INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

Bell & Howell Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA

UMI
800-521-0600
The Quadrilateral Relation and Line Tension Measurements in Liquid-Liquid-Fluid Systems

by

Pu Chen

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Mechanical and Industrial Engineering
University of Toronto

© Copyright by Pu Chen 1998
The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

L’auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L’auteur conserve la propriété du droit d’auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-41415-9
Abstract

The concept of line tension arises as a natural and necessary extension of the requirements of a fundamental equation when applied to systems with multiphase boundary curves. Despite being a well-defined thermodynamic quantity, line tension had not been quantified satisfactorily. The major problems associated with previous experiments are: (i) the chosen three-phase contact line systems in which necessary contact angles can be readily measured are often complicated, leading to difficulties in experimental control; (ii) the theoretical models used in data analysis are not straightforward, resulting in significant errors in line tension calculation.

In view of these difficulties, study of the simplest possible configuration of three-phase contact line systems, i.e., a liquid lens, was chosen. To find a straightforward correlation between line tension and measurable quantities, the contact line Quadrilateral Relation was first developed, which is a generalization of the classical Neumann triangle relation including line tension effects. The Relation is derived using the minimum free energy principle, and the result is graphically represented by a quadrilateral whose four sides are three surface tensions and a line tension term. From this graphical representation, it is easy to derive various forms
of the Quadrilateral Relation and to evaluate which form(s) would be appropriate for a particular experimental situation. For liquid lens systems, the line tension can be expressed as a function of three surface tensions, diameter of the lens, and two angles at the contact line.

The experimental procedure developed consists of (i) image acquisition (to obtain the cross-sectional image of liquid lenses), (ii) image analysis (to perform edge detection and extract the coordinates of the lens profile), and (iii) numerical analysis (to compute experimental data and generate line tension values according to the properly formulated theoretical expression). For four alkane-water-air systems (hexadecane, tetradecane, dodecane, and decane), the line tension is found to be negative and of the order of $10^6$ J/m. This result is confirmed by both static and dynamic measurements. Furthermore, the absolute value of the line tension is found to increase with increasing hydrocarbon chain-length.
Acknowledgements

I would like to thank my supervisor, Professor A.W. Neu~îln, who introduced me to the interesting and challenging field of surface thermodynamics. He provided me with advice and support throughout my studies and spent time in helping me to improve my English.

I would also like to thank all my past and present colleagues of the Laboratory for Applied Surface Thermodynamics for their help, advice and support. In particular, I would like to thank S.S. Susnar and C. Mak for many stimulating conversations and assistance in conducting experiments throughout this study, A. Joyti, R.M. Prokop, D. Kwok and José M. Alvarez for their friendship and encouragement, and Z. Policova for her valuable advice on many experimental aspects. I would like to express my appreciation to O.I. del Río and A. Amirfazli for their assistance with software problems, C. Mak for compiling Appendix C, and S.S. Susnar for helping in hardware development.

I would also like to express my gratitude to Professor J. Gaydos for insightful discussion on many theoretical issues.

I am indebted to my wife, Qin, and my son, Patrick. Qin’s patience and support have been a real contribution to my study. Patrick’s joyful play has been a constant source of inspiration for me in the pursuit of knowledge.

It is with great appreciation and thanks that I acknowledge the continued and valuable support and encouragement of my parents, Mr. and Mrs. F. Chen.

My financial support was provided by the Provincial Government (Ontario Graduate
Scholarship), the University of Toronto (Open Fellowship) and the Department of Mechanical and Industrial Engineering through the availability of tutorialship and the opportunity to lecture.
# Table of Contents

Abstract ........................................................................................................................... ii

Acknowledgments ........................................................................................................... iv

Table of Contents ........................................................................................................ vi

List of Tables ................................................................................................................ x

List of Figures ............................................................................................................... xi

1. Introduction ............................................................................................................... 1

1.1 Literature Review .................................................................................................. 4
  1.1.1 Drop-Size Dependence of Contact Angles ....................................................... 6
    1.1.1.1 Thin Film Systems ..................................................................................... 6
    1.1.1.2 Liquid-Solid Systems ............................................................................... 8
  1.1.2 Critical Particle Size and Heterogeneous Nucleation ........................................ 9
    1.1.2.1 Critical Particle Size ................................................................................ 10
    1.1.2.2 Heterogeneous Nucleation ...................................................................... 11

1.2 Motivation and Objectives ................................................................................. 13
  1.2.1 Necessity of the Tension .................................................................................. 16
  1.2.2 Objectives of the Thesis ............................................................................... 18

2. Theoretical Development: The Quadrilateral Relation for Three-Phase Contact Lines .............................................................................................................. 19

2.1 Thermodynamics of Surfaces ............................................................................ 20
  2.1.1 The Dividing Surface ..................................................................................... 20
  2.1.2 The Fundamental Equation of Surfaces .......................................................... 22

2.2 Thermodynamics of Lines ................................................................................... 24

2.3 The Quadrilateral Relation for Three-Phase Contact Lines ............................... 26
  2.3.1 Derivation of the Quadrilateral Relation .......................................................... 30
  2.3.2 Variants of the Quadrilateral Relation .............................................................. 35
  2.3.3 Applications of the Quadrilateral Relation to Specific Geometries ................. 40
    2.3.2.1 Arrangement (i): A Liquid Lens ............................................................... 41
2.3.2.2 Arrangement (ii): A Pendant Drop in Contact with a Second Immiscible Liquid ........................................ 42
2.3.2.3 Arrangement (iii): A Cone-Shaped Capillary ................................................................. 45

2.4 Summary ........................................................................................................................................ 48

3. Line Tension Measurement I: An Application of the Quadrilateral Relation to Liquid Lens Systems .................................................................................................................... 50

3.1 Theoretical Analysis .................................................................................................................. 50

3.2 Experimental .................................................................................................................................. 53
  3.2.1 Materials ................................................................................................................................... 53
  3.2.2 Interfacial (Surface) Tensions ................................................................................................. 54
  3.2.3 Experimental design ............................................................................................................... 56
  3.2.4 Image analysis ........................................................................................................................ 59
  3.2.5 Line tension calculation ......................................................................................................... 67

3.3 Results ............................................................................................................................................ 68
  3.3.1 Determination of the Appropriate Sign in Equation (3-1) ....................................................... 68
  3.3.2 Line Tension Results from Static Measurements ................................................................. 69
  3.3.3 Line Tension Results from Dynamic Measurements .......................................................... 72

3.4 Discussion ..................................................................................................................................... 74
  3.4.1 Possible Sources of Error in Line Tension Measurements ...................................................... 74
  3.4.2 Impossibility of Zero Line Tension .......................................................................................... 75
  3.4.3 Quadrilateral Pictograph of a Negative Line Tension ............................................................ 78

3.5 Summary ...................................................................................................................................... 78

4. Line Tension Measurement II: Lens-Size Dependence of Contact Angles in Liquid Lens Systems ........................................................................................................................................ 81

4.1 Theoretical Analysis .................................................................................................................. 82

4.2 Experimental .................................................................................................................................. 86
  4.2.1 Experimental Procedure ......................................................................................................... 86
  4.2.2 Line Tension Calculation ....................................................................................................... 87

4.3 Results ............................................................................................................................................ 88
  4.3.1 Method I: Line Tension from Individual Lenses ...................................................................... 88
    4.3.1.1 Comparison between Advancing and Receding Contact Angles .................................. 93
4.3.2 Method II: Line Tension Calculations from the Lens-Size Dependence of Contact Angles ........................................ 95
4.3.2.1 Line Tension Calculation from a Single Surface Tension and Lens-Size Dependence of Contact Angle .................. 97

4.4 Discussion ......................................................................................................................... 99
4.4.1 Rate Dependence of the Contact Angle and the Line Tension ........................................ 99
4.4.2 Lens-Size Dependence of Contact Angles .......................................................... 100

4.5 Summary .......................................................................................................................... 101

5. Line Tension Measurement III: Chain-Length Dependence of Line Tension in the Alkane-Water-Air System ........... 103

5.1 Experimental ...................................................................................................................... 104
5.1.1 Materials ..................................................................................................................... 104
5.1.2 Interfacial (Surface) Tensions .................................................................................. 105
5.1.3 Image Analysis ......................................................................................................... 106

5.2 Results and Discussion ..................................................................................................... 117
5.2.1 Improvement from the Edge Detection and Image Analysis Scheme ...................... 117
5.2.2 Line Tension as a Function of the Alkane Chain-Length ........................................... 121
5.2.3 Lens-Size Dependence of Line Tension ............................................................... 127

5.3 Summary .......................................................................................................................... 129

6. Summary and Conclusions ............................................................................................... 130

7. Future Work ....................................................................................................................... 134

7.1 Other Three-Phase Contact Line Systems .................................................................... 134

7.2 Combination of Line Tension and Film Tension Measurements ................................ 135

7.3 New Strategy to Determine Contact Angles .................................................................. 136

Appendix A. The Modified Young Equation of Capillarity in Line Tension Measurement ......................................................... 138

Appendix B. Heterogeneous Nucleation Theory and its Application to Line Tension Measurement ....................................................... 140
Appendix C. Programs for Analysing the Liquid Lens Profile and Computing Line Tension ................................................................. 145

C.1 Program I: TLT.MinA ......................................................................................... 145
C.2 Program II: TLT.MaxD ......................................................................................... 167
C.3 Program III: LT.MinA ......................................................................................... 182
C.4 Program IV: LT.MaxD ......................................................................................... 199

Appendix D. Film Tension Measurements ................................................................................................. 213

D.1 Background ........................................................................................................... 213
D.2 Experimental ......................................................................................................... 215
  D.2.1 Materials ........................................................................................................... 215
  D.2.2 Sample Preparation and Experimental Procedure ........................................... 216
  D.2.3 Interfacial Tension Measurement ....................................................................... 218
  D.2.4 Experimental Set-Up ........................................................................................ 218
D.3 Results .................................................................................................................... 219
  D.3.1 Hexadecane-Water ............................................................................................ 221
    D.3.1.1 Static Measurements .................................................................................. 221
    D.3.1.2 Dynamic Measurements ............................................................................ 225
    D.3.1.3 Interfacial Tensions ................................................................................... 235
  D.3.2 Tetradecane-Water ............................................................................................ 236
  D.3.3 Dodecane-Water ............................................................................................... 236
D.4 Discussion ................................................................................................................ 239
D.5 Conclusions ............................................................................................................. 243

References ..................................................................................................................... 244
List of Tables

Table 1-1 Comparison of Line Tension Values

Table 3-1 Line Tension versus Diameters of the Dodecane Liquid Lens

Table 4-1 Linear Regression Results of the Three Derivatives for Leg 3 in Fig. 4-2

Table 4-2 Line Tension $\sigma \, (\mu J/m)$ as calculated by Various Methods

Table 5-1 Interfacial or Surface Tensions (mJ/m²) and Mass Densities (g/cm³) of Alkanes and Water under Mutual Saturation, at $25^\circ$C

Table 5-2 Line Tensions of Alkane-Water-Air Three-Phase Contact Lines

Table 5-3 Line Tension versus the Diameter of a Dodecane Liquid Lens on the Air-Water Surface

Table D-1 Interfacial Tensions and Film Tensions (mJ/m²) from Static Measurements
List of Figures

Fig. 1-1 (a) Profile of a liquid lens floating on the surface of a second immiscible liquid. $\gamma_1$ and $\gamma_2$ are the surface tensions of the floating liquid and the base liquid; $\gamma_{12}$ is the interfacial tension between the two liquids. $\kappa$ is the curvature of the three-phase contact line, in the horizontal direction. (b) The Liquid lens is pulled up with a capillary so that the the contact line is above the horizontal surface of the base liquid.

