A.1 Estimation of the drop contact line velocity for water at room temperature.

R(mm)	R ² (mm ²)	$\Delta R/\Delta t$ (mm/s)									
		H=10(mm)	H=20	H=30	H=40	H=50	H=60	H=70	H=80	H=90	H=100
2	4	14.70	29.39	44.09	58.78	73.48	88.18	102.87	117.57	132.26	146.96
3	9	6.53	13.06	19.59	26.13	32.66	39.19	45.72	52.25	58.78	65.32
4	16	3.67	7.35	11.02	14.70	18.37	22.04	25.72	29.39	33.07	36.74
5	25	2.35	4.70	7.05	9.41	11.76	14.11	16.46	18.81	21.16	23.51
6	36	1.63	3.27	4.90	6.53	8.16	9.80	11.43	13.06	14.70	16.33
7	49	1.20	2.40	3.60	4.80	6.00	7.20	8.40	9.60	10.80	12.00
8	64	0.92	1.84	2.76	3.67	4.59	5.51	6.43	7.35	8.27	9.19
9	81	0.73	1.45	2.18	2.90	3.63	4.35	5.08	5.81	6.53	7.26
10	100	0.59	1.18	1.76	2.35	2.94	3.53	4.11	4.70	5.29	5.88
11	121	0.49	0.97	1.46	1.94	2.43	2.91	3.40	3.89	4.37	4.86
12	144	0.41	0.82	1.22	1.63	2.04	2.45	2.86	3.27	3.67	4.08
Flow velocity $\bar{V}$ (mm/s)		45.93	91.85	137.78	183.70	229.63	275.55	321.48	367.40	413.33	459.25
Flow rate Q (ml/s)		0.37	0.74	1.11	1.48	1.85	2.22	2.59	2.95	3.32	3.69

Table A.2 Estimation of the drop contact line velocity for ethanol at room temperature.

R(mm)	$R^2(\text{mm}^2)$	$\Delta R/\Delta t \text{ (mm/s)}$									
		H=10(mm)	H=20	H=30	H=40	H=50	H=60	H=70	H=80	H=90	H=100
2	4	5.69	11.38	17.07	22.76	28.46	34.15	39.84	45.53	51.22	56.91
3	9	2.53	5.06	7.59	10.12	12.65	15.18	17.71	20.24	22.76	25.29
4	16	1.42	2.85	4.27	5.69	7.11	8.54	9.96	11.38	12.81	14.23
5	25	0.91	1.82	2.73	3.64	4.55	5.46	6.37	7.28	8.20	9.11
6	36	0.63	1.26	1.90	2.53	3.16	3.79	4.43	5.06	5.69	6.32
7	49	0.46	0.93	1.39	1.86	2.32	2.79	3.25	3.72	4.18	4.65
8	64	0.36	0.71	1.07	1.42	1.78	2.13	2.49	2.85	3.20	3.56
9	81	0.28	0.56	0.84	1.12	1.41	1.69	1.97	2.25	2.53	2.81
10	100	0.23	0.46	0.68	0.91	1.14	1.37	1.59	1.82	2.05	2.28
11	121	0.19	0.38	0.56	0.75	0.94	1.13	1.32	1.51	1.69	1.88
12	144	0.16	0.32	0.47	0.63	0.79	0.95	1.11	1.26	1.42	1.58
Flow velocity $\bar{V}$ (mm/s)		17.79	35.57	53.36	71.14	88.93	106.71	124.50	142.28	160.07	177.85
Flow rate Q (ml/s)		0.14	0.29	0.43	0.57	0.72	0.86	1.00	1.14	1.29	1.43

Table A.3 Estimation of the drop contact line velocity for hexadecane at room temperature.

R(mm)	$\Delta R/\Delta t$ (mm/s) (Water)									
	H=10(mm)	H=20	H=30	H=40	H=50	H=60	H=70	H=80	H=90	H=100
2	5.71	27.95	50.18	72.41	94.65	116.88	139.12	161.35	183.59	205.82
4	3.49	9.05	14.61	20.17	25.73	31.29	36.84	42.40	47.96	53.52
6	1.86	4.33	6.80	9.27	11.74	14.21	16.68	19.15	21.62	24.09
8	1.13	2.52	3.91	5.30	6.69	8.08	9.47	10.86	12.25	13.64
10	0.76	1.65	2.54	3.43	4.31	5.20	6.09	6.98	7.87	8.76
12	0.54	1.16	1.78	2.39	3.01	3.63	4.25	4.86	5.48	6.10

R(mm)	$\Delta R/\Delta t$ (mm/s) (Ethanol)									
	H=10(mm)	H=20	H=30	H=40	H=50	H=60	H=70	H=80	H=90	H=100
2	10.20	24.90	39.59	54.29	68.99	83.68	98.38	113.07	127.77	142.47
4	3.11	6.79	10.46	14.13	17.81	21.48	25.16	28.83	32.50	36.18
6	1.47	3.10	4.73	6.37	8.00	9.63	11.26	12.90	14.53	16.16
8	0.85	1.77	2.69	3.60	4.52	5.44	6.36	7.28	8.20	9.11
10	0.55	1.14	1.73	2.32	2.90	3.49	4.08	4.67	5.25	5.84
12	0.39	0.80	1.20	1.61	2.02	2.43	2.84	3.24	3.65	4.06

R(mm)	$\Delta R/\Delta t$ (mm/s) (Hexadecane)									
	H=10(mm)	H=20	H=30	H=40	H=50	H=60	H=70	H=80	H=90	H=100
2	6.10	28.86	51.63	74.39	97.16	119.92	142.69	165.45	188.22	210.98
4	1.91	4.44	6.97	9.50	12.03	14.56	17.09	19.62	22.15	24.68
6	0.78	1.69	2.60	3.51	4.42	5.33	6.24	7.15	8.06	8.97
8	0.42	0.88	1.35	1.81	2.27	2.74	3.20	3.67	4.13	4.60
10	0.26	0.54	0.82	1.10	1.38	1.66	1.94	2.23	2.51	2.79
12	0.18	0.36	0.55	0.74	0.93	1.12	1.30	1.49	1.68	1.87

Table A.4 Estimations of the drop contact line velocities for water, ethanol and hexadecane with surface tension effects.

Figure A.1 Relation between the drop contact line velocity $\Delta R/\Delta t$ and the square of radius R^2 of three measuring liquids with or without considering surface tension effects, when $H=50$ mm.

Appendix B:

Calculation of Chemical Potential Control

B.1 Chemical potential difference across the drop interface

Three different measuring liquids were adopted for use in this experiment. They were distilled water, ethanol and hexadecane, as discussed in Section 5.1. This experiment was performed on a patterned solid surface, a 20 mm × 20 mm square inlay with low contact angle that is surrounded by a surface with high contact angle (refer to Section 4.4). The drop grew and spread gradually from a central hole into the square inlay zone, before it was restrained by the boundary of the inner square as explained in Section 3.3. At the boundary the contact angle of the drop advanced from a low angle to a higher one. The radius of drop's contact line, x , would be close to the half of the inner square length, i.e., $x=0.01$ m, when the drop reached the boundary of the inner square. Thus, the chemical potential difference across an ethanol or hexadecane drop interface, $\Delta\mu$, can be estimated using Equation (4.17). The results are listed in Table B.1. It has been demonstrated that Equation (4.16) may be used up to 30°, when the dimensionless drop radius, B , lies between 1 and 1000 (Hartland and Hartley, 1976).

Water is a slightly different situation than either ethanol or hexadecane, since water droplets had larger contact angles (~50°-110°, except on the SAM I thiol with *Si* wafer substrate coated with gold; refer to Chapter 5), and the radius of water drop's contact line, x_{water} , is nearly equal to the drop radius R . However, the chemical potential difference across the water drop interface can be estimated as

$$\begin{aligned}\Delta\mu &= R_g T \ln \left(1 + \frac{2\gamma_{lv}}{Px_{water}} \right) = \frac{8314}{18.02} \times (273 + 20) \times \ln \left(1 + \frac{2 \times 0.07275}{101325 \times 0.01} \right) \\ &= 19.4 (\text{J/kg})\end{aligned}$$

which indicates that the chemical potential difference across a water drop interface is also relatively small, although it is greater than those of either ethanol or hexadecane.