Fig. 2-1 Schematics of (a) a liquid lens and (b) a blow-up of a region of the three phase contact line. $\gamma^{(1)}$, $\gamma^{(2)}$ and $\gamma^{(3)}$ denote the surface tensions of the interfaces between bulk phases $V_3$ and $V_1$, $V_1$ and $V_2$, and $V_2$ and $V_3$, respectively. $m_i$ and $n_i$ ($i=1,2,3$) depict the tangential and normal directions of the interfaces. $\sigma \kappa$ represents the line tension $\sigma$ contribution to the force balance at a point of the contact line with $t$ as the tangent. $\delta r$ denotes an arbitrary variation in the position of the point.

Fig. 2-2 Schematics of (a) a side-view of a three phase contact line, and (b) a quadrilateral which is composed of three surface tensions $\gamma^{(1)}$, $\gamma^{(2)}$, and $\gamma^{(3)}$, and a line tension contribution $\sigma \kappa$.

Fig. 2-3 Schematic of a pendant drop in contact with a second liquid. $\gamma^{(1)}$ and $\gamma^{(2)}$ are the surface tensions of the pendant liquid and the second liquid; $\gamma^{(3)}$ is the interfacial tension between the two liquids; $\sigma \kappa$ represents the line tension contribution to the quadrilateral relation.

Fig. 2-4 Schematic of a cone-shaped capillary. $\gamma^{(1)}$, $\gamma^{(2)}$ and $\gamma^{(3)}$ are the surface tensions of liquid-fluid (air), solid-fluid and solid-liquid; $\sigma \kappa$ represents the line tension contribution to the quadrilateral relation; $P_N$ is the normal stress component of solid surface.

Fig. 3-1 Schematic of a pendant/ floating liquid lens in contact with a second liquid. $\gamma^{(1)}$ and $\gamma^{(2)}$ are the surface tensions of the pendant liquid and the second liquid; $\gamma^{(3)}$ is the interfacial tension between the two liquids; $\sigma \kappa$ represents the line tension contribution to the quadrilateral relation. Contact angles $\theta_1$ and $\theta_2$ are measured in the experiment, which can be used to calculate necessary contact angles in Eq. (3-1) to obtain line tension: The angles in the quadrilateral relation can be obtained from $\theta_{kl} = \theta_1$, $\theta_{lk} = \pi - \theta_2$, and $\theta_{12} = \pi - \theta_1 + \theta_2$.

Fig. 3-2 Experimental setup for surface tension measurement under mutual saturation condition.
Fig. 3-3  Schematic of the experimental setup. The pendant/floating drop of dodecane is supported by a Teflon capillary (needle). Upon lowering the needle with a stepper motor, a three-phase contact line is formed among dodecane, water and air.

Fig. 3-4  An image acquired for the cross section of a pendant/floating liquid lens of dodecane in contact with water.

Fig. 3-5  A drop profile acquired from an image (as in Fig. 3-4) through an image detection scheme. The distance between A and A' is 6.69 mm, representing the diameter of the liquid lens. The bottom picture is an enlargement of the portion enclosed by a rectangle in the top picture, where 30 pixel points along each of the interfaces AB and AC, starting from the intersection point A, are used in the linear curve-fit.

Fig. 3-6  The slope of the fitted straight line to the interface AB in Fig. 3-5 against the number of pixel points used in the fit, which indicates a steady value of the slope, also with a relatively small fluctuation, in the region of 20 to 40 pixel points. The errors associated with each slope are the standard errors in the linear curve-fit.

Fig. 3-7  The slope of the fitted straight line to the interface AC in Fig. 3-5 against the number of pixel points used in the fit, which indicates a steady value of the slope, also with a relatively small fluctuation, in the region of 20 to 40 pixel points. The errors associated with each slope are the standard errors in the linear curve-fit.

Fig. 3-8  The diameter, two contact angles corresponding to the slopes of the air-dodecane interface and air-water interface (relating to the contact angles in Fig. 3-1 by \( \theta_1 = \theta_{kl} \) and \( \theta_2 = \theta_{kl} + \theta_{12} - \pi \), and line tension plotted as a function of time up to 6 min. The values of the diameter and line tension are entered into Table 3-1.

Fig. 3-9  The diameter, two contact angles corresponding to the slopes of the air-dodecane interface and air-water interface, and line tension versus time in a dynamic mode, where the drop-size is controlled by adjustment of the drop volume of dodecane. The intercept at time zero of the fitted straight line to the line tension values yields a line tension of \( -1.39 \pm 0.05 \times 10^{-6} \) J/m (0.05 is the standard error limit in the linear regression), comparable to the values in the static experiment (Table 3-1).

Fig. 3-10 Quadrilateral diagram with four sides representing three surface (interfacial) tensions (dodecane-air, water-air and dodecane-water) and a line tension contribution (dodecane-water-air three-phase contact line) in proportion, using the contact angles obtained from the actual experiment (corresponding to Fig. 3-4). Because of the minuteness of the line tension relative to the surface tension, the resulting quadrilateral diagram looks like a classical Neumann triangle (top portion of the figure). With a magnification of 100 times, the contribution of this
small, negative line tension can be seen, which constitutes the fourth side of the quadrilateral (bottom portion of the figure). The negative line tension contribution to the quadrilateral diagram results in crossing of the two surface tension sides, although the topology of the quadrilateral remains intact.

Fig. 4-1 The diameter, two contact angles defining the slopes of the dodecane-air interface and water-air interface (cf. Fig. 3-1), and line tension plotted as a function of time, for individual static lenses.

Fig. 4-2 The diameter, two contact angles defining the slopes of the dodecane-air interface and water-air interface, and line tension versus time. The lens size is varied by adjustment of the drop volume of dodecane at a rate of 1 min per cycle, i.e., 92.2 μm/s of the contact line movement. The intercept at time zero of the fitted straight line yields a line tension of -1.4 ± 0.1 × 10⁻⁶ J/m (0.1 is the standard error limit in the linear regression).

Fig. 4-3 The diameter, two contact angles defining the slopes of the dodecane-air interface and water-air interface, and line tension versus time. The lens size is varied by adjustment of the drop volume of dodecane at a rate of 3.5 min per cycle, i.e., 23.2 μm/s of the contact line movement. The intercept at time zero of the fitted straight line yields a line tension of -1.3 ± 0.1 × 10⁻⁶ J/m (0.1 is the standard error limit in the linear regression). The slight decline in line tension is due to gradual accumulation of impurities at the interface and the contact line regions.

Fig. 4-4 The diameter, two contact angles defining the slopes of the dodecane-air interface and water-air interface, and line tension versus time. The lens size is varied by adjustment of the drop volume of dodecane at a rate of 16 min per cycle, i.e., 4.75 μm/s of the contact line movement. The intercept at time zero of the fitted straight line yields a line tension of -1.1 ± 0.1 × 10⁻⁶ J/m (0.1 is the standard error limit in the linear regression). The slight decline in line tension with time is due to gradual accumulation of impurities at the interface and the contact line regions.

Fig. 4-5 The lens-size dependence of contact angle at three different speeds of advancing and receding the contact line (a) 1 min per cycle, (b) 3.5 min per cycle, and (c) 16 min per cycle. At lower speeds (b) and (c), the difference between the advancing contact angle and the receding contact angle is attributed to gradual accumulation of impurities to the interfaces and the three-phase contact line.

Fig. 5-1 A typical image acquired of the cross section of a pendant/floating liquid lens of alkane on the water surface.

Fig. 5-2 The intensity or graylevel of the pixel change across the edge of the liquid lens from higher values on the bright background of the image to lower values inside
the dark image. The Sobel values reach a maximum at the pixel location that corresponds to the edge of the lens at \( x = 267 \). After refining the location of the edge to sub-pixel resolution, \( x = 266.9 \).

**Fig. 5-3** A drop profile (top) acquired from the image in Fig. 5-1 through the edge detection scheme with sub-pixel resolution. The distance between \( A \) and \( A' \) is 6.8 mm, representing the diameter of the liquid lens. The bottom picture is an enlargement of the portion enclosed by the rectangle in the top picture, where 30 pixel points along each of the interfaces AB and AC, starting from the intersection point \( A \), are used in the linear curve-fit (see text).

**Fig. 5-4** A drop profile (top) acquired from the image in Fig. 5-1 through the edge detection scheme with pixel resolution. The distance between \( A \) and \( A' \) is 6.7 mm, representing the diameter of the liquid lens. The bottom picture is an enlargement of the portion enclosed by the rectangle in the top picture, where 30 pixel points along each of the interfaces AB and AC, starting from the intersection point \( A \), are included. Note that two steps occur in the lower portion of the curve (bottom picture) because of the limitation of pixel resolution in edge detection.

**Fig. 5-5** Illustration of the procedure for locating the intersection point \( A \): 1) finding the maximum distance, \( d \), of a point on the interfaces to the straight line BC, and 2) finding the smallest angle, \( \theta \), between the two fitted straight lines, one to the left and the other to the right of a point which is within the range of ten pixel points away from the point \( A \).

**Fig. 5-6** The contact angles \( \theta_1 \) and \( \theta_2 \) obtained from a linear curve-fit as a function of the number of the points used in the fitting procedure, which indicates a steady value, also with a relatively small fluctuation, in the region of 20 to 40 points. The errors associated with each slope are the standard errors in the linear curve-fit. In addition, the correlation coefficients associated with the curve-fits appear to reach the plateau when using 20 points in the fitting procedure, and a further increase in the number of the points does not result in a significant increase in the correlation coefficient value.

**Fig. 5-7** The diameter, two contact angles, and line tension versus time in a dynamic experiment for a dodecane liquid lens on the water surface. The results are obtained from the image analysis scheme described in the text. Compared with the results in Fig. 5-8 (see below), which are obtained from the original image analysis scheme used in Chapter 3, this present version of image analysis, including edge detection with sub-pixel resolution, significantly reduces the scatter in the contact angles and hence in the line tension.

**Fig. 5-8** The diameter, two contact angles, and line tension versus time in a dynamic
experiment for a dodecane liquid lens on the water surface. The results are obtained from the original image analysis scheme used in Chapter 3 with pixel resolution in edge detection. Note that the data show a relatively large scatter, compared with those in Fig. 5-7.