B.2 Equilibrium of vapour in contact with liquid

When the liquid/vapour system of a measuring liquid is in equilibrium, the chemical potentials in both phases must be the same, i.e., $\mu_l = \mu_k$, where μ_l and μ_k stand for the chemical potentials of the measuring liquid in the liquid phase and in the vapour phase, respectively (Moran and Shapiro, 1999). The chemical potential of the liquid phase, μ_l , is also known as the Gibbs function per mole pure liquid, expressed as

$$\mu_l = \frac{G}{n} = g(T, P) \quad (\text{B.1})$$

where, n is the mole number of the liquid. The vapour is assumed to be an ideal gas mixture (air and vapour of the measuring liquid) whereupon μ_k equals the Gibbs function per mole estimated at temperature T and the partial pressure P_k of the vapour

$$\mu_k = g(T, P_k) \quad (\text{B.2})$$

Thus, equilibrium between the liquid and the vapour phases can be expressed as

$$g(T, P_k) = g(T, P) \quad (\text{B.3})$$

or

$$h(T, P_k) - Ts(T, P_k) = h(T, P) - Ts(T, P) \quad (\text{B.4})$$

using the definition $g = h - Ts$. Modeled as an ideal gas, the vapour enthalpy is assumed to be equal to the saturated vapour value, h_g^{sat} , at temperature T , i.e., $h(T, P_k) \approx h_g^{sat}$. Furthermore, the difference between the specific entropy of the vapour and the specific entropy at the corresponding saturated vapour state is

$$s(T, P) = s_g^{sat}(T) - R_g \ln\left(\frac{P_k}{P_{sat}}\right) \quad (B.5)$$

The enthalpy of the liquid is obtained by

$$h(T, P) \approx h_f^{sat} + v_f^{sat} (P - P_{sat}) \quad (B.6)$$

where, h_f^{sat}, v_f^{sat} are the saturated liquid specific enthalpy and the specific molar volume at temperature T . Furthermore, the entropy of the liquid is nearly equal to the saturated liquid specific entropy s_f^{sat} at temperature T , i.e., $s(T, P) \approx s_f^{sat}(T)$. Combining the expressions from Equations (B.1) to (B.6) gives

$$h_g^{sat} - T(s_g^{sat} - R_g \ln \frac{P_k}{P_{sat}}) = h_f^{sat} + v_f^{sat} (P - P_{sat}) - Ts_f^{sat} \quad (B.7a)$$

or

$$R_g T \ln \frac{P_k}{P_{sat}} = v_f^{sat} (P - P_{sat}) - [(h_g^{sat} - h_f^{sat}) - T(s_g^{sat} - s_f^{sat})] \quad (B.7b)$$

At equilibrium, the molar Gibbs functions of both phases are equal ($g_g^{sat} = g_f^{sat}$), hence the term in the square brackets in Equation (B.7b) vanishes, which leads to the following simplified form

$$\frac{P_k}{P_{sat}} = \exp \frac{v_f^{sat} (P - P_{sat})}{R_g T} \quad (B.8)$$

Taking water at 20°C as a typical experimental example gives

$$\frac{v_f^{sat} (P - P_{sat})}{R_g T} = \frac{1.0018 \times 10^{-3} \times (101325 - 0.02339 \times 10^5)}{\frac{8314}{18.02} \times (273 + 20)} = 7.34 \times 10^{-4}$$

As a consequence,

$$\frac{P_k}{P_{sat}} = \exp(7.34 \times 10^{-4}) = 1.00073$$

The above calculation shows that there is little difference between the partial pressure of the vapour, in the air in contact with the measuring liquid, and the saturated pressure of the measuring liquid, i.e., $P_k \approx P_{sat}$.

B.3 Pressure and chemical potential variations with height

Equation (4.20) permits the partial pressures and chemical potentials in the air, corresponding to all three measuring liquid, with different heights (the vessel height and the drop height) at different temperatures, to be calculated. The results are tabulated in Tables B.2 through B.5. A 50% relative humidity was used to calculate the water's partial pressure at the top of the vessel, P_{k2} . For ethanol and hexadecane, the partial pressures at the top of the vessel were assumed to be zero.

B.4 Comparison with the previous sessile drop arrangements in chemical potential control

As shown in Figure B.3a, in this experimental system the liquid drop has a certain height, which is very small (refer to Table B.5), so the chemical potential difference between the flat liquid-vapour surface and the top of the curved drop can be obtained as

$$\Delta\mu = R_g T \ln\left(\frac{P_{sat}}{P_k}\right) \quad (\text{B.9})$$

Consider a water drop at 20°C. Saturation pressure across a flat water surface is $P_{sat}=0.02339$ bar (Moran and Shapiro, 1999) and $P_k=0.02280$ bar at the drop height ≈ 10 mm (calculated by Equation (4.20)), so the chemical potential difference is

$$\Delta\mu = RT \ln\left(\frac{P_{sat}}{P_k}\right) = \frac{8314}{18.02} \times (273 + 20) \times \ln\left(\frac{0.02339}{0.02280}\right) = 3453.7 \text{ (J/kg)}$$

However, the saturation pressure of the liquid in the vapour phase across a curved surface (a drop surface) would be different from the one across a flat surface, i.e., $P_{sat}^{drop} \neq P_{sat}$, because the pressure of a drop is not equal to the pressure of a flat liquid surface, i.e., $P_l \neq P \approx 1 \text{ atm}$ (refer to Equation (2.1)). The pressure of an axisymmetric drop can be obtained by Laplace's Equation (3.1) and the saturation temperature corresponding to this pressure is given by Clausius-Clapeyron equation (Kondepudi and Prigogine, 1998),

$$\frac{d \ln P}{dT} = \frac{\Delta H_{vap}}{RT^2} \quad (\text{B.10})$$

This equation is also written in its integrated form,

$$\ln P_2 - \ln P_1 = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (\text{B.11})$$

where ΔH_{vap} is defined as the molar enthalpy of the transition. Therefore, for a drop of 10 mm radius, Equation (B.11) can be rewritten as

$$\ln P_l^{0.01} - \ln P = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T} - \frac{1}{T^{0.01}} \right) \quad (\text{B.12})$$

The saturation temperature $T^{0.01}$ corresponding to the pressure of the water drop, $P_l^{0.01}$, could be estimated as follows

$$T^{0.01} = 1 / \left[\frac{1}{(293 + 100)} - \frac{\ln(1 + 2 \times 0.07275 / 0.01 / 101325) \times 8314}{18.02 \times 2257 \times 1000} \right] = 373.00408 \text{ (K)}$$

The difference between the saturation temperature with respect to the pressure of the drop and the saturation temperature with respect to the pressure of the flat liquid surface (1 atm) is

$$\Delta T = T^{0.01} - T = 0.00408(\text{K})$$

The saturation pressure at 20°C across the water drop surface could be obtained by

$$\begin{aligned} P_{sat}^{0.01} &= \exp \left[\frac{\Delta H_{vap}}{R} \left(\frac{1}{T} - \frac{1}{T + \Delta T} \right) - \ln P_{sat} \right] \\ &= \exp \left[\frac{2454.1 \times 18.02 \times 1000}{8314} \left(\frac{1}{293} - \frac{1}{293.00408} \right) + \ln(0.02339) \right] \\ &= 0.023396(\text{bar}) \end{aligned}$$

Thus,

$$\Delta \mu = RT \ln \left(\frac{P_{sat}^{0.01}}{P_k} \right) = \frac{8314}{18.02} \times (273 + 20) \times \ln \left(\frac{0.023396}{0.02280} \right) = 3488.3(\text{J/kg})$$

In the conventional sessile drop arrangements, illustrated by Figure B.3b, the experiments were performed in open, still air, so the chemical potential difference, between the saturated water in the vapour phase around the drop and the partial pressure of the water in the air, was larger. For a relatively big drop ($R=10$ mm), it can be obtained as

$$\Delta \mu = RT \ln \left(\frac{P_{sat}^{0.01}}{50\% P_{sat}} \right) = \frac{8314}{18.02} \times (273 + 20) \times \ln \left(\frac{0.023396}{50\% \times 0.02339} \right) = 93736.6(\text{J/kg})$$

Likewise, for a small drop ($R=1$ mm), the saturation pressure also can be estimated using Equations (B.10) to (B.12) and the chemical potential difference is given by

$$\Delta \mu = RT \ln \left(\frac{P_{sat}^{0.001}}{50\% P_{sat}} \right) = \frac{8314}{18.02} \times (273 + 20) \times \ln \left(\frac{0.023449}{50\% \times 0.02339} \right) = 94043.6(\text{J/kg})$$

Moreover, there is a chemical potential difference between the saturated water in the vapour phase around the small drop and the one around the big drop, obtained by

$$\Delta\mu = RT \ln\left(\frac{P_{sat}^{0.001}}{P_{sat}^{0.01}}\right) = \frac{8314}{18.02} \times (273 + 20) \times \ln\left(\frac{0.023449}{0.023396}\right) = 305.9(\text{J/kg})$$

In these sessile drop arrangements, the chemical potential variation of the liquid phase between a small drop ($R=1$ mm) and a big drop ($R=10$ mm) will occur and should be considered. It can be estimated in size as

$$\Delta\mu = \mu_{ls} - \mu_{lb} = R_g T \ln\left(\frac{P_{ls}}{P_{lb}}\right) \quad (\text{B.13})$$

where μ_{ls} and μ_{lb} denote the liquid phase chemical potentials for a small and a big drop, respectively; the pressures P_{ls} and P_{lb} denote the pressures of the small drop and the big drop, respectively. Therefore, taking water drops as an example gives

$$\begin{aligned} \Delta\mu &= R_g T \ln\left(\frac{P_{ls}}{P_{lb}}\right) = \frac{8314}{18.02} \times 293 \times \ln\left(\frac{101325 + 2 \times 0.07275 / 0.001}{101325 + 2 \times 0.07275 / 0.01}\right) \\ &= 174.6(\text{J/kg}) \gg 0 \end{aligned}$$

Those above results indicate that the chemical potential can have a significant affect to other sessile drop arrangements.

Contact angle (deg)	Ethanol		Hexadecane	
	Drop radius R (m)	Chemical potential $\Delta\mu$ (J/kg)	Drop radius R (m)	Chemical potential $\Delta\mu$ (J/kg)
5	1.89129	1.308E-02	1.31368	4.49E-03
10	0.94926	2.606E-02	0.65935	8.94E-03
15	0.63688	3.884E-02	0.44237	1.332E-02
20	0.48195	5.132E-02	0.33476	1.761E-02
25	0.39004	6.342E-02	0.27092	2.176E-02
30	0.32967	7.503E-02	0.22899	2.574E-02
35	0.28738	8.607E-02	0.19961	2.953E-02

Table B.1 Drop's contact angle dependence of chemical potential ($\Delta\mu$ is estimated using Equation (4.17)).

z (mm)	17°C			18°C			19°C			20°C			21°C		
	P_k (bar)	ϕ (%)	μ_k (J/g)	P_k (bar)	ϕ (%)	μ_k (J/g)	P_k (bar)	ϕ (%)	μ_k (J/g)	P_k (bar)	ϕ (%)	μ_k (J/g)	P_k (bar)	ϕ (%)	μ_k (J/g)
5	0.01914	98.75	-529.33	0.02038	98.75	-522.68	0.02171	98.75	-516.01	0.02309	98.74	-509.39	0.02456	98.75	-502.78
10	0.0189	97.5	-531.02	0.02013	97.51	-524.39	0.02143	97.51	-517.72	0.02280	97.49	-511.1	0.02425	97.51	-504.5
15	0.01865	96.26	-532.74	0.01987	96.27	-526.11	0.02116	96.27	-519.45	0.02251	96.25	-512.84	0.02394	96.27	-506.24
20	0.01841	95.01	-534.48	0.01961	95.02	-527.86	0.02089	95.02	-521.2	0.02222	95.01	-514.6	0.02363	95.03	-508.01
25	0.01817	93.77	-536.25	0.01936	93.78	-529.63	0.02061	93.78	-522.97	0.02193	93.76	-516.38	0.02332	93.78	-509.79
30	0.01793	92.52	-538.04	0.0191	92.53	-531.42	0.02034	92.53	-524.77	0.02164	92.52	-518.18	0.02301	92.54	-511.6
40	0.01745	90.03	-541.69	0.01858	90.04	-535.08	0.01979	90.04	-528.45	0.02106	90.03	-521.87	0.02239	90.05	-515.3
50	0.01697	87.54	-545.45	0.01807	87.55	-538.85	0.01924	87.55	-532.23	0.02048	87.54	-525.66	0.02178	87.56	-519.11
60	0.01648	85.05	-549.31	0.01756	85.06	-542.73	0.0187	85.06	-536.12	0.01989	85.05	-529.57	0.02116	85.06	-523.03
80	0.01551	80.05	-557.4	0.01653	80.07	-550.85	0.0176	80.07	-544.26	0.01873	80.06	-537.74	0.01991	80.08	-531.22
100	0.01455	75.06	-566.03	0.01549	75.07	-559.5	0.0165	75.08	-552.94	0.01756	75.07	-546.45	0.01867	75.08	-539.96
120	0.01358	70.06	-575.25	0.01446	70.07	-568.76	0.0154	70.08	-562.22	0.01639	70.06	-555.77	0.01743	70.08	-549.31
160	0.01164	60.04	-595.9	0.01239	60.05	-589.47	0.0132	60.06	-583	0.01404	60.05	-576.63	0.01494	60.05	-570.25
200	0.00969	50	-620.37	0.01032	50.01	-614.03	0.01099	50.02	-607.64	0.01170	50	-601.37	0.01244	50.01	-595.09

Table B.2 Partial pressure P_k and chemical potential μ_k variations of water, with height at different temperatures, where ϕ is the relative humidity (μ_k is estimated using Equation (4.22)).

z (mm)	22°C			23°C			24°C			25°C		
	P_k (bar)	ϕ (%)	μ_k (J/g)	P_k (bar)	ϕ (%)	μ_k (J/g)	P_k (bar)	ϕ (%)	μ_k (J/g)	P_k (bar)	ϕ (%)	μ_k (J/g)
5	0.02612	98.75	-496.11	0.02773	98.67	-489.64	0.02948	98.75	-482.91	0.0313	98.77	-476.28
10	0.02579	97.51	-497.84	0.02738	97.43	-491.37	0.02911	97.51	-484.64	0.03091	97.53	-478.02
15	0.02546	96.27	-499.58	0.02703	96.19	-493.12	0.02874	96.27	-486.4	0.03051	96.29	-479.78
20	0.02513	95.02	-501.35	0.02668	94.95	-494.9	0.02837	95.03	-488.18	0.03012	95.05	-481.56
25	0.0248	93.78	-503.15	0.02633	93.7	-496.7	0.02799	93.78	-489.98	0.02973	93.81	-483.37
30	0.02448	92.54	-504.96	0.02598	92.46	-498.52	0.02762	92.54	-491.81	0.02933	92.56	-485.21
40	0.02382	90.04	-508.68	0.02528	89.97	-502.25	0.02688	90.05	-495.54	0.02854	90.08	-488.95
50	0.02316	87.55	-512.5	0.02458	87.48	-506.08	0.02614	87.57	-499.38	0.02776	87.59	-492.81
60	0.0225	85.06	-516.43	0.02388	84.99	-510.03	0.02539	85.07	-503.34	0.02697	85.09	-496.78
80	0.02118	80.07	-524.66	0.02248	80	-518.29	0.02391	80.09	-511.62	0.02538	80.1	-505.08
100	0.01986	75.07	-533.44	0.02108	75	-527.1	0.02241	75.09	-520.44	0.0238	75.11	-513.94
120	0.01853	70.06	-542.83	0.01967	70	-536.52	0.02092	70.09	-529.89	0.02221	70.1	-523.43
160	0.01588	60.03	-563.87	0.01685	59.97	-557.64	0.01793	60.06	-551.05	0.01903	60.06	-544.67
200	0.01322	49.97	-588.83	0.01403	49.92	-582.7	0.01493	50	-576.16	0.01584	50	-569.89

Table B.2 (continued) Partial pressure P_k and chemical potential μ_k variations of water, with height at different temperatures, where ϕ is the relative humidity (μ_k is estimated using Equation (4.22)).

z (mm)	17°C			18°C			19°C			20°C			21°C		
	P_k (bar)	ϕ (%)	μ_k (J/g)	P_k (bar)	ϕ (%)	μ_k (J/g)	P_k (bar)	ϕ (%)	μ_k (J/g)	P_k (bar)	ϕ (%)	μ_k (J/g)	P_k (bar)	ϕ (%)	μ_k (J/g)
5	0.04751	97.57	-159.46	0.05053	97.56	-156.76	0.05372	97.57	-154.08	0.05709	97.56	-151.39	0.06064	97.58	-148.71
10	0.04632	95.13	-160.78	0.04927	95.12	-158.09	0.05238	95.13	-155.41	0.05567	95.13	-152.72	0.05913	95.16	-150.04
15	0.04513	92.68	-162.15	0.04801	92.68	-159.46	0.05104	92.7	-156.78	0.05425	92.7	-154.09	0.05762	92.73	-151.42
20	0.04394	90.24	-163.55	0.04674	90.24	-160.86	0.0497	90.26	-158.18	0.05282	90.26	-155.5	0.05611	90.3	-152.83
25	0.04274	87.79	-164.99	0.04548	87.79	-162.3	0.04835	87.82	-159.63	0.0514	87.83	-156.95	0.0546	87.86	-154.28
30	0.04155	85.33	-166.47	0.04421	85.34	-163.79	0.047	85.37	-161.12	0.04997	85.38	-158.44	0.05308	85.42	-155.77
40	0.03916	80.42	-169.58	0.04167	80.44	-166.9	0.0443	80.47	-164.23	0.0471	80.49	-161.56	0.05004	80.53	-158.9
50	0.03676	75.49	-172.88	0.03912	75.51	-170.21	0.0416	75.55	-167.56	0.04423	75.58	-164.89	0.04699	75.63	-162.23
60	0.03435	70.55	-176.43	0.03656	70.58	-173.76	0.03888	70.62	-171.11	0.04134	70.65	-168.45	0.04394	70.71	-165.8
80	0.02952	60.63	-184.35	0.03143	60.68	-181.7	0.03343	60.72	-179.07	0.03555	60.76	-176.43	0.03779	60.82	-173.8
100	0.02467	50.67	-193.75	0.02627	50.72	-191.12	0.02795	50.76	-188.51	0.02973	50.8	-185.89	0.03161	50.86	-183.28
120	0.0198	40.66	-205.27	0.02109	40.71	-202.66	0.02243	40.75	-200.09	0.02387	40.79	-197.5	0.02538	40.85	-194.91
160	0.00997	20.48	-241.16	0.01063	20.53	-238.62	0.01132	20.55	-236.16	0.01205	20.58	-233.66	0.01282	20.63	-231.17
200	5.1E-05	0.104	-517.61	7.1E-05	0.137	-501.72	7.1E-05	0.129	-503.45	8.1E-05	0.139	-498.11	9.1E-05	0.147	-493.56