Fig. 5-9a  The diameter, two contact angles, and line tension plotted as a function of time up to 60 s in the static mode of the experiment for hexadecane. The errors are all at the 95% confidence level. The scatter in the data appears to increase with decreasing alkane chain-length (from Figs. 5-9a to 5-9d).

Fig. 5-9b  The diameter, two contact angles, and line tension plotted as a function of time up to 60 s in the static mode of the experiment for tetradecane. The errors are all at the 95% confidence level. The scatter in the data appears to increase with decreasing alkane chain-length.

Fig. 5-9c  The diameter, two contact angles, and line tension plotted as a function of time up to 60 s in the static mode of the experiment for dodecane. The errors are all at the 95% confidence level. The scatter in the data appears to increase with decreasing alkane chain-length.

Fig. 5-9d  The diameter, two contact angles, and line tension plotted as a function of time up to 60 s in the static mode of the experiment for decane. The errors are all at the 95% confidence level. The scatter in the data appears to increase with decreasing alkane chain-length.

Fig. B-1  Cap-shaped nucleus situated on the surface of a planar substrate.

Fig. C-1  Sample image of a liquid lens system.

Fig. C-2  Sample profile file. These are the edge coordinates of Fig. C-1. The file has been truncated to fit onto a page.
   Filename: s055.02.plt

Fig. C-3  Example of a typical input file for TLT.MinA or TLT.MaxD.
   Filename: input

Fig. C-4  Example of a typical output file for TLT.MinA.
   Filename: output

Fig. C-5  Example of a typical output file for TLT.MaxD
   Filename: output
Fig. C-6 Example of a typical input file for LT.MinA or LT.MaxD. This is the input file used in the sample analysis.

Filename: *input*

Fig. C-7 Example of a typical output file for LT.MinA. These are the results of the sample analysis.

Filename: *output*

Fig. C-8 Example of a typical output file for LT.MaxD

Filename: *output*

Fig. D-1 Experimental set-up for film tension measurements. To form a film, the capillary is raised up into the alkane phase by a micromanipulator positioned above the cuvette (step 1 to step 2). Then, using a micro-syringe connected to the other end of the capillary, a minute amount of alkane is withdrawn into the capillary (step 2). Finally, the capillary is lowered down into the water phase, and an air bubble coated with an alkane film is formed at the tip of the capillary by pumping air through the tube slowly (step 3).

Fig. D-2 Schematic of the experimental set-up for tension measurements using ADSA-P.

Fig. D-3 A typical image and its profile (right) of an air bubble coated with a hexadecane film, inside the water phase. The film tension analysed by ADSA-P from this single image is 80.60 mJ/m². It is noted that the profile is smooth.

Fig. D-4 A typical static hexadecane film tension measurement over a time span of 5 min, which results in a film tension of 80.60 ± 0.01 mJ/m² at the 95% confidence level.

Fig. D-5 A typical image of an air bubble after rupture of hexadecane film and its profile. The interfacial tension from this single image is 72.70 mJ/m². Note that two kinks appear in the neck region of the cross-sectional profile of the air bubble, as indicated by arrows, indicating the presence of a ring of hexadecane.

Fig. D-6a Consecutive images of an air bubble showing the hexadecane film rupture at $t = 0.64$ s. Before film rupture, the tension is approximately 80.0 mJ/m²; after film rupture, the tension is approximately 72.6 mJ/m². The former represents film tension and the latter interfacial tension; the error limits associated with each tension value represent 95% confidence limits. The image at $t = 0.64$ s is blurred due to vibration accompanying film rupture, and hence it cannot be analysed by ADSA.

Fig. D-6b Profiles of the consecutive images (Fig. D-6a) of an air bubble showing the hexadecane film rupture at $t = 0.64$ s. The image at $t = 0.64$ s is blurred due to
vibration accompanying film rupture, and hence it cannot be analysed by ADSA.

Fig. D-6c The neck regions of images at $t = 0.32$ and $3.15$ s (in Fig. D-6b) are magnified, where a smooth profile is seen for the bubble with film (A), but kinks appear after film rupture (B).

Fig. D-7 Dynamic tension measurement for the hexadecane-water system; the air bubble surface area is increased at a rate of $3.05 \pm 0.02$ mm$^2$/s, corresponding to a volume increase at a rate of $2.12 \pm 0.02$ mm$^3$/s. (The errors represent the standard deviations from the linear regression procedure). An approximately $7.4$ ml/m$^2$ sudden drop in tension accompanies film rupture. A linear curve fit to the tension values before film rupture is also shown.

Fig. D-8 Dynamic tension measurement for the hexadecane-water system, similar to that in Fig. D-7, except that the air bubble surface area is increased at a rate of $0.61 \pm 0.01$ mm$^2$/s, corresponding to a volume increase at a rate of $0.44 \pm 0.01$ mm$^3$/s. The decrease in tension accompanying film rupture is again $7.4$ ml/m$^2$.

Fig. D-9 Dynamic tension measurement for the hexadecane-water system, similar to that in Fig. D-7, except that the air bubble surface area is increased at a rate of $0.52 \pm 0.02$ mm$^2$/s, corresponding to a volume increase at a rate of $0.36 \pm 0.01$ mm$^3$/s. The tension decrease upon film rupture is also $7.4$ ml/m$^2$.

Fig. D-10 Dynamic tension measurement for the dodecane-water system, similar to that in Fig. D-7; the air bubble surface area is increased at a rate of (a) $1.04 \pm 0.01$ mm$^2$/s, (b) $0.90 \pm 0.03$ mm$^2$/s and (c) $0.84 \pm 0.02$ mm$^2$/s. Film rupture is accompanied by a decrease in tension of approximately $4.0$ ml/m$^2$. A linear curve fit to the tension values before film rupture is also shown in (a) and (b). In (c) a change in slope occurs at about $76$ ml/m$^2$, and two linear curve fits to the two branches are shown.

Fig. D-11 Schematic of a thick alkane layer on an air bubble with a relatively small surface area at the beginning of an expansion experiment. The two surface tension vectors, of the inner and outer surfaces of the alkane layer, are not parallel, resulting in a smaller total tension value than the sum of water-alkane interfacial tension and alkane surface tension.
Chapter 1

Introduction

The concept of line tension and its definition arise as a natural and necessary extension of the requirements of a fundamental equation [1] when applied to systems with multiphase boundary curves. Thus, just as surface tension is the two-dimensional analogue of bulk pressure, so is line tension the one-dimensional analogue of surface tension. Line tension, denoted by the symbol $\sigma$, is defined in complete analogy to the accepted thermodynamic definitions for bulk pressure and surface tension; it represents the excess free energy per unit length of a multiphase boundary curve and has the units of force (e.g., N or J/m). If $\sigma$ is positive, it operates so as to fold-in surface regions along the boundary where several surfaces meet and to constrict the length of the contact line. If $\sigma$ is negative, it tends to expand the length of the contact line [2-4].

Practical applications of line tension can be found in many industrial and biological processes, such as nucleation, condensation [4-30], stabilization of emulsions and foams by fine particles [12-15,31-34], spray paint, ink jet printing, molten metal casting, deposition and retention of inhaled particles [35-38], microbial and cell adhesion [2,12-15], and other similar processes involving moving contact lines. For instance, in dropwise condensation and nucleation, a positive line tension may pinch-off the droplet from the solid surface in an attempt to reduce the contact line length. If this occurs, one would expect that the dropwise versus the filmwise mode of heat transfer would be enhanced. Depending on the magnitude
of line tension and the size of the system or characteristic length scale, line tension may have an significant impact on these processes [2].

In the deposition of spherical particles in the human respiratory tract [35], the fate of particles deposited on the airway surfaces will depend on physical and chemical properties of the particle, and mucociliary clearance mechanisms. Particles will initially be wetted to a certain extent by the surfactant film, causing particle displacement towards the epithelium by surface forces and, depending on the surface tension, will become totally submerged [36,37]. The physical forces affecting displacement of fibres and other particles through the air-water interface and their interaction with cell membranes will likely be affected by the shape and size of particles. The description of particle-surface film interactions by surface forces [38] is incomplete unless line tension is included. The modification of the contact angle by line tension may promote or hinder particle wetting and displacement into the aqueous phase. It has been found [39] that particles of irregular shape, especially with sharp edges, will resist the immersion into a liquid because of the line tension effect. The particles tend to float such that the three-phase contact occurs at an edge. Therefore, line tension effects must be considered for the interaction between the air-water interface and particles of different size, shape and surface characteristics, and for particle displacement at the airway surface.

However, despite line tension being a well-defined thermodynamic quantity [40-42] and having numerous applications, there are still a large number of problems associated with determining both the magnitude and sign of the line tension [2,3]. From both theoretical and experimental points of view, line tension has been ascribed a positive sign as well as a negative one, and the order of magnitude has been reported ranging from $10^{-12}$ to $10^{-5} \text{ J/m}$ [4-
Selected line tension values and the methods used are listed in Table 1-1. There is little consensus on the value of line tension, although studies have been conducted since the mid-nineteen thirties. It may be expected that different material systems would have different line tension values, the question would be how much these values can differ. Can they differ by seven orders of magnitude? Further, can they change the sign? In fact, these significant discrepancies in line tension value are often reported for similar material systems [4-34,54-63] (Table 1-1). It is necessary to re-evaluate these line tension measurements and the methodologies employed.

Table 1-1 Comparison of Line Tension Values

<table>
<thead>
<tr>
<th>Researcher (s)</th>
<th>Arrangement</th>
<th>Value (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaydos et al. [55]</td>
<td>Sessile Drop&lt;sup&gt;a&lt;/sup&gt;</td>
<td>+2 to 6 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
</tr>
<tr>
<td>Li et al. [56]</td>
<td>Sessile Drop&lt;sup&gt;b&lt;/sup&gt;</td>
<td>+1 to 3 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
</tr>
<tr>
<td>Langmuir [43]</td>
<td>Liquid Lens&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-6.2 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
</tr>
<tr>
<td>Torza, Mason [54]</td>
<td>Emulsion Bubbles&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-6 to +58 x 10&lt;sup&gt;-9&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ivanov et al. [12]</td>
<td>Bubble in Surfactant Soln.&lt;sup&gt;e&lt;/sup&gt;</td>
<td>-12 to +3 x 10&lt;sup&gt;-8&lt;/sup&gt;</td>
</tr>
<tr>
<td>Harkins [45]</td>
<td>Liquid Lens&lt;sup&gt;f&lt;/sup&gt;</td>
<td>+1 to 10 x 10&lt;sup&gt;-11&lt;/sup&gt;</td>
</tr>
<tr>
<td>Kolarov et al. [16]</td>
<td>Common Black Film&lt;sup&gt;g&lt;/sup&gt;</td>
<td>-1.7 x 10&lt;sup&gt;10&lt;/sup&gt;</td>
</tr>
<tr>
<td>Churaev et al. [51,53]</td>
<td>Thin Film&lt;sup&gt;h&lt;/sup&gt;</td>
<td>-1 x 10&lt;sup&gt;-10&lt;/sup&gt;</td>
</tr>
<tr>
<td>Platikanov et al. [33,34]</td>
<td>Newton Black Film&lt;sup&gt;i&lt;/sup&gt;</td>
<td>-0.8 to +1.2 x 10&lt;sup&gt;-10&lt;/sup&gt;</td>
</tr>
<tr>
<td>de Feijter, Vrij [65,66]</td>
<td>Thin Film&lt;sup&gt;j&lt;/sup&gt;</td>
<td>-10&lt;sup&gt;12&lt;/sup&gt;</td>
</tr>
<tr>
<td>Scheludko [21,23]</td>
<td>Heterogeneous Nucleation&lt;sup&gt;k&lt;/sup&gt;</td>
<td>-1.9 x 10&lt;sup&gt;10&lt;/sup&gt;</td>
</tr>
<tr>
<td>Navascues et al. [7,8]</td>
<td>Heterogeneous Nucleation&lt;sup&gt;l&lt;/sup&gt;</td>
<td>-4 to +0.5 x 10&lt;sup&gt;-10&lt;/sup&gt;</td>
</tr>
</tbody>
</table>
Notes: The materials used for each type of experiment are as follows: a) alkanes on Teflon (FEP); b) dodecane and ethylene glycol on FC-721 (a fluorocarbon), Zonyl FSC (a fluorosurfactant) and DDOA (dimethyldioctadecylammonium); c) tetradecane on water; d) oil in water; e) air bubbles in sodium dodecyl sulfate aqueous solutions; f) nonvolatile oil on water; g) sodium dodecyl sulfate added in an NaCl aqueous solution; h) surfactant films; i) sodium lauryl sulfate added in an NaCl aqueous solution; j) soap films; k) water on n-hexadecane, 2-bromotoluene, decalin and tetrachloroethylene; l) water on mercury and chromous iodide on quartz. Further discussion of some of these experiments is given below.