Table B.3 Partial pressure P_k and chemical potential μ_k variations of ethanol, with height at different temperatures, where ϕ is the relative humidity (P_{sat} of ethanol at different temperatures refer to Ref. [5]) (μ_k is estimated using Equation (4.22)).

z (mm)	22°C			23°C			24°C			25°C		
	P_k (bar)	φ (%)	μ_k (J/g)	P_k (bar)	φ (%)	μ_k (J/g)	P_k (bar)	φ (%)	μ_k (J/g)	P_k (bar)	φ (%)	μ_k (J/g)
5	0.06435	97.55	-146.05	0.06838	97.7	-143.3	0.07245	97.6	-140.69	0.0768	97.6	-138.03
10	0.06276	95.13	-147.38	0.06669	95.28	-144.64	0.07066	95.19	-142.03	0.0749	95.19	-139.37
15	0.06116	92.71	-148.76	0.06499	92.86	-146.02	0.06887	92.78	-143.4	0.07301	92.78	-140.75
20	0.05956	90.28	-150.17	0.06329	90.43	-147.43	0.06707	90.36	-144.82	0.07111	90.36	-142.17
25	0.05795	87.85	-151.62	0.06159	88	-148.89	0.06527	87.94	-146.28	0.0692	87.94	-143.63
30	0.05635	85.41	-153.12	0.05989	85.57	-150.39	0.06347	85.51	-147.78	0.06729	85.52	-145.13
40	0.05313	80.53	-156.26	0.05647	80.68	-153.53	0.05986	80.64	-150.92	0.06346	80.65	-148.28
50	0.04989	75.63	-159.6	0.05304	75.78	-156.87	0.05623	75.75	-154.27	0.05962	75.76	-151.64
60	0.04665	70.71	-163.18	0.0496	70.86	-160.46	0.05258	70.84	-157.87	0.05576	70.86	-155.24
80	0.04013	60.83	-171.19	0.04267	60.97	-168.49	0.04525	60.96	-165.91	0.04799	60.99	-163.31
100	0.03357	50.88	-180.7	0.0357	51.01	-178.02	0.03787	51.02	-175.46	0.04016	51.03	-172.89
120	0.02696	40.87	-192.37	0.02868	40.98	-189.72	0.03043	40.99	-187.19	0.03226	41	-184.66
160	0.01361	20.63	-228.75	0.01448	20.69	-226.21	0.01537	20.71	-223.77	0.01628	20.69	-221.44
200	8.1E-05	0.123	-501.51	8.1E-05	0.116	-503.21	9.1E-05	0.123	-498.6	4.1E-05	0.052	-543.89

Table B.3 (continued) Partial pressure P_k and chemical potential μ_k variations of ethanol, with height at different temperatures, where φ is the relative humidity (P_{sat} of ethanol at different temperatures refer to Ref. [5]) (μ_k is estimated using Equation (4.22)).

z (mm)	17°C			18°C			19°C			20°C			21°C		
	P_k (bar)	ϕ (%)	μ_k (J/g)	P_k (bar)	ϕ (%)	μ_k (J/g)	P_k (bar)	ϕ (%)	μ_k (J/g)	P_k (bar)	ϕ (%)	μ_k (J/g)	P_k (bar)	ϕ (%)	μ_k (J/g)
5	1.1E-06	97.48	-146.4	1.2E-06	97.99	-145.7	1.3E-06	97.92	-145.04	1.5E-06	97.69	-144.37	1.7E-06	97.63	-143.69
10	1E-06	94.98	-146.68	1.2E-06	95.48	-146	1.3E-06	95.41	-145.32	1.4E-06	95.19	-144.64	1.6E-06	95.13	-143.97
15	1E-06	92.49	-146.96	1.1E-06	92.98	-146.3	1.3E-06	92.9	-145.6	1.4E-06	92.68	-144.93	1.6E-06	92.63	-144.26
20	9.9E-07	89.99	-147.25	1.1E-06	90.47	-146.5	1.2E-06	90.4	-145.9	1.4E-06	90.18	-145.23	1.5E-06	90.13	-144.55
25	9.6E-07	87.49	-147.55	1.1E-06	87.96	-146.8	1.2E-06	87.89	-146.2	1.3E-06	87.68	-145.53	1.5E-06	87.63	-144.86
30	9.3E-07	84.99	-147.86	1E-06	85.46	-147.2	1.2E-06	85.38	-146.51	1.3E-06	85.17	-145.84	1.4E-06	85.13	-145.17
40	8.8E-07	79.99	-148.51	9.8E-07	80.45	-147.8	1.1E-06	80.36	-147.16	1.2E-06	80.17	-146.49	1.4E-06	80.13	-145.82
50	8.2E-07	74.99	-149.19	9.2E-07	75.43	-148.5	1E-06	75.34	-147.85	1.1E-06	75.16	-147.19	1.3E-06	75.12	-146.52
60	7.7E-07	69.99	-149.93	8.6E-07	70.42	-149.2	9.6E-07	70.32	-148.59	1.1E-06	70.15	-147.93	1.2E-06	70.12	-147.26
80	6.6E-07	59.99	-151.57	7.4E-07	60.4	-150.9	8.2E-07	60.29	-150.24	9.1E-07	60.14	-149.58	1E-06	60.12	-148.92
100	5.5E-07	50	-153.51	6.1E-07	50.37	-152.8	6.8E-07	50.25	-152.19	7.6E-07	50.13	-151.54	8.5E-07	50.12	-150.89
120	4.4E-07	40	-155.89	4.9E-07	40.35	-155.2	5.5E-07	40.22	-154.58	6.1E-07	40.12	-153.94	6.8E-07	40.12	-153.29
160	2.2E-07	20	-163.26	2.5E-07	20.3	-162.5	2.7E-07	20.15	-161.99	3.1E-07	20.09	-161.38	3.4E-07	20.11	-160.74
200	1E-10	0.009	-245.02	3E-09	0.249	-209.5	1E-09	0.075	-222.03	1E-09	0.067	-222.79	1.8E-09	0.108	-217.2

Table B.4 Partial pressure P_k and chemical potential μ_k variations of hexadecane, with height at different temperatures, where ϕ is the relative humidity. (The saturated pressure P_{sat} of hexadecane at different temperatures was calculated using

$$\ln P_{sat} = A - \frac{B}{T} + C \ln T + \frac{DP_{sat}}{T^2}, \text{ with constants } A=89.06, B=12411.3, C=-10.58, \text{ and } D=15200 \text{ (Reid et al., 1987)}.$$

z (mm)	22°C			23°C			24°C			25°C		
	P _k (bar)	φ(%)	μ _k (J/g)	P _k (bar)	φ(%)	μ _k (J/g)	P _k (bar)	φ(%)	μ _k (J/g)	P _k (bar)	φ(%)	μ _k (J/g)
5	1.8E-06	97.54	-143.03	2E-06	97.54	-142.35	2.3E-06	97.61	-141.69	2.5E-06	97.53	-141.02
10	1.8E-06	95.04	-143.31	2E-06	95.05	-142.63	2.2E-06	95.11	-141.97	2.5E-06	95.03	-141.3
15	1.7E-06	92.54	-143.6	1.9E-06	92.56	-142.92	2.2E-06	92.61	-142.26	2.4E-06	92.53	-141.59
20	1.7E-06	90.04	-143.89	1.9E-06	90.08	-143.22	2.1E-06	90.11	-142.56	2.3E-06	90.03	-141.89
25	1.7E-06	87.54	-144.2	1.8E-06	87.59	-143.52	2E-06	87.6	-142.87	2.3E-06	87.53	-142.2
30	1.6E-06	85.04	-144.51	1.8E-06	85.11	-143.83	2E-06	85.1	-143.18	2.2E-06	85.03	-142.52
40	1.5E-06	80.04	-145.17	1.7E-06	80.13	-144.49	1.9E-06	80.1	-143.84	2.1E-06	80.03	-143.18
50	1.4E-06	75.04	-145.87	1.6E-06	75.16	-145.19	1.7E-06	75.1	-144.55	1.9E-06	75.04	-143.88
60	1.3E-06	70.04	-146.61	1.5E-06	70.19	-145.93	1.6E-06	70.1	-145.3	1.8E-06	70.04	-144.64
80	1.1E-06	60.04	-148.28	1.3E-06	60.24	-147.59	1.4E-06	60.1	-146.98	1.6E-06	60.04	-146.32
100	9.4E-07	50.04	-150.25	1.1E-06	50.3	-149.55	1.2E-06	50.1	-148.96	1.3E-06	50.04	-148.32
120	7.6E-07	40.05	-152.67	8.5E-07	40.36	-151.94	9.3E-07	40.1	-151.39	1E-06	40.04	-150.76
160	3.8E-07	20.05	-160.16	4.3E-07	20.47	-159.32	4.7E-07	20.09	-158.92	5.2E-07	20.04	-158.33
200	1E-09	0.054	-224.31	1.2E-08	0.579	-198.06	2E-09	0.087	-218.27	1E-09	0.039	-226.59

Table B.4 (continued) Partial pressure P_k and chemical potential μ_k variations of hexadecane, with height at different temperatures, where ϕ is the relative humidity. (The saturated pressure P_{sat} of hexadecane at different temperatures was calculated using

$$\ln P_{sat} = A - \frac{B}{T} + C \ln T + \frac{DP_{sat}}{T^2}, \text{ with constants } A=89.06, B=12411.3, C=-10.58, \text{ and } D=15200 \text{ (Reid et al., 1987)).}$$

θ (deg)	Ethanol				Hexadecane			
	Drop height (mm)	P_k (bar)	$\Delta\mu$ (J/g)	μ_k/μ_{sat} (%)	Drop height (mm)	P_k (bar)	$\Delta\mu$ (J/g)	μ_k/μ_{sat} (%)
5	0.1647	0.05846	0.04606	0.034	0.1802	1.522E-06	0.00187	0.0013
10	0.3281	0.05842	0.08799	0.062	0.359	1.52E-06	0.0115	0.008
15	0.4891	0.05837	0.12932	0.089	0.535	1.519E-06	0.02098	0.0146
20	0.6463	0.05833	0.16972	0.116	0.707	1.518E-06	0.03026	0.021
25	0.7986	0.05828	0.2089	0.142	0.8736	1.516E-06	0.03925	0.0272
30	0.9448	0.05824	0.24653	0.167	1.0336	1.515E-06	0.04789	0.0332
35	1.0838	0.0582	0.28235	0.191	1.1857	1.514E-06	0.05611	0.0389

Table B.5 Pressure and chemical potential variations with the drop height ($\Delta\mu$ is estimated using Equation (B.9)).

Figure B.1 Profiles of pressure variations with the vessel height at different temperatures listed from Tables B.2 to B.4, where “w-17” denotes water at 17°C, “e” represents ethanol and “h” represents hexadecane.

Figure B.2 Chemical potential variations of measuring liquids with the vessel height at different temperatures, which are listed from Tables B.2 to B.4.

Figure B.3 (a) Drop spreading experimental system; (b) conventional sessile drop experimental arrangement.

References:

- [1] Hartland, S., and Hartley, R., *Axisymmetric Fluid-Liquid Interfaces: tables giving the shape of sessile and pendant drops and external menisci, with examples of their use*, Elsevier Scientific Pub. Co., New York, **1976**
- [2] Kondepudi, D., and Prigogine, I., *Modern Thermodynamics: from heat engines to dissipative structures*, Wiley, New York, **1998**
- [3] Moran, M. J., and Shapiro, H. N., *Fundamentals of Engineering Thermodynamics*, Wiley, New York, **1999**
- [4] Reid, R. C., Prausnitz, J. M., and Poling, B. E., *The Properties of Gases and Liquids*, McGraw-Hill, New York, **1987**
- [5] Ohe, S., http://www.s-ohe.com/Ethanol_cal.html

Appendix C:
Image Processing Programs
(MATLAB)

```
% --- Image noise reduction and edge detection, and the coordinates of a drop profile
acquisition ---

clear all;
close all;

% --- Input an image file, called 'corner.jpg' ---
image_matrix = imread('corner.jpg');

% --- Remove the noise using median filtering ---
nonoise_image = medfilt2(image_matrix);

% --- Display the figures ---
imshow(nonoise_image);
figure;
subplot(2,1,1), imshow(image_matrix); title('Original Image');
subplot(2,1,2), imshow(nonoise_image); title('Smoothed Image');

% --- Detect the edge (the drop profile) using Sobel operator ---
bw1 = edge(nonoise_image, 'sobel');
figure;
imshow(bw1);

% --- Write the edge image to a JPEG format ---
imwrite(bw1, 'edge.jpg');

% --- Set up the image coordinates ---
temp = size(image_matrix);
row = temp(1);
column = temp(2);

y(:, 1) = [row:-1:1]';
for i = 2 : column,
    y(:, i) = y(:, 1);
end

x(1, :) = [1:1:column];
for i = 2 : row,
    x(i, :) = x(1, :);
end
```

```
% --- Search for the edge and save data points on the edge in a matrix, called 'edges' ---
count = 0;
temp = size(bw1);
for i = 1: temp(1),
    for j = 1 : temp(2),
        if bw1(i, j) > 0.5
            count = count + 1;
            edges(count, 1:2) = [x(i, j) y(i, j)];
        end
    end
end
% --- Overlap the detected edge on the original image ---
image_matrix(i, j) = 250.0;
end
end
figure;
plot(edges(:, 1), edges(:, 2), '*'), grid on;
xlabel('X (pixels)');
ylabel('Y (pixels)');
title('Drop profile');
figure;
imshow(image_matrix);

% --- Save the matrix 'edges' to a data file, called 'drop_profile.dat' ---
temp = size(edges);
fid = fopen('g:/ping/image/drop_profile', 'W');
for i = 1: temp(1),
    fprintf(fid, '%12.3f %12.3f', [edges(i, 1) edges(i, 2)]);
    fprintf(fid, '\n');
end
fclose(fid);
```

% --- Best-fit lines and 95% confidence intervals on two straight sides of a square ---

```
clear all;  
close all;
```

```
image_matrix = imread('corner.jpg');  
temp = size(image_matrix);  
row = temp(1);  
column = temp(2);
```

% --- Input Excel data files of two straight lines and the curved line ---

```
s1 = xlsread('levelline');  
s2 = xlsread('verticalline');  
s3 = xlsread('circle');
```

```
x1 = s1(:, 1);  
y1 = s1(:, 2);
```

```
x2 = s2(:, 2);  
y2 = s2(:, 1);
```

```
x3 = s3(:, 1);  
y3 = s3(:, 2);
```

% --- Fit a linear model, i.e., linear regression ---

```
[p1, s1] = polyfit(x1, y1, 1);  
[p2, s2] = polyfit(x2, y2, 1);
```

% --- Find out the 95% confidence interval ---

```
alpha = 1 - 0.95;  
[yp1, delta1] = polyconf(p1, x1, s1, alpha);  
[yp2, delta2] = polyconf(p2, x2, s2, alpha);
```

```
figure;  
plot(x1, y1, '.');  
hold on;  
plot(y2, x2, '.');  
plot(x3, y3, '.');  
xlabel('X (pixels)');  
ylabel('Y (pixels)');  
hold on;  
plot(x1, yp1, 'r-', x1, yp1 + delta1, 'g--', x1, yp1 - delta1, 'g--');  
plot(yp2, x2, 'r-', yp2 + delta2, x2, 'g--', yp2 - delta2, x2, 'g--'), grid on;
```

```
% --- Nonlinear least squares fit on a curve ---

clear all;
close all;

circle = xlsread('circle');

tic;

x = circle(:, 1);
y = circle(:, 2);
temp = size(x);

% --- Initially guess on the center and the radius of a circle ---
best_sse1 = 10000;
best_parameter = [rand*50 rand*50 rand*50];

for counter = 1 : 100,

    parameter = [best_parameter(1)+randn*2 best_parameter(2)+randn*2
best_parameter(3)+randn*2];
    parameter = fminsearch( 'processmodel', parameter );

% --- Verify the results ---
    sse1 = 0;
    for i = 1 : temp(1);
        sse1 = sse1 + ( ( x(i) - parameter(1))^2 + (y(i) - parameter(2))^2 )^0.5 -
        parameter(3) )^2;
    end

    if best_sse1 > sse1
        best_sse1 = sse1;
        best_parameter = parameter;
    end

end

% --- Display best_sse1 ---
sse1 = 0;
for i = 1 : temp(1);
    sse1 = sse1 + ( ( x(i) - best_parameter(1))^2 + (y(i) - best_parameter(2))^2 )^0.5 -
    best_parameter(3) )^2;
end
```

```
best_sse1
best_parameter

% --- Save the best parameters to a data file, called 'best_parameter.mat'
save best_parameter best_parameter;

figure;
plot(x, y, '*');
hold on;

% --- Plot the best-fit circle using the estimated parameters ---
theta = [0:pi/50:2.0*pi];

r = best_parameter(3);
x1 = cos(theta) * r + best_parameter(1);
y1 = sin(theta) * r + best_parameter(2);

plot(x1, y1, '-', best_parameter(1), best_parameter(2), 'rh'), grid on;
xlabel('X (pixels)');
ylabel('Y (pixels)');

toc;
```


% --- Function of 'processmodel' ---

```
function sse = processmodel( parameter )
```

```
circle = xlsread('circle');
```

```
x = circle(:, 1);
```

```
y = circle(:, 2);
```

```
temp = size(x);
```

```
sse = 0;
```

```
for i = 1 : temp(1);
```

```
    sse = sse+(((x(i) - parameter(1))^2 + (y(i) - parameter(2))^2)^0.5 - parameter(3))^2;
```

```
end
```

Appendix D:

ADSA-P Program
(FORTRAN)

```

PROGRAM MAIN
IMPLICIT REAL*8 (A-H,O-Z)
CHARACTER*20 FILNAM
LOGICAL*1 NAME(60)
COMMON/INPUT/ X(2000),Z(2000),GRAVTY,DELRHO,GAMA,Q(4),ZMAX,
+ NPTS,NCYCL,INCRNT,ISTAT,NAME
GRAVTY=980.62
DELRHO=0.9982
GAMA=0.0
ZMAX=0.4163
NPTS=2
NCYCL=3
INCRNT=300
ISTAT=2
WRITE(6,*) 'ENTER NAME OF DATA FILE (NAME <20 CHARACTERS) '
READ(5,100) FILNAM
WRITE(6,*) 'ENTER THE NUMBER OF DATA POINTS '
READ(5,*) NPTS
100 FORMAT(A20)
OPEN(UNIT=1,STATUS='OLD',FILE=FILNAM)
DO 10 I=1,NPTS
    READ(1,*) X(I),Z(I)
    WRITE(6,*) X(I),Z(I)
10 CONTINUE
CALL ADSA
CLOSE(UNIT=1)
STOP
END

SUBROUTINE ADSA
C .....
C . Subroutine INTFCE calls to subroutines: INIT, SYSEQ, and SOLVE..
C . (this version does not contain the error analysis part)
C . The parameters which are defined in the COMMON INPUT
C . statement have the following interpretation:
C .
C . X(K),Z(K) .. K=1,2...,NPTS, are measured points on the
C . interface profile (if NPTS > 100 it is necessary
C . to increase the length of all the arrays of
C . length 100, accordingly).
C . GRAVTY ..... Gravitational acceleration vector. GRAVTY is
C . assigned a positive value for sessile drop and
C . it is assigned a negative value for pendant drop
C . DELRHO ..... Density difference, ( > 0), between the two bulk
C . phases.
C . GAMA ..... A known value of the surface tension, or zero.
C . ZMAX ..... Measured distance between the drop base and the
C . coordinate reference plane.
C . NAME ..... Title for the run. Use up to 60 characters.
C . NCYCL ..... Number of optimization cycles.
C . INCRNT ..... An approximate number of integration steps along
C . one half of the meridian curve.
C .....
IMPLICIT REAL*8(A-H,O-Z)
CHARACTER*1 NAME*60
DIMENSION Q0(4),EQ0(4),EQQ0(4,4),F0(3)
COMMON/INPUT/ X(2000),Z(2000),GRAVTY,DELRHO,GAMA,Q(4),ZMAX,
+ NPTS,NCYCL,INCRNT,NAME
COMMON/BLOCK1/ F(3),G(3),H(3),ERR,EQ(4),EQQ(4,4),SOLAST
+ ,SMAX,DELS

```

```

C      . . . . .
C      . Subroutine INIT is called to obtain      .
C      . first values of Q(I) and DELS      .
C      . . . . .
      KSOL=1
      IF (GAMA.NE.0.D0) KSOL=2
      CALL INIT(KSOL,PI)
      IF (KSOL.EQ.1) THEN
        K=-5
        ALFA=0.005D0
        M=0
        A=DABS (GRAVTY)/GRAVTY
      ELSE
        ALFA=DELRHO*GRAVTY/GAMA
      END IF

C      . . . . .
C      . Implementing the combined optimization method. Q(4) is the .
C      . loading parameter; applicable only when KSOL=1.      .
C      . . . . .
      DO 16 L=1,NCYCL
        DELS=DELS/(2**(L-1))
        WRITE (6,28) L,DELS
        ERR0=1.0D10
        ER0=ERR0
        GO TO (1,12),KSOL
1       MJOB=3
        CALL SYSEQ(KSOL,MJOB)
        CALL PRINT
        IF (DABS (ERR0-ERR)/ERR.LT.1.0D-9) GO TO 3
        ERR0=ERR
        DO 2 I=1,3
          IF (DABS (EQ(I)).GT.1.0D-9) GO TO 9
2       CONTINUE
3       IF (DABS (ER0-ERR)/ERR.LT.1.0D-9.OR.
+         DABS (EQ(4)).LT.1.0D-9) GO TO 16
        IF (ERR.GT.ER0) GO TO 10
        ER0=ERR
        IF (K.LE.3) ALFA=ALFA*2
        IF (ALFA.GT.1) ALFA=1
        DO 4 I=1,4
          Q0(I)=Q(I)
          EQ0(I)=EQ(I)
          DO 4 J=1,4
4         EQQ0(I,J)=EQQ(I,J)
        CALL SOLVE(4)
        DEL4=EQ(4)
        M=0
5       DEL=DEL4*ALFA
        WRITE (6,100) M,K,ALFA
100      FORMAT(2X,' *** ',I2,2X,I2,2X,D12.5,' ***')
        Q(4)=Q0(4)-DEL
        IF ((A-DABS (Q(4))/Q(4)).NE.0.D0) GO TO 27
        DO 6 I=1,3
          Q(I)=Q0(I)
          EQ(I)=EQ0(I)-EQQ0(I,4)*DEL
          DO 6 J=1,3
6         EQQ(I,J)=EQQ0(I,J)
        K=1
7       CALL SOLVE(3)
        DO 8 I=1,3

```

```

8      Q(I)=Q(I)-EQ(I)
      GO TO 1
9      K=K+1
      IF (K.LE.5) GO TO 7
10     ALFA=ALFA/2
      M=M+1
      IF (M.NE.9) GO TO 5
      DO 11 I=1,4
          IF (EQ0(I).GT.1.D-5) GO TO 27
11     Q(I)=Q0(I)
C     .....
C     . Solving for the case when GAMA is specified .
C     .....
12     CONTINUE
13     MJOB=3
      Q(4)=ALFA*Q(3)*Q(3)
      CALL SYSEQ(KSOL,MJOB)
      CALL PRINT
      IF (DABS(ERR0-ERR)/ERR.LT.1.0D-9) GO TO 16
      ERR0=ERR
      DO 15 I=1,3
          IF (DABS(EQ(I)).GT.1.0D-9) THEN
              CALL SOLVE(3)
              DO 14 J=1,3
14                 Q(J)=Q(J)-EQ(J)
                    GO TO 13
              END IF
15     CONTINUE
16     CONTINUE
C     .....
C     . Integrating the Laplacian curve to determine the value .
C     . of the contact angle at Z+Q(2)=ZMAX, ( Z=Q(3)*F(2) ), and .
C     . the values of the surface area and the volume of the drop. .
C     .....
      IF (ZMAX.EQ.0) GO TO 24
      A=0
      V=0
      A1=0
      V1=0
      S0=0
      J=1
      MJOB=1
      DO 17 I=1,3
17         F(I)=0
18     S1=S0+DELS
      CALL I2EULR(S0,S1,Q(4),MJOB)
      SS=Q(3)*F(2)+Q(2)-ZMAX
      IF (SS.GT.0) THEN
19         DLS=(Q(3)*F(2)+Q(2)-ZMAX)/(Q(3)*DSIN(F(3)))
          IF (DABS(DLS/SMAX).LT.1.D-9) J=2
          S1=S0-DLS
          S0=SOLAST
          DELS=S1-S0
          DO 20 I=1,3
20             F(I)=F0(I)
              CALL I2EULR(S0,S1,Q(4),MJOB)
              GO TO (19,21),J
          END IF
21     A2=F(1)*DSIN(F(3))
      A=A+0.5D0*DELS*(A1+A2)