1.1 Literature Review

The determination of line tension has been pursued theoretically as well as experimentally. Gibbs [50] is the first to speculate that line tension might have a negative value and gave an example of two soap-bubbles adhering to each other. Harkins [45] pointed out that a given amount of material had a higher energy in an edge than anywhere else. He further used a simplified molecular theory and calculated that the line tension of the edge of a lens of oil containing a single row of molecules should be positive and on the order of $10^{-11}$ to $10^{-10}$ J/m [45]. Churaev et al. [51] produced calculations for the line tension of a thin film on a bulk liquid, and their results were on the order of $-10^{-9}$ to $-10^{-10}$ J/m. They suggested that the sign of line tension may change from negative to positive as the profile of the transition zone between the wetting film coating a liquid surface and the meniscus of the bulk liquid changes from gently to steeply sloping [51]. Clearly, significantly different results were
obtained.

In principle, line tension can be estimated using statistical mechanics, thereby considering the molecular interactions of the three bulk phases in the contact line region [69]. However, theoretical calculations at present do not resolve the issue completely; the value of line tension has been found to be sensitive to the model used for the calculation [4,70,71]. Particularly, because of the lack of knowledge about the molecular interactions at short range, the models based on statistical thermodynamics often lead to extremely complicated expressions and do not give exact solutions. This situation is similar to that in two-phase equilibrium, where exact solutions for surface tension are available only in some special cases [4,70,71].

These difficulties in theoretical estimation of line tension make the experimental determination necessary and important. Because of the small magnitude of line tension, experimental determination of this quantity has proven to require considerable ingenuity in experimental design [46,47]. Moreover, line tension cannot be measured directly; therefore, indirect approaches must be adopted. There are two general types of approaches: (a) measuring the geometric parameters, such as contact angles, of a three-phase contact line configuration, and inferring the line tension through theoretical correlations [12-15,33,43,46,47,54-68]; (b) observing the critical size of a bubble (or a solid particle) or measuring critical supersaturation for the condensation of vapour on a substrate, and again obtaining the line tension through theoretical correlations [6-8,18-32].
1.1.1 Drop-Size Dependence of Contact Angles

A number of geometric arrangements of three-phase contact line systems have been investigated, where geometric parameters are evaluated and related to line tension [12-15,33,43,46,47,54-68]. In these measurements, the essential information to obtain is the drop-size dependence of contact angles. Cases may or may not involve films.

1.1.1.1 Thin Film Systems

A typical film system consists of a small circular Newton black film (coated on a small bubble, separating two gas phases) in contact with a bulk phase of aqueous solution, from which the film is generated [65]. The presence of line tension is expected along the contact line between the black film and the bulk liquid [33,67]. The drop-size dependence of contact angles is measured, from which information about film tension and line tension can be extracted through theoretical correlations. Platikanov et al. [33,34] found that the value of line tension was of order of $10^{-10}$ J/m and dependent on the salt concentration. In a system consisting of sodium dodecyl sulfate and sodium chloride (NaCl) solutions, the line tension was found to change the sign, from positive to negative as the NaCl concentration increased. The NaCl concentration at the transition was approximately 0.36 M [4,33].

Based on similar thin film systems, Kralchevsky et al. [13-15] found line tension to be of the order of $10^{-8}$ J/m. However, their line tension values depend on not only the salt concentration but also the curvature of the contact line between the film and the bulk solution.
There are two points worth noting: First, there is an apparent discrepancy between the line tension values in the work of Kralchevsky et al. and that of Platikanov et al.; the former exceed the latter by two orders of magnitude. There have been explanations from both groups [72,73]; however, one important issue that has not been dealt with is the dynamic effect in their systems. It may well be that equilibrium has never been reached in their experiments with Newton black films; thus, the theoretical relations based on the assumption of equilibrium may seriously deviate from the actual experimental conditions. It is known that surface properties, such as surface tension, of a surfactant solution will be time-dependent before the system reaches or approaches equilibrium, and the equilibration can be as long as hours [74-77]. Therefore, considerable effort has to be put into the study of dynamic effects before reliable line tension data may be claimed from these film systems.

The second point to be noted is the result of the curvature dependence of line tension. This result was obtained from a dynamic film system while the contact line was changing in size. One has to differentiate between the effect due to dynamic status and that due to the curvature of the contact line before drawing any conclusion with respect to line tension variations. However, current literature reports have not been able to resolve this issue. On the other hand, from a thermodynamic point of view, line tension has been tacitly assumed to be independent of curvature, just as surface tension is independent of curvature under the theory of Gibbs' moderate curvature [2,78-80]. In a proper thermodynamic analysis, line tension appears explicitly in the Young equation or the Neumann triangle relation (i.e., the mechanical equilibrium conditions for dividing lines) at the lowest level of generality, i.e., the same level in the hierarchy at which the classical Laplace equation is the appropriate
equilibrium condition. Since the theoretical relations developed [13-15] is based on the moderate curvature hypothesis, i.e., curvature effects are neglected in the mechanical equilibrium conditions, the line tension results should be curvature independent. The curvature-dependent line tension reported, on the other hand, would indicate some defects existing in these experiments and/or theoretical analyses. In situations where line tension would depend on curvature, more general equilibrium conditions would apply [78] (see also chapter 2).

1.1.1.2 Liquid-Solid Systems

In the methods of the drop-size dependence of contact angles for measuring line tension, there exist other approaches, which do not involve thin films. For example, by studying liquid drops placed on a liquid-liquid interface, modified by a monolayer, Schürch et al. were able to measure line tension and found its value to be on the order of $10^{-8}$ J/m [46,47]. Recently, by measuring the contact angles of liquids on a solid surface, Gaydos and Neumann [55], and Li and Neumann [56] found line tension to range from $1 \times 10^{-6}$ to $6 \times 10^{-6}$ J/m. In these studies, the method employed is based on measurement of the drop-size dependence of contact angle of a liquid on a solid surface, or a surface that has little deformability and can be approximated to be a rigid, planar surface [46,47,55,56].

The line tension is related to the contact angle information through the modified Young equation of capillarity [78]. If the substrate is a horizontal, planar, smooth, homogeneous, and rigid surface, the sessile drop will be axisymmetric and the three-phase
contact line will be a circle. Thus, the line tension can be obtained through the slope of \( \cos \theta \) vs. \( 1/R \) (\( \theta \) is the contact angle and \( R \) the radius of curvature of the contact line) (see Appendix A).

However, by measuring the drop-size dependence of contact angle of sessile drops on solid surfaces, both positive and negative line tensions have been reported [46,47,54-64,68]. Moreover, the order of magnitude of the line tensions ranged from \( 10^{-11} \) to \( 10^{-5} \) J/m [46,47,54-64,68]. It is difficult to understand that line tension can be either positive or negative and that it can change over several orders of magnitude among chemically and energetically similar solid-liquid systems.

It has been speculated that line tension values may be influenced by the vapour environment [63] or by the difficulties in interpreting the contact angles measured on solid surfaces where contact angle hysteresis exists [81-85]. Contact angle phenomena are complicated; many factors can play a role, including surface chemical reaction, solid dissolution and swelling, and liquid retention upon the receding of contact lines [86,87]. Unless all these factors are considered, a sensible contact angle interpretation may not be achieved. Recently, a careful study of several organic liquids on a Self-Assembled Monolayer (SAM) surface was conducted [86], and a positive line tension of the order of \( 10^{-6} \) J/m has been obtained for this liquid-solid-vapour system.

1.1.2 Critical Particle Size and Heterogeneous Nucleation

The second general type of approach for measuring line tension is to observe the
critical size of a bubble (or a solid particle) or to measure critical supersaturation for the condensation of vapour on a substrate [6-8,18-32]. Compared with the methods using the drop-size dependence of contact angles, these two approaches require a much more complicated theoretical correlation between the line tension and the measurable quantities.

1.1.2.1 Critical Particle Size

In the method of observing the critical size of a bubble or particle, only positive line tension can be measured. This method is based on the fact that a particle is hindered by a force or energy barrier due to positive line tension when the particle is pressed into a fluid-liquid interface. If the particle size, \( R \), is small, the line tension effect, \( \sigma/R \), is significant [31,32]. The external force (e.g., gravity) must overcome this force barrier before pressing the particle into the interface. There exists a critical size of the particle below which the particle cannot penetrate into the interface. Using this method, a line tension of \( 10^{-10} \) J/m was found from a system consisting of small glass spheres in a \( 10^{-2} \) M aqueous octyltrimethylammonium bromide solution [31].

However, there is a certain degree of ambiguity in determination of the critical size of particles, and statistical distributions of particles in contact with the interface and those without such contact have to be obtained and analysed in the measurement. This makes the method not only tedious but also less accurate. Furthermore, in deriving the theoretical relation between line tension and relevant measurable quantities (e.g., surface tension, contact angle, and the critical particle size), the deformation of the interface due to the particle (with
different sizes) penetration has not been dealt with satisfactorily, thereby leading to errors in line tension calculation [34].

1.1.2.2 Heterogeneous Nucleation

Another method categorized into this second general type of approach for obtaining line tension is to measure critical supersaturation for the condensation of vapour on a substrate, i.e., heterogeneous nucleation [6-8,18-30]. It is anticipated that a nucleation process will be sensitive to the presence of line tension because of the extremely small size of nuclei of the new phase. In particular, reduction in critical supersaturation and a change in nucleation mechanism from barrier to barrierless condensation are expected when line tension is negative. Since the actual quantity experimentally determined is critical supersaturation, an essential part of this method is a theoretical correlation between this measurable quantity and line tension.