```

```

      A1=A2
      V2=F(1)*A2
      V=V+0.5D0*DELS*(V1+V2)
      V1=V2
      SOLAST=S0
      DO 22 I=1,3
22      F0(I)=F(I)
      GO TO (18,23),J
C --> Surface area
23      A=2*PI*Q(3)*Q(3)*A
C --> Volume
      V=PI*Q(3)*Q(3)*Q(3)*V
C --> Contact radius
      XC=Q(3)*F(1)
C
C      . . . . .
C      .   Printing the computational results. .
C      . . . . .
24      IF (Q(4).NE.0) GO TO 25
      GAMA=-0.0D0
      GO TO 26
C --> Surface tension
25      GAMA=DELRHO*GRAVITY*Q(3)*Q(3)/Q(4)
C --> Contact angle
26      PHI=F(3)*180/PI
      WRITE (6,29) NAME,Q(1),Q(2),Q(3),GAMA,A,V,PHI,XC
      WRITE (6,*) NAME,Q(1),Q(2),Q(3),GAMA,A,V,PHI,XC
      WRITE (2,29) NAME,Q(1),Q(2),Q(3),GAMA,A,V,PHI,XC
      RETURN
27      WRITE(2,30)
      WRITE (6,30)
28      FORMAT(' ',/,20X,I2,' OPTIMIZATION CYCLE.'/
+           20X,'INCREMENTAL ARC-LENGTH, DELS :',D15.8/)
29      FORMAT(' ',5X,///15X,'COMPUTATIONAL RESULTS: ',/,14X,24('.'))//
+           8X,'SAMPLE: ',A60//
+           10X,'A. Origin of the drop coordinate system :'/
+           40X,'X0 (cm) ',10('.'),D13.6/40X,'Z0 (cm) ',10('.'),D13.6/
+           10X,'B. Radius of curvature at origin (cm) ',10('.'),D13.6/
+           10X,'C. Surface tension (ergs/cm sq.) ',15('.'),D13.6/
+           10X,'D. Surface area (cm sq.) ',23('.'),D13.6/
+           10X,'E. Volume (cm cu.) ',29('.'),D13.6/
+           10X,'F. Contact angle (degrees) ',21('.'),D13.6/
+           10X,'G. Contact radius (cm) ',25('.'),D13.6/)
30      FORMAT(' ',/,3X,'** TERMINAL ERROR. CHECK THE INPUT DATA. **')
      RETURN
      END
C
      SUBROUTINE INIT(KSOL,PI)
C
C      . . . . .
C      .   In subroutine INIT the first values of array Q are determined. .
C      . . . . .
      IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER*1 NAME*60
      COMMON/INPUT/ X(2000),Z(2000),GRAVITY,DELRHO,GAMA,Q(4),ZMAX,
+           NPTS,NCYCL,INCRNT,NAME
      COMMON/BLOCK1/ R(6),E(6),A,B,C,D,F,G,H,O,DEL,DEL1,E0,E00,ALFA,
+           Q1,Q2,E3,E6,E5,DUM,SMAX,DELS
      COMMON/BLOCK2/ T(124),P(124)
C
      PI=DACOS(-1.D0)
      A=0

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```

      B=0
      DO 2 I=1,NPTS
        IF (Z(I).LT.A) GO TO 1
        M=I
        A=Z(I)
1      IF (DABS(X(I)).LT.B) GO TO 2
        K=I
        B=DABS(X(I))
2      CONTINUE
C      . . . . .
C      . Constructing the merit function E(1) and its first and second .
C      . partial derivatives E(I) I=2,...,6, with respect to Q(1) and .
C      . Q(2). . . . .
C      . . . . .
      A=0
      B=0
      DO 3 I=1,NPTS
        A=A+X(I)
3      B=B+Z(I)
      Q(1)=A/NPTS
      Q2=4*DABS(X(K)-Q(1))
      DEL=Q2/12
      Q(2)=B/NPTS-Q2
      Q2=Q2+B/NPTS
      ALFA=0.05D0
      E0=1.D10
      E00=E0
      L=-5
      K=0
      INI=1
4      CONTINUE
      DO 5 I=1,6
        R(I)=0
5      E(I)=0
      DO 6 I=1,NPTS
        A=X(I)-Q(1)
        B=Z(I)-Q(2)
        D=DSQRT(A*A+B*B)
        C=1/D
        F=C*C*C
        R(1)=R(1)+D
        R(2)=R(2)+A*C
        R(3)=R(3)+B*C
        R(4)=R(4)+A*A*F-C
        R(5)=R(5)+A*B*F
6      R(6)=R(6)+B*B*F-C
      DO 7 I=1,6
7      R(I)=R(I)/NPTS
      DO 8 I=1,NPTS
        A=X(I)-Q(1)
        B=Z(I)-Q(2)
        D=DSQRT(A*A+B*B)
        C=1/D
        F=C*C*C
        G=R(2)-A*C
        H=R(3)-B*C
        O=D-R(1)
        E(1)=E(1)+O*O
        E(2)=E(2)+O*G
        E(3)=E(3)+O*H

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      E(4)=E(4)+G*G+O*(R(4)+C-A*A*F)
      E(5)=E(5)+G*H+O*(R(5)-A*B*F)
8      E(6)=E(6)+H*H+O*(R(6)+C-B*B*F)
C      . . . . .
C      . Locating the initial position of the center .
C      . of the fitted circle. .
C      . . . . .
      IF (INI.EQ.0) GO TO 11
      IF (Q(2).GT.Q2) GO TO 9
      K=K+1
      T(K)=E(1)
      P(K)=Q(2)
      Q(2)=Q(2)+DEL
      GO TO 4
9      A=1.D10
      DO 10 I=1,K
          IF (T(I).GT.A) GO TO 10
          J=I
          A=T(I)
10     CONTINUE
      Q(2)=P(J)
      INI=0
      GO TO 4
C      . . . . .
C      . Optimization method using the combined INCREMENTAL LOADING .
C      . method and the NEWTON-RAPHSON method. The loading parameter is .
C      . Q(1). .
C      . . . . .
11     IF (DABS(E0-E(1))/E(1).LT.1.D-9) GO TO 12
      E0=E(1)
      IF (DABS(E(3)).GT.1.D-9) GO TO 15
12     IF (DABS(E00-E(1))/E(1).LT.1.D-9. OR .DABS(E(2)).LT.1.D-9)
+      GO TO 16
      E00=E(1)
      IF (L.LE.3) ALFA=ALFA*2
      IF (ALFA.GT.1) ALFA=1
      E3=E(3)
      E5=E(5)
      E6=E(6)
      DEL1=(E3-E6*E(2)/E5)/(E5-E6*E(4)/E5)
      Q1=Q(1)
      Q2=Q(2)
13     DEL=DEL1*ALFA
      Q(1)=Q1-DEL
      Q(2)=Q2
      E(3)=E3-DEL*E5
      E(6)=E6
      L=L+1
14     Q(2)=Q(2)-E(3)/E(6)
      GO TO 4
15     L=L+1
      IF (L.LE.5) GO TO 14
      ALFA=ALFA/2
      GO TO 13
C      . . . . .
C      . Establishing the first values of Q(I) and DELS. .
C      . . . . .
16     Q(2)=Q(2)-R(1)
      Q(3)=R(1)
      Q(4)=0

```



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      IF (KSOL.EQ.2) Q(4)=DELRHO*GRAVITY*Q(3)*Q(3)/GAMA
      SMAX=PI-2*DATAN(DABS((X(M)-Q(1))/(Z(M)-Q(2))))
      DELS=SMAX/INCRNT
      RETURN
      END
C
      SUBROUTINE SYSEQ(KSOL,MJOB)
C . . . . .
C . In subroutine SYSEQ the objective function and its 1-st and
C . 2-nd partial derivatives are constructed. For every datum point,
C . the routine locates initially a point on the calculated curve
C . which is closest to the datum point and then calculates the
C . function value and the derivatives at that point. The global set
C . of equations is obtained by summing up these individual
C . expressions.
C . Subroutine SYSEQ calls subroutine I2EULR.
C . . . . .
      IMPLICIT REAL*8(A-H,O-Z)
      CHARACTER*1 NAME*60
      COMMON/INPUT/ X(2000),Z(2000),GRAVITY,DELRHO,GAMA,Q(4),ZMAX,
+       NPTS,NCYCL,INCRNT,NAME
      COMMON/BLOCK1/ F(3),G(3),H(3),ERR,EQ(4),EQQ(4,4),SOLAST,
+       SMAX,DELS
      COMMON/BLOCK2/ F0(3),G0(3),H0(3),ERRSQ(2000),ESQ(4),QQ(10),
+       L(2000),LP(2000),IK(25),JK(25)
      Q1=Q(1)
      Q2=Q(2)
      Q3=Q(3)
      Q4=Q(4)
      ERR=0
      DO 1 I=1,4
         EQ(I)=0
         DO 1 J=1,4
1          EQQ(I,J)=0
      SOLAST=0
      DO 2 I=1,3
         F(I)=0
         F0(I)=0
         G0(I)=0
2          H0(I)=0
      DO 3 I=1,NPTS
         L(I)=I
         LP(I)=1
         A=X(I)
         B=Z(I)
         IF (A.LT.Q1) LP(I)=-1
3          ERRSQ(I)=(Q1-A)*(Q1-A)+(Q2-B)*(Q2-B)
      M0=NPTS
      KL=0
C . . . . .
C . Locating the point Sm on the curve X=X(S), Z=Z(S)
C . ( X=Q3*F(1), Z=Q3*F(2) ), which is closest to a datum
C . point (X(NPIV),Z(NPIV)).
C . . . . .
      DO 22 NP=1,NPTS
         KJOB=1
         S0=SOLAST
4          S1=S0+DELS
5          CALL I2EULR(S0,S1,Q4,MJOB)
         IF (KJOB.NE.1) GO TO 11

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      DO 8 N=1,M0
        M=L(N)
        A=Q3*F(1)+LP(M)*(Q1-X(M))
        B=Q3*F(2)+Q2-Z(M)
        SQI=A*A+B*B
        IF (SQI-ERRSQ(M)) 6,6,7
6      ERRSQ(M)=SQI
        GO TO 8
7      KL=KL+1
        IK(KL)=M
        JK(KL)=N
8      CONTINUE
        IF (KL.NE.0) GO TO 10
        SOLAST=S0
        DO 9 I=1,3
          F0(I)=F(I)
          G0(I)=G(I)
9          H0(I)=H(I)
        GO TO 4
10     NPIV=IK(KL)
        K=LP(NPIV)
        MJOB=1
        KJOB=2
11     A=Q3*F(1)+K*(Q1-X(NPIV))
        B=Q3*F(2)+Q2-Z(NPIV)
        COS=DCOS(F(3))
        SIN=DSIN(F(3))
        APB=A*COS+B*SIN
        BMA=B*COS-A*SIN
        IF (DABS(F(2)).LT.1.0D-12) GO TO 14
        ESS=BMA*(2+Q4*F(2)-SIN/F(1))+Q3
        IF (KJOB.EQ.3) GO TO 15
        SQI=APB/ESS
        S1=S0-SQI
        IF (DABS(SQI/SMAX).GT.1.0D-9) GO TO 12
        MJOB=3
        KJOB=3
12     S0=SOLAST
        DO 13 I=1,3
          F(I)=F0(I)
          G(I)=G0(I)
13     H(I)=H0(I)
        GO TO 5
C      . . . . .
C      .   Constructing the objective function ERR, and its 1-st and .
C      . 2-nd partial derivatives EQ(I) and EQQ(I,J), respectively. .
C      . . . . .
14     MJOB=3
        ESS=Q3+Q2-Z(NPIV)
15     CONTINUE
        ESQ(1)=K*COS
        ESQ(2)=SIN
        ESQ(3)=APB/Q3+F(1)*COS+F(2)*SIN
        ESQ(4)=BMA*G(3)+Q3*(G(1)*COS+G(2)*SIN)
        QQ(1)=1
        QQ(2)=0
        QQ(3)=K*F(1)
        QQ(4)=K*Q3*G(1)
        QQ(5)=1
        QQ(6)=F(2)

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      QQ(7)=Q3*G(2)
      QQ(8)=F(1)*F(1)+F(2)*F(2)
      QQ(9)=A*G(1)+B*G(2)+Q3*(F(1)*G(1)+F(2)*G(2))
      QQ(10)=Q3*(A*H(1)+B*H(2)+Q3*(G(1)*G(1)+G(2)*G(2)))
      ERR=ERR+A*A+B*B
      EQ(1)=EQ(1)+K*A
      EQ(2)=EQ(2)+B
      GO TO (16,17),KSOL
C  --> Solving with four variables
16  IV=4
      EQ(3)=EQ(3)+A*F(1)+B*F(2)
      EQ(4)=EQ(4)+Q3*(A*G(1)+B*G(2))
      GO TO 18
C  --> Solving with three variables
17  IV=3
      Q4Q3=(Q4+Q4)/Q3
      EQ4=Q3*(A*G(1)+B*G(2))
      ESQ(3)=ESQ(3)+ESQ(4)*Q4Q3
      QQ(3)=QQ(3)+QQ(4)*Q4Q3
      QQ(4)=QQ(5)
      QQ(5)=QQ(6)+QQ(7)*Q4Q3
      QQ(6)=QQ(8)+(QQ(9)+QQ(10)+Q4Q3+EQ4/Q3)*Q4Q3
      EQ(3)=EQ(3)+A*F(1)+B*F(2)+EQ4*Q4Q3
18  CONTINUE
      IJ=0
      ESS=Q3/ESS
      DO 19 I=1,IV
          SQI=-ESQ(I)*ESS
          DO 19 J=I,IV
              IJ=IJ+1
19          EQQ(I,J)=EQQ(I,J)+ESQ(J)*SQI+QQ(IJ)
      M0=M0-1
      IF (M0.EQ.0) GO TO 23
      DO 20 I=1,M0
          IF (I.LT.JK(KL)) GO TO 20
          L(I)=L(I+1)
20  CONTINUE
      KL=KL-1
      IF (KL.GT.0) GO TO 10
      DO 21 I=1,3
          F(I)=F0(I)
          G(I)=G0(I)
21  H(I)=H0(I)
22  CONTINUE
23  CONTINUE
      DO 24 I=1,IV
          DO 24 J=I,IV
24  EQQ(J,I)=EQQ(I,J)
      RETURN
      ENTRY PRINT
      WRITE (6,100) ERR,(Q(I),I=1,4),(EQ(I),I=1,4)
100 FORMAT(' ',/,2X,'Value of error function:'/5X,D19.12/
+         22X,'Value of Q(I), I=1,4: '/,4(25X,D15.8/),
+         42X,'Value of EQ(I), I=1,4: '/,4(45X,D15.8/))
      RETURN
      END
C
      SUBROUTINE I2EULR(S0,S1,Q4,K)
C  . . . . .
C  . I2EULR is a second order implicit EULER METHOD of integration. .

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C . This subroutine will do a single step integration of the system .
C . of first order ordinary differential equations: .
C .           V'(S)=U(S,V(S)), V=(F(3),G(3),H(3)) .
C . given the initial condition V0=V(S0). .
C . . . . .
  IMPLICIT REAL*8 (A-H,O-Z)
  DIMENSION DELF(3), DELG(3), DELH(3)
  COMMON/BLOCK1/ F(3), G(3), H(3), DUM(24)
  DELS=S1-S0
  DEL=DELS/2
  IF (F(1).EQ.0) THEN
    DO 1 I=1,3
      F(I)=DELS
      G(I)=0
      H(I)=0
1    F(2)=F(2)*DEL
      S0=S1
      RETURN
    END IF
C . . . . .
C . Calculating the increments DELF(3), DELG(3) and DELH(3). .
C . . . . .
  SIN=DSIN(F(3))
  COS=DCOS(F(3))
  PS1=SIN/F(1)
  PC1=COS/F(1)
  PS2=PS1/F(1)
  A1=DEL*SIN
  A2=-DEL*COS
  A3=DEL*PS2
  A4=DEL*Q4
  A5=1+DEL*PC1+A1*A3+A2*A4
  B1=DELS*COS
  B2=DELS*SIN
  B3=DELS*(2+Q4*F(2)-PS1)+B1*A3+B2*A4
  DELF(3)=B3/A5
  DELF(2)=B2-A2*DELF(3)
  DELF(1)=B1-A1*DELF(3)
  GO TO (7,2,2),K
2  PS3=PS2/F(1)
  PC2=PC1/F(1)
  B1=-(DELS*SIN+DEL*COS*DELF(3))*G(3)
  B2=(DELS*COS-DEL*SIN*DELF(3))*G(3)
  B3=DELS*(G(1)*(PS2-PS3*DELF(1))+F(2)+Q4*G(2)-PC1*G(3))+
+ DEL*(PC2*G(3)*DELF(1)+DELF(2)+(PC2*G(1)+PS1*G(3))*DELF(3))
  B3=B3+B1*A3+B2*A4
  DELG(3)=B3/A5
  DELG(2)=B2-A2*DELG(3)
  DELG(1)=B1-A1*DELG(3)
  GO TO (5,5,3),K
3  G3G3=G(3)*G(3)
  G1G1=G(1)*G(1)
  G1G3=G(1)*G(3)
  PC3=PC2/F(1)
  B2=(G3G3*COS+H(3)*SIN)
  B3=G3G3*SIN-H(3)*COS
  B1=-DELS*B2+DEL*(B3*DELF(3)-2*COS*G(3)*DELG(3))
  B2=-(DELS*B3+DEL*(B2*DELF(3)+2*SIN*G(3)*DELG(3)))
  B3=DELS*(PS3*(G1G1*(3/F(1)-2)-H(1))+G1G3*(2*(PC2-PC3)
+ -PS2*DELF(3))+2*(G(2)-PS3*G(1)*DELG(1))+PC2*(G(3)*DELG(1)

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+   +G(1)*DELG(3))+PS1*(G3G3+G(3)*DELG(3))+PS2*H(1)+Q4*H(2)
+   -PC1*H(3)-PC3*G1G1*DELF(3)+DELG(2))+DEL*(PC2*(H(3)*DELF(1)
+   +H(1))+G3G3*(PC1-PS2*DELF(1))+PS1*H(3))
  B3=B3+B1*A3+B2*A4
  DELH(3)=B3/A5
  DELH(2)=B2-A2*DELH(3)
  DELH(1)=B1-A1*DELH(3)
C   . . . . .
C   .   Performing the integration step: V(I+1)=V(I)+DELV(I).   .
C   . . . . .
  DO 4 I=1,3
    4   H(I)=H(I)+DELH(I)
    5   CONTINUE
    DO 6 I=1,3
      6   G(I)=G(I)+DELG(I)
      7   CONTINUE
    DO 8 I=1,3
      8   F(I)=F(I)+DELF(I)
    S0=S1
    RETURN
  END
C
  SUBROUTINE SOLVE(N)
C   . . . . .
C   .   This subroutine does a gaussian elimination on the   .
C   .   augmented matrix of the linear system of equations: .
C   .   [A(N,N)]x{X(N)}={B(N)}, .
C   .   and it does the backward substitution in the solution .
C   .   of the above system of equations. The solution vector .
C   .   is returned in B(N). .
C   . . . . .
  IMPLICIT REAL*8 (A-H,O-Z)
  COMMON/BLOCK1/ DUM(10),B(4),A(4,4),DUMY(3)
  M=N-1
  DO 3 I=1,M
    L=I+1
    DO 2 J=L,N
      S=A(J,I)/A(I,I)
      DO 1 K=L,N
        1   A(J,K)=A(J,K)-S*A(I,K)
        2   B(J)=B(J)-S*B(I)
      3   CONTINUE
    B(N)=B(N)/A(N,N)
    K=N
    DO 5 I=2,N
      L=K
      K=K-1
      S=B(K)
      DO 4 J=L,N
        4   S=S-A(K,J)*B(J)
        5   B(K)=S/A(K,K)
    RETURN
  END

```

Source: Rotenberg, Y., "The determination of the shape of non-axisymmetric drops and the calculation of surface tension, contact angle, surface area and volume of axisymmetric drops", *Ph. D. Thesis*, University of Toronto, 1983