The existing theoretical analysis [6-8,18-30] starts out with an expression of the free energy of formation for a cap-shaped nucleus on a planar solid substrate (Appendix B). This free energy is the grand canonical potential [1] (although some authors [17-22] used this free energy without identifying it as the name of grand canonical potential). To obtain explicit expressions for the free energy terms, the geometry of the nucleus droplet is necessarily idealized as a portion of a sphere. Then, the free energy of nucleus formation can be expressed as a function of the radius of curvature of the spherical surface of the nucleus and the contact angle of the nucleus on the solid substrate. The critical contact angle $\theta$ and radius
of curvature \( r \) are obtained through an analysis of the equilibrium stability conditions for the nucleus droplet [6-8,18-30]. These critical values are then related to the supersaturation, defined as \( P_v / P_e \) (\( P_v \) is the vapour pressure of a supersaturation system, and \( P_e \) that of a saturated one), through the Gibbs-Thomson equation. The nucleation rate is given by the Volmer equation [88] (Appendix B).

Through the theoretical analysis, the following predictions can be made [6-8,17-21]: (i) the nucleation barrier will be modified by the presence of line tension and hence the nucleation rate will be affected; (ii) the nucleation contact angle will be smaller when line tension is negative, and the nucleation contact angle will be larger when line tension is positive; (iii) there will be a limit to the minimum size of the nucleus if line tension is positive; (iv) spontaneous (i.e., barrierless) nucleation of cap-shaped droplets is possible if line tension is negative; (v) homogeneous nucleation will be more favourable than heterogeneous one when positive line tension becomes sufficiently large.

However, there are several drawbacks in the above theoretical analysis for heterogeneous nucleation: First, the use of grand canonical potential is appropriate only when a (thermodynamic) system is under constant temperature and chemical potentials [1,78]; however, in the nucleation experiments reported [6-8,18-30] this is not the case. These nucleation experiments were conducted under the condition of varying chemical potentials due to the variation in vapour pressure. The appropriate free energy form in these systems would be the Gibbs free energy, which is very different from the grand canonical potential. Second, so far, complete analysis has been carried out only for spherical, cap-shaped nuclei; real nuclei may not assume a spherical shape due to the boundary condition at the three-phase
contact line. Considering the small magnitude of line tension, such a spherical approximation may well smear the possible line tension effects. Third, in order to calculate a line tension value, several theoretical steps are needed, and the result is expected to be sensitive to the values used as input parameters. Fourth, a very sensitive tool for observing the onset of nuclei is required as the nucleus embryos are small. Finally, as the nucleus embryos are so small, curvature effects may have to be considered in the three-phase contact line system.

With all these questions, it may not be surprising that discrepancies exist in the line tension value obtained from similar nucleation experiments [7,8,18,24-27,30]. For example, in water vapour nucleation on a hexadecane substrate, Scheludko et al. [17-22] reported a line tension value ranging from \(-3.2 \times 10^{-10}\) to \(-1.6 \times 10^{-10}\) J/m, while Mitchell [30] gave a value of several orders of magnitude smaller, yet Hwo et al. [25,26] reported a zero line tension.

1.2 Motivation and Objectives

From the above literature review, it is apparent that further studies are needed to provide a better understanding of line tension and the parameters that affect its magnitude and sign. One of the problems associated with the experiments mentioned above is that the chosen three-phase line system is often complicated, and the theoretical model used in the data analysis is not always straightforward. For example, in the measurement of the drop-size dependence of contact angle on a solid surface, both negative and positive line tension have been claimed [57-68, 81-83]. One possible explanation for the discrepancies observed in the measured values of line tension is the imperfection of the solid surfaces used in the
experiments: surface roughness, heterogeneity (and hence contact angle hysteresis), surface deformability and reactivity can all alter the contact angles from the values on the corresponding ideal solid surfaces. Unless advancing contact angles are used, one cannot use the modified Young equation to interpret the measurement and estimate line tension [86]. For three-phase contact line systems involving surfactant or monolayer formation, the equilibration of surface phases and further line phases becomes important and can often complicate measuring equilibrium line tension [12-15].

Recently, careful experiments have been conducted on liquid-solid-air systems, where reliable contact angle data were collected [86]. From these experiments, a line tension was found to be positive and of the order of $10^{-6}$ J/m. To study the line tension in liquid-liquid-air systems, a relatively simple three-phase contact line configuration is needed. A liquid lens is probably the simplest system consisting of a three-phase contact line, which is formed at the intersection of three interfaces among the two liquids and the ambient fluid phase, e.g., air (Fig. 1-1a). (Although similar systems were studied by Langmuir [43], serious mistakes in his theoretical analysis have been pointed out [44]. A new treatment is required in order to estimate line tension correctly.)

The surfaces created in a liquid lens system will be homogeneous and smooth; with the high purities of the two liquids used, the equilibrium of the three-phase contact line can be reached quickly after the liquid lens is formed. However, to extract line tension values, a relation between the line tension and the parameters measurable in the experiment has to be established. This relation should correlate the contact angles formed at the three-phase contact line directly to the line tension. As seen in the analysis of heterogeneous nucleation,
Fig. 1-1

(a) Profile of a liquid lens floating on the surface of a second immiscible liquid. $\gamma_1$ and $\gamma_2$ are the surface tensions of the floating liquid and the base liquid, respectively; $\gamma_{12}$ is the interfacial tension between the two liquids. $\kappa$ is the curvature of the three-phase contact line, in the horizontal direction.

(b) The Liquid lens is pulled up with a capillary so that the the contact line is above the horizontal surface of the base liquid.
overly complicated theory, involving multiple steps of approximation, can easily obliterate the possible effect of line tension.

The traditional description of a liquid lens system is through the classical Neumann triangle relation [89] which relates the three contact angles formed by the three interfaces at the contact line to the surface tensions of these interfaces. The effect of line tension has been neglected. As a first step, it would be interesting to test how well the classical Neumann triangle relation can describe a liquid lens system. As mentioned in the Literature Review, there are experiments even indicating zero line tension, i.e., non-existence of line tension. If the classical Neumann triangle relation fails to describe the liquid lens system, then such a claim will be disproved.

1.2.1 Necessity of Line Tension

In this section, a strategy to test the classical Neumann triangle relation is presented. Then, the results of relevant experimental work are shown to test this classical relation. Finally, the line tension is introduced to explain the discrepancy between the experiment and the prediction of the classical Neumann triangle relation.

For the liquid lens system shown in Fig. 1-1a, the classical Neumann triangle relation may be written as [90]

\[ \gamma_2 \cos \theta_2 = \gamma_1 \cos \theta_1 + \gamma_{12} \cos \theta_{3x} \]  

(1-1)

where \( \gamma_1 \) and \( \gamma_2 \) are the surface tensions of the floating drop and of the base liquid, and \( \gamma_{12} \)
is the interfacial tension between the two liquids; $\theta_1$ is the contact angle between the direction of $\gamma_1$ and the horizontal direction $\kappa$, $\theta_2$ is the angle between $\gamma_2$ and $-\kappa$, and $\theta_{3k}$ that between $\gamma_{12}$ and $\kappa$; $\kappa$ denotes the curvature of the three-phase contact line. Equation (1-1) involves the contact angle $\theta_{3k}$, spanned by the interface between the two liquids, which cannot be easily observed. Therefore, in order to verify the classical Neumann triangle relation, it is desirable to reformulate Eq. (1-1) so that the contact angle $\theta_{3k}$ will not be needed.

One way to do this is to use a cosine expression of the classical Neumann triangle relation, in which only one contact angle, $\theta_{12}$, between $\gamma_1$ and $\gamma_2$ is involved [3,91]

$$\gamma_{12}^2 = \gamma_1^2 + \gamma_2^2 + 2 \gamma_1 \gamma_2 \cos \theta_{12}$$  \hspace{1cm} (1-2)

However, since the three-phase contact line may be depressed below the horizontal surface of the base liquid (Fig. 1-1a), it may be difficult to measure this angle accurately. This problem can be circumvented by elevating the three-phase contact line as shown in Fig. 1-1b (see Chapter 3 for details). The design depicted in Fig. 1-1b allows for a direct measurement of the contact angle $\theta_{12}$ by acquiring a cross-sectional image of the liquid lens [3]. The validity of the classical Neumann triangle relation can then be tested by obtaining the three surface tensions and by measuring $\theta_{12}$: It has been demonstrated [3,91] that, for a dodecane-water-air three-phase system, the contact angle $\theta_{12}$ experimentally measured is significantly different from the one predicted by Eq. (1-2). Details are shown in Fig. 1-1. This discrepancy necessarily led to an interpretation of the data in terms of line tension. The effect of line tension would modify the mechanical equilibrium condition at the three-phase contact line and hence provide a correct explanation for the contact angle measured.
To evaluate line tension effects on contact angles in the present liquid lens system, an appropriate way is to modify the classical Neumann triangle relation by including line tension contributions to the equilibrium condition at the three-phase contact line. Once a modified Neumann triangle relation is obtained, a suitable experiment must be designed for liquid lens systems so that the necessary parameters can be measured for determining line tension. As will be shown in the following chapters, measurement of a single contact angle is insufficient to estimate the line tension from the modified Neumann triangle relation. Advanced image analysis schemes are required to obtain the experimental information that would allow for a line tension calculation.

1.2.2 Objectives of the Thesis

To summarize, the objectives of the thesis are:

(1) to generalize the classical Neumann triangle relation by including line tension effects, i.e., develop a Quadrilateral Relation for three-phase contact line systems,

(2) to design an experiment by applying the Quadrilateral Relation to liquid lens systems for measuring line tension, and

(3) to perform measurements using a series of liquids to evaluate and further verify the line tension results.
Chapter 2

Theoretical Development: The Quadrilateral Relation for Three-Phase Contact Lines

The purpose of this chapter is to explore theoretical possibilities and to develop a theoretical model which can relate line tension to contact angles directly for liquid-liquid-fluid three-phase contact line systems. However, before these theoretical developments, the basic thermodynamic concepts of lines will be presented, and in particular the definition of line tension will be discussed. As mentioned in the Introduction, the thermodynamics of lines is developed in complete analogy to the accepted thermodynamics of surfaces [42,78,92]. Therefore, surface thermodynamics will be reviewed first, where the concept of the Gibbs dividing surface is introduced. Since the systems under consideration are often macroscopic in size, i.e., the radii of curvature of surfaces and lines are much larger than the thickness of the surfaces and the width of the multiphase contact lines, Gibbs' moderate curvature approximation [42,78,92] can be adopted. As a consequence, the effects of bending moments associated with high curvatures [2,42,78,80,92] will be neglected.

This chapter consists of three parts. The first part is a review of thermodynamics of surfaces and of lines. The treatment will be Gibbsian in the sense that it is based on his concept of the dividing surface and the dividing line. The second part is a derivation of a modified form of the Neumann triangle relation including line tension effects. This will result in the Quadrilateral Relation for three-phase contact line systems. The third part is the
application of the Quadrilateral Relation to a number of geometries of contact line systems that have or could be used in experimental studies.

2.1 Thermodynamics of Surfaces

2.1.1 The Dividing Surface

A molecule in the neighborhood of the interface (surface) between any two bulk phases will experience a different environment from that if the same molecule were deep within a similar bulk phase. Consequently, the density of the various components and their energy and entropy densities in the neighborhood of the interface will be different from the corresponding densities in the bulk phases. Furthermore, the time-averaged densities will likely change gradually and continuously from one bulk phase to the other, not in a discontinuous or stepwise fashion. For an equilibrium system which is subject to external body and/or surface forces, and which is sufficiently small so that the interfacial regions need consideration (i.e., the boundaries are not infinitely remote), one finds that the energy, entropy and mass densities will be functions of position, which will vary slowly through each bulk phase due to the influence of gravity or other external body forces, and will, in general, vary rapidly across the interface. In most cases of interest, the influence of the interface is limited and does not extend beyond several molecular diameters (about 10^{-9}-10^{-8} m) into the bulk phases [92]. Therefore, it may be considered to a first approximation, as done by Gibbs [42,93,94], as a two-dimensional mathematical boundary between the two bulk phases which
both extend uniformly right up to the dividing surface.

From the Gibbsian point of view, the dividing surface or surface of discontinuity is a mathematically constructed surface of only two dimensions which is "sensibly" placed within the thin interface region, separating the two bulk regions. Bulk properties in each phase are assumed to persist uniformly right up to the dividing surface, and the excess properties, formed as a result of this assumed model for the interface, are attributed to the dividing surface. Therefore, the dividing surface, which is initially constructed as a geometric surface of bulk separation, is transformed into a thermodynamic, autonomous system. This system is governed by a suitable fundamental equation for the interface which is dependent only on excess or surface quantities [92,95]. Surface or excess quantities like the internal energy are then defined as

\[ U^{(A)} = U_t^{(V)} - U^{(a)} - U^{(b)} \]  

(2-1)

where the quantities denoted by the superscripts \( (\alpha) \) and \( (\beta) \) are those for the hypothetical bulk systems \( (\alpha) \) and \( (\beta) \) that extend right up to the dividing surface. The variable \( U^{(A)} \) represents the difference in energy between the real system of total energy \( U_t^{(V)} \), with an interface of nonzero volume, and a hypothetical system of energy \( (U^{(a)} + U^{(b)}) \) in which the phases \( (\alpha) \) and \( (\beta) \) are completely uniform right up to the dividing surface. Thus, \( U^{(A)} \) represents the excess energy arising from the Gibbsian model of an interface, or equivalently it represents the total internal energy of the surface phase.

Similarly, \( S^{(A)} \) represents the difference in entropy between the real system and a hypothetical system consisting of the two bulk phases which are uniform right up to the
dividing surface. $S^{(A)}$ is then the corresponding total surface entropy for the interface between the bulk phases (α) and (β). Finally, the surface mass of component $i$, $N_i^{(A)}$, can be defined. It should be noted that, in the process of introducing a dividing surface to model the interfacial region, the total energy, entropy, and mass of the real system do not change, i.e., the extensive quantities of the system are all conserved [92].

2.1.2 The Fundamental Equation of Surfaces

The fundamental equation for a moderately curved surface (interface) [2,42,78,80,92] can be readily established by considering the modes in which the internal energy $U^{(A)}$ of the surface can be changed. There is the possibility of transfer of mass and heat into and out of the surface. Instead of the volume as in the case of a bulk phase, the mechanical energy transfer here is associated with the surface area $A$. The work done in generating a surface area increment $dA$ is $\gamma dA$, where $\gamma$ is the surface tension. Overall, one obtains

$$dU^{(A)} = TdS^{(A)} + \gamma dA + \sum \mu_i dN_i^{(A)}$$

(2-2)

where $T$ is the temperature, $\mu_i$ is the chemical potential of component $i$. Alternatively, the fundamental equation for the surface may be expressed as

$$U^{(A)} = U^{(A)}[S^{(A)}, A, N_i^{(A)}]$$

(2-3)

The surface tension, defined as
\[ \gamma = \left( \frac{\partial U^{(A)}}{\partial A} \right)_{S^{(A)}, N_i^{(A)}} \quad (2-4) \]

is the two-dimensional counterpart of the three-dimensional bulk pressure \( P \). Both quantities are isotropic, but the surface or interfacial tension is tensile rather than compressive like the pressure.

Corresponding to Eq. (2-2), the Euler relation for the surface can be written as

\[ U^{(A)} = TS^{(A)} + \gamma A + \sum \mu_i N_i^{(A)} \quad (2-5) \]

From here one can easily write down free energy forms through the Legendre transformation [1]. For example, the grand canonical potential (free energy) can be readily written as

\[ \Omega^{(A)} = U^{(A)} - TS^{(A)} - \sum \mu_i N_i^{(A)} = \gamma A \quad (2-6) \]

and in differential form

\[ d\Omega^{(A)} = -S^{(A)} dT + \gamma dA - \sum N_i^{(A)} d\mu_i \quad (2-7) \]

It can be seen that the grand canonical potential would be the appropriate thermodynamic potential (free energy) when the system is in both thermal and chemical equilibrium, i.e., under the condition of constant temperature and chemical potential.
2.2 Thermodynamics of Lines

As suggested originally by Gibbs [96], the lines in which surfaces meet should be treated in a manner entirely analogous to that in which surfaces are treated. Following this line of thought, one extrapolates the properties of the dividing surfaces by assuming that the fundamental equation for each surface holds at every point of the surface right up to the dividing line. The dividing line, or the line of discontinuity is a mathematically constructed line of only one dimension, which is "sensibly" placed within the narrow multiphase contact line region. Thus, the actual quantities of internal energy, entropy, and masses (or mole numbers) in the vicinity of the dividing line are represented partially by the extrapolated volume density, partially by the extrapolated surface densities, and partially by whatever is remaining (i.e., the excess) that is attributed to the dividing line in the form of linear densities.

Under the Gibbs moderate curvature assumption, the fundamental equation for a line [2,42,78,80,92] can be readily established by considering the modes in which the internal energy $U^{(L)}$ of the line can be changed. Similar to the case of surfaces, there is the possibility of transfer of mass and heat into and out of the line. Instead of the surface area in the case of a surface phase, the mechanical energy transfer here is associated with the length of the line $L$. The work done in generating a line length increment $dL$ is $\sigma dL$, where $\sigma$ is the line tension. Overall, one obtains

$$dU^{(L)} = T dS^{(L)} + \sigma dL + \sum \mu_i dN_i^{(L)}$$

(2-8)

where $T$ is the temperature, $\mu_i$ is the chemical potential of component $i$. Alternatively, the
fundamental equation for the surface may be expressed as

$$ U^{(L)} = U^{(L)}[S^{(L)}, L, N_i^{(L)}] $$

(2-9)

The line tension is then defined as

$$ \sigma = \left( \frac{\partial U^{(L)}}{\partial L} \right)_{S^{(L)}, N_i^{(L)}} $$

(2-10)

which is the one-dimensional counterpart of the two-dimensional surface tension. Both quantities are tensile, rather than compressive like their three-dimensional counterpart, bulk pressure.

Corresponding to Eq. (2-8), the Euler relation for the line can be written as

$$ U^{(L)} = TS^{(L)} + \sigma L + \sum \mu_i N_i^{(L)} $$

(2-11)

Therefore, one can easily write down free energy forms through the Legendre transformation [1]. For example, the grand canonical potential (free energy) can be readily written as

$$ \Omega^{(L)} = U^{(L)} - TS^{(L)} - \sum \mu_i N_i^{(L)} = \sigma L $$

(2-12)

and in differential form

$$ d\Omega^{(L)} = -S^{(L)}dT + \sigma dL - \sum N_i^{(L)} d\mu_i $$

(2-13)

It can be seen that the grand canonical potential would be the appropriate thermodynamic potential (free energy) when the system is in both thermal and chemical equilibrium, i.e.,
under the condition of constant temperature and chemical potential.

2.3 The Quadrilateral Relation for Three-Phase Contact Lines

With the thermodynamic background above, one is in the position to explore theoretical possibilities to generalize the classical Neumann triangle relation and to investigate the role of line tension in the mechanical equilibrium condition of multiphase boundary curve systems.

As mentioned earlier, the classical Neumann triangle relation was suggested over a century ago [89] for a liquid lens system in relating the three surface tensions of the three interfaces that intersect at the contact line. Over the last few decades, it was found that this relation must be modified by line tension. Pethica [40] was the first to modify the Young equation of capillarity by including a line tension contribution in the equilibrium condition of a sessile drop on a solid surface. Lane [97] modified Pethica’s analysis and applied his results to the case of a small liquid volume wetting a conical pore (i.e., to model a liquid in contact with an inclined rather than a flat solid surface). Torza and Mason [54] obtained the force balance conditions for the attachment of two drops, and Pujado and Scriven [44] corrected Langmuir’s original analysis [43] of the equilibrium conditions of a bubble or a drop pressed against another fluid interface in the gravitational field. All these force balance or equilibrium conditions can be, in principle, converted to a generalized Neumann triangle relation [78] where line tension is incorporated. In 1977, Boruvka and Neumann [78] obtained a general Neumann triangle relation which includes not only line tension but also higher order curvature
terms such as geodesic curvatures and torsion. Recently, Ivanov, Kralchevsky and Nikolov [12] re-derived the force balance conditions by a variational approach.

However, there are several drawbacks with current expressions: (i) All of this work, except that of Boruvka and Neumann, is based on some specific geometries, (ii) a clear conversion from the force balance conditions (which are normally represented by two orthogonal force balance equations) to a type of "cosine rule" Neumann triangle relation (in which cosines of contact angles are explicitly involved in the equation of tensions) has not been provided. Such a conversion can be practical, as demonstrated in situations where the classical Neumann triangle relation [89] is employed, and (iii) no corresponding graphical representation, i.e., a pictograph similar to the classical Neumann triangle, has been developed for the situation where line tension effects are noticeable.

To address these limitations, a generalization of the Neumann triangle relation to include line tension will first be derived, without restriction to any specific geometry of a three phase line system. Then, a graphical representation of a quadrilateral relation is developed. Such a quadrilateral relation is composed of the three surface tensions associated with the three intersecting interfaces and a line tension at the intersection. The interpretation of experimental data, and especially data obtained from liquid lens capillary systems, would be enhanced by a clear picture of the manner in which the classical Neumann triangle relation is altered by the presence of line tension. Such a representation would be useful in all situations where the classical Neumann triangle relation has been traditionally employed. One obvious benefit that arises from this representation is a simple, geometric method for manipulating the quadrilateral pictograph to obtain either a cosine rule expression or a force balance equation.
projected in a particular direction. Experimental concerns would dictate the choice of
variables in the cosine rule expression, and simple considerations, based on the quadrilateral
geometry, would provide the methodology for choosing which quantities would need to be
measured. In the present case, the quadrilateral relation would be expected to be applied to
the liquid lens system, providing a direct relation between the contact angles and the line
tension.

In the next section, a suitable free energy representation for capillary systems is chosen
and then, on the basis of the grand canonical free energy, a modified form of the Neumann
triangle relation that includes a line tension contribution is derived. To avoid undue
complexity, the investigation is restricted to a three-phase lens system with just one line
tension term and the usual three surface tensions (Fig. 2-1a). It is also assumed that the
adjacent surfaces forming the contact line are both uniform and isotropic, which, of course,
will be satisfied by most fluid phases. Finally, it is assumed that the contact line occurs in a
plane of constant external potential, $\phi (r)$, so that $\nabla \phi (r) = 0$. This assumption does not limit
the analysis, as it is consistent with virtually all experimental situations considered in the
literature [3-49,51-68]. Once the quadrilateral relation is developed and a clear physical
meaning provided, application will be discussed to a number of typical geometries that exist
or could exist in experimental studies on line tension.
Fig. 2-1 Schematics of (a) a liquid lens and (b) a blow-up of a region of the three phase contact line. $\gamma^{(1)}, \gamma^{(2)}$ and $\gamma^{(3)}$ denote the surface tensions of the interfaces between bulk phases $V_3$ and $V_1$, $V_1$ and $V_2$, and $V_2$ and $V_3$, respectively. $\mathbf{m}_i$ and $\mathbf{n}_i$ ($i=1,2,3$) depict the tangential and normal directions of the interfaces. $\sigma \kappa$ represents the line tension $\sigma$ contribution to the force balance at a point of the contact line with $\mathbf{t}$ as the tangent. $\delta \mathbf{r}$ denotes an arbitrary variation in the position of the point.
2.3.1 Derivation of the Quadrilateral Relation

The classical Neumann triangle relation is the appropriate boundary condition when the three surfaces which intersect to form the contact line are all deformable and the contribution from line tension is ignored. When one of the surfaces is rigid, the Young equation is the appropriate boundary condition. In the general formulation, these boundary conditions can be quite complex because they would include a detailed analysis of the higher-order curvature dependence of both the surface and the line boundaries [78]. In practice, however, the mechanical equilibrium conditions for capillary systems with complex geometry are not of immediate necessity in many experimental studies that deal with either spherical or axisymmetric systems. Furthermore, most estimates of line tension have been performed using capillary systems which are axisymmetric and where the surfaces forming the contact line are deformable. Thus, the consideration is restricted to the equilibrium of three bulk phases which meet in a line of three-phase contact (Fig. 2-1).

Macroscopically, the locus of points that form the contact line is one-dimensional and locally linear (i.e., there are no higher-order curvature effects); it is analogous to the macroscopically two-dimensional and locally planar interface between two bulk phases. It is possible to define an excess free energy per unit length, or line tension, that is associated with the contact line (cf. Eq. (2-12)) and to write down the total free energy as the sum

$$\Omega_t = \Omega^{(V_1)} + \Omega^{(V_2)} + \Omega^{(V_3)} + \Omega^{(A_1)} + \Omega^{(A_2)} + \Omega^{(A_3)} + \Omega^{(L)}$$  \hspace{1cm} (2-14)

where the first three terms on the right-hand side are the grand canonical potentials of the
three bulk phases with volumes $V_1$, $V_2$ and $V_3$; the next three terms are the grand canonical potentials of the three surfaces with areas $A_1$, $A_2$ and $A_3$; the last term is the free energy of the contact line with a length $L$. At equilibrium, $\Omega$, is minimized when the system is under the condition of constant temperature, chemical potentials, and total volume of the composite system, i.e.,

$$\delta (V_1 + V_2 + V_3) = 0$$

(2-15)

According to Eqs. (2-6) and (2-12), the variation of the total free energy, $\delta \Omega$, can be written as

$$\delta \Omega_i = \delta \int \int \int -P^{(1)} dV + \delta \int \int \int -P^{(2)} dV + \delta \int \int \int -P^{(3)} dV$$

$$+ \delta \int \int \gamma^{(1)} dA + \delta \int \int \gamma^{(2)} dA + \delta \int \int \gamma^{(3)} dA + \delta \int \sigma dL$$

(2-16)

where $P^{(1)}$, $P^{(2)}$ and $P^{(3)}$ are the pressures of the three bulk phases $V_1$, $V_2$ and $V_3$; $\gamma^{(1)}$, $\gamma^{(2)}$ and $\gamma^{(3)}$ are the surface tensions for surfaces $A_1$, $A_2$ and $A_3$; $\sigma$ is the line tension of the three phase contact line $L$. The minimum free energy principle requires that the above variation vanishes, i.e., $\delta \Omega_i = 0$.

Allowing for arbitrary variations of the position vector $r$ inside the volume $V$, one has

$$\delta \Omega^{(V)} = \delta \int \int \int -P dV$$

$$= \int \int \int -\delta P dV + \int \int \int -P \delta dV$$

$$= \int \int \int -\nabla P \cdot \delta r dV + \int \int \int -P (\nabla \cdot \delta r) dV$$

(2-17)
where the first term on the right-hand side is the virtual work done by the external field, and the second term

$$\delta W_i^{(e)} = \iiint P \delta V = \iiint P (\nabla \cdot \delta r) dV$$  \hspace{1cm} (2-18)

is the virtual work done by internal forces. After employing the relation

$$\nabla \cdot (-P \delta r) = -\nabla P \cdot \delta r - P (\nabla \cdot \delta r)$$  \hspace{1cm} (2-19)

and Gauss' divergence theorem for the virtual work of the internal forces, Eq. (2-17) reduces to

$$\delta \Omega^{(v)} = \iint - P (n \cdot \delta r) dA$$  \hspace{1cm} (2-20)

where \(n\) is the unit normal to the surface which encloses the bulk volume under consideration. Equation (2-20) represents the bulk phase variation of a point along the contact line.

For each bulk phase in our present three-phase contact line system (Fig. 2-1), one has identical expressions; that is,

$$\delta \Omega^{(v)} = \iint - P^{(1)} (n_1 \cdot \delta r) dA_1 - \iint - P^{(1)} (n_2 \cdot \delta r) dA_2$$  \hspace{1cm} (2-21)

where \(n_1\) and \(n_2\) are the unit normals to the surfaces \(A_1\) and \(A_2\) that bound the volume \(V\), as indicated in Fig. 1. Likewise, the variations of the next two volume work terms (bulk variations) corresponding to the arbitrary variation \(\delta r\) can be written as

$$\delta \Omega^{(v)} = \iint - P^{(2)} (n_2 \cdot \delta r) dA_2 - \iint - P^{(2)} (n_3 \cdot \delta r) dA_3$$  \hspace{1cm} (2-22)
and

$$\delta \Omega^{(V)} = \iint -P^{(3)}(n_3 \cdot \delta r) \, dA_3 - \iint -P^{(3)}(n_1 \cdot \delta r) \, dA_1$$  \hfill (2-23)

where \(n_3\) is the unit normal to the surface \(A_3\).

The corresponding surface phase variations involve both surface and line contributions and may, in analogy with Eq. (2-17), be written as

$$\delta \Omega^{(A)} = \iint \nabla_2 \gamma \cdot \delta r \, dA + \iint \gamma (\nabla_2 \cdot \delta r) \, dA = \iint \nabla_2 \cdot (\gamma \delta r) \, dA$$  \hfill (2-24)

When using the surface analogue of Gauss' divergence theorem [103], Eq. (2-24) becomes

$$\delta \Omega^{(A)} = -\iint \gamma J (n \cdot \delta r) \, dA - \int \gamma (m \cdot \delta r) \, dL$$  \hfill (2-25)

where \(J\) is the mean curvature of the surface \(A\), and \(m\) is the unit vector tangent to the surface \(A\) and coincident with the direction of the surface tension force, i.e., the inward directed binormal to the contact line (Fig. 2-1b). Using this relation, one may write the first surface phase variation in response to an arbitrary variation of the position, \(\delta r\), of the point along the contact line

$$\delta \Omega^{(A_1)} = -\iint \gamma^{(1)} J_1 (n_1 \cdot \delta r) \, dA_1 - \int \gamma^{(1)} (m_1 \cdot \delta r) \, dL$$  \hfill (2-26)

where the mean curvature \(J_1\) and binormal \(m_1\) refer to the first surface \(A_1\). Similarly, the other surface phase variations are given by
\[ \delta \Omega^{(A_2)} = - \int \int \gamma^{(2)} J_2 (n_2 \cdot \delta r) dA_2 - \int \gamma^{(2)} (m_2 \cdot \delta r) dL \]  \hspace{1cm} (2-27)

and

\[ \delta \Omega^{(A_3)} = - \int \int \gamma^{(3)} J_3 (n_3 \cdot \delta r) dA_3 - \int \gamma^{(3)} (m_3 \cdot \delta r) dL \]  \hspace{1cm} (2-28)

where \( J_2 \) and \( J_3 \) are the mean curvatures of the surfaces \( A_2 \) and \( A_3 \), and \( m_2 \) and \( m_3 \) are the unit tangents to the surfaces \( A_2 \) and \( A_3 \), respectively.

Finally, the variation of the linear work term in response to the variation of the positions of points along the contact line is written as

\[ \delta \Omega^{(L)} = \delta \int \sigma dL = \int \nabla \cdot (\sigma \delta r) dL = - \int \sigma \kappa \cdot \delta r dL \]  \hspace{1cm} (2-29)

where \( \kappa \) is the curvature vector of the contact line, and the scalar product \( \kappa \cdot \delta r \) represents the extension in length of the contact line per unit length.

Substitution of the bulk, surface, and line variation expressions (using Eqs. (2-21) - (2-23), (2-26) - (2-28), and (2-29)) into the necessary equilibrium condition \( \delta \Omega_i = 0 \) yields

\[ \delta \Omega_i = - \int \int \left[ \gamma^{(1)} J_1 + (P^{(1)} - P^{(3)}) \right] n_1 \cdot \delta r dA_1 \\
- \int \int \left[ \gamma^{(2)} J_2 + (P^{(2)} - P^{(1)}) \right] n_2 \cdot \delta r dA_2 \\
- \int \int \left[ \gamma^{(3)} J_3 + (P^{(3)} - P^{(2)}) \right] n_3 \cdot \delta r dA_3 \\
- \int (\gamma^{(1)} m_1 + \gamma^{(2)} m_2 + \gamma^{(3)} m_3 + \sigma \kappa) \cdot \delta r dL \]  \hspace{1cm} (2-30)

With the variation \( \delta r \) unrestricted, each integrand must independently equal zero in order to satisfy the necessary condition of minimum free energy. The first three area related integrands result in the usual Laplace equation of capillarity. The last integrand yields the equilibrium
condition for the contact line

\[ \gamma^{(1)} m_1 + \gamma^{(2)} m_2 + \gamma^{(3)} m_3 + \sigma \kappa = 0 \] (2-31)

This is a generalization of the Neumann triangle relation with the line tension effects included. This is at the same level in the hierarchy at which the classical Laplace equation is the appropriate equilibrium condition for surfaces [78].

To represent the above relation graphically, one begins with the classical Neumann triangle relation and then adds an additional (line tension) vector \( \sigma \kappa \) to the triangle of surface tensions. The resulting diagram is a quadrilateral which contains three surface tensions and one line tension, see Fig. 2-2. Within the scope of the present consideration, the surfaces and the line are uniform and isotropic, so that the quadrilateral should be in a plane since the three surface tensions are all normal to the tangent direction, \( t = n \times m \), of the three phase contact line. The line curvature \( \kappa \) is also normal to \( t \).

In the contact line quadrilateral relation, the line tension term always occurs in association with the curvature \( \kappa \). If \( \kappa \) is small (i.e., the radius of the curvature of the contact line is large, compared to the ratio of the line tension and the surface tension), the line tension contribution to the force balance becomes negligible and the classical Neumann triangle is recovered.

2.3.2 Variants of the Quadrilateral Relation

To be able to interpret relation (2-31) in the context of experimental situations, it is
Fig. 2-2  Schematics of (a) a side-view of a three phase contact line, and (b) a quadrilateral which is composed of three surface tensions $\gamma^{(1)}$, $\gamma^{(2)}$, and $\gamma^{(3)}$, and a line tension contribution $\sigma \kappa$. 
desirable to convert the planar vectorial relation that is given in Eq. (2-31) into two equivalent, orthogonal scalar relations. This is accomplished by projecting the vector expression into two orthogonal directions to achieve independent and equivalent scalar force balance equations about the contact line. This may be demonstrated by selecting two directions such that one direction (denoted by the $x$ unit vector) is along the direction in which the line tension force operates; that is, the direction in which the vector $\kappa$ points, and the other direction (denoted by the $y$ unit vector) is perpendicular. With this choice of directions, one may write the vector expression (Eq. (2-31)) as two scalar expressions projected in the two directions

\[ x \text{-direction:} \]
\[ \sigma \kappa + \gamma^{(1)} \cos \theta_{k1} + \gamma^{(2)} \cos(\theta_{k1} + \theta_{12}) + \gamma^{(3)} \cos \theta_{3x} = 0 \]  \hspace{1cm} (2-32)

\[ y \text{-direction:} \]
\[ \gamma^{(1)} \sin \theta_{k1} + \gamma^{(2)} \sin(\theta_{k1} + \theta_{12}) - \gamma^{(3)} \sin \theta_{3x} = 0 \]  \hspace{1cm} (2-33)

which eliminates the line tension term from the force balance equation in the $y$ direction. Identical expressions, applicable to axisymmetric liquid lens systems, can be obtained from the balance of forces in the radial and vertical directions by appropriate mathematical manipulation [104].

It may be seen that both of these projected equations contain the possibility of at least three independent angles since $\theta_{12} + \theta_{23} + \theta_{3x} + \theta_{k1} = 2\pi$. In addition, this particular choice of projection directions eliminates the line tension term from the force balance condition in the $y$-direction. If the surface tensions can be obtained by an independent means, then evaluation of the line tension will involve the measurement of a minimum of two angles. The
choice of angles is arbitrary, but the experimental situation may dictate a preferable pair. This can be realized by mathematical manipulation of the contact line quadrilateral. Consider one of the two diagonals of the quadrilateral, which divides the quadrilateral into two triangles. Within each divided triangle, one can use the cosine rule to write down an expression for the square of the length of this diagonal by using the other two sides of this triangle and the contact angle between them. From the two triangles, an equation containing two contact angles, three surface tensions and one line tension follows. For example, if one uses the contact angle $\theta_{12}$ between the directions of the surface tensions $\gamma^{(1)}$ and $\gamma^{(2)}$, and the contact angle $\theta_{3\kappa}$ between the directions of the surface tension $\gamma^{(3)}$ and the line tension $\sigma\kappa$ (see Fig. 2-2), a scalar cosine rule relation is achieved

$$[\gamma^{(1)}]^2 + [\gamma^{(2)}]^2 + 2\gamma^{(1)}\gamma^{(2)} \cos\theta_{12} = [\gamma^{(3)}]^2 + (\sigma\kappa)^2 + 2\gamma^{(3)}\sigma\kappa \cos\theta_{3\kappa}(2-34)$$

In Eq. (2-34) the two contact angles occur at opposite corners of the quadrilateral (Fig. 2-2). A similar equation may be written by using the remaining pair of opposite corner contact angles. If one knows a priori that the line tension term $\sigma\kappa$ is much smaller than the surface tension terms, then the square of the line tension term may be dropped in favour of the remaining terms and Eq. (2-34) simplifies to

$$[\gamma^{(1)}]^2 + [\gamma^{(2)}]^2 + 2\gamma^{(1)}\gamma^{(2)} \cos\theta_{12} = [\gamma^{(3)}]^2 + 2\gamma^{(3)}\sigma\kappa \cos\theta_{3\kappa} (2-35)$$

which may be used to obtain an estimate of $\sigma\kappa$ provided the two selected angles can be measured. Wallace and Schürch [46,47] used an analogous approach to select a liquid-liquid-fluid system for estimating $\sigma$ that approximately satisfied $\theta_{23} + \theta_{3\kappa} = \pi$ so that they only
needed to measure the angle $\theta_{12}$. Equation (2-35) is consistent with the classical Neumann triangle relation in the limit $(\sigma \kappa) \rightarrow 0$.

Another scalar form of the force balance at the three phase contact line may also be easily obtained from the quadrilateral, by expressing one of the four quantities (three surface tensions and one line tension) in terms of the remaining three. If the interest is to find the line tension, the cosine rule gives the expression (see Fig. 2-2b)

$$\begin{align*}
(\sigma \kappa)^2 &= [\gamma^{(1)}]^2 + [\gamma^{(2)}]^2 + [\gamma^{(3)}]^2 \\
&+ 2\gamma^{(1)}\gamma^{(2)}\cos\theta_{12} + 2\gamma^{(2)}\gamma^{(3)}\cos\theta_{23} + 2\gamma^{(3)}\gamma^{(1)}\cos\theta_{31}
\end{align*}
$$

where

$$\theta_{31} = \theta_{3\kappa} + \theta_{\kappa 1}
$$

and

$$\theta_{12} + \theta_{23} + \theta_{31} = 2\pi
$$

It is interesting to note that only two independent contact angles are involved in Eq. (2-36), and that they are adjacent to each other. Equation (2-36) can also be obtained by summing the squares of Eqs. (2-32) and (2-33). Three other equalities may be obtained from Eq. (2-36) by permutation of $\sigma \kappa, \gamma^{(1)}, \gamma^{(2)}, \gamma^{(3)}$ and their corresponding contact angles.

Resolving the force balance in all four directions that lie, respectively, in the three interfaces and the one line tension direction, and that are all perpendicular to the three phase contact line, one has
The four equations form a set of dependent homogeneous equations for the surface and line tensions; thus, the determinant of coefficients vanishes, i.e.,

\[
\begin{vmatrix}
1 & \cos\theta_{12} & \cos(\theta_{3k} + \theta_{k1}) & \cos\theta_{k1} \\
\cos\theta_{12} & 1 & \cos\theta_{23} & \cos(\theta_{23} + \theta_{3k}) \\
\cos(\theta_{3k} + \theta_{k1}) & \cos\theta_{23} & 1 & \cos\theta_{3k} \\
\cos\theta_{k1} & \cos(\theta_{k1} + \theta_{12}) & \cos\theta_{3k} & 1
\end{vmatrix} = 0
\]  

(2-40)

which demonstrates that any one of Eqs. (2-39) follows from the other three. As a consequence of their homogeneity, Eqs. (2-39) determine only ratios of tensions, rather than the tension themselves.

2.3.3 Applications of the Quadrilateral Relation to Specific Geometries

It is possible to demonstrate the utility of the various equivalent forms of the Quadrilateral Relation by considering several common geometries that have or could be used to measure line tension. In particular, (i) a liquid lens, (ii) a pendant drop in contact with a second immiscible liquid, and (iii) a cone-shaped capillary will be considered. In each case, the corresponding expression for mechanical equilibrium at the contact line will be given and how one could obtain an estimate of the line tension from the selected geometry will be
2.3.2.1 Arrangement (i): A Liquid Lens

One of the benefits of using liquid lenses is that the three phase contact line involves only liquids which permit smooth contact line formation, and no solid surface has to be considered in terms of its surface tension and surface preparation. By using conventional methods, liquid-liquid and liquid-fluid surface tensions can be easily determined to a relatively high degree of accuracy. As mentioned above, in order to apply the quadrilateral relation, one has to determine at least two contact angles along with three surface tensions to evaluate the line tension. As depicted in Fig. 2-2, for an axisymmetric liquid lens, the contact angles $\theta_{kl}$ and $\theta_{l2}$ may be the two angles which are easiest to measure. The angle $\theta_{l2}$ may be obtained by optical methods while $\theta_{kl}$ can be measured through the observation of the slope of the tangent to the liquid lens surface against the horizontal. If these two angles are used, the cosine quadrilateral equation (2-36) would be rewritten by rotating the corresponding surface and line tension quantities to yield the expression

$$\gamma^{(3)} = (\sigma \kappa)^2 + [\gamma^{(1)}]^2 + [\gamma^{(2)}]^2 + 2\sigma \kappa \gamma^{(1)} \cos \theta_{kl} + 2\gamma^{(1)} \gamma^{(2)} \cos \theta_{l2} + 2\gamma^{(2)} \sigma \kappa \cos \theta_{2\kappa}$$ (2-41)

where the sum of the three contact angles is $2\pi$. Equation (2-41) is quadratic with respect to the line tension $\sigma$, and its solution may be easily obtained once the curvature of the three phase line $\kappa$ is known. The radius of this curvature may be measured by determining the distance between the two edges of the liquid lens (i.e., the diameter of the three phase contact
line), and this may be achieved either through the top view of the liquid lens or proper optical reflection methods.

If one of the liquids has a much higher mass density than the other, then it is unlikely that it deforms to a significant level when the lighter liquid is deposited onto it. The resulting three phase contact line system can then be approximated as a sessile drop system [46,47]. In this situation, only the force balance in the direction along the flat (or nearly flat) surface is needed. From Eq. (2-32), this condition can be written as

$$\sigma_k + \gamma^{(1)} \cos \theta_{k1} - \gamma^{(2)} + \gamma^{(3)} = 0$$  \hspace{1cm} (2-42)

where $\theta_{k1}$ is the contact angle conventionally defined for a sessile drop on a solid surface. However, there are only a limited number of liquid lens systems that approximately satisfy the conditions necessary to use a sessile drop type approximation. The first and only attempt using this approach was made by Wallace and Schürch [46,47]. On the other hand, there is a large number of liquid lens systems where the sessile drop approximation is not valid; hence, one has to use the more general Quadrilateral Relation, one form of which is given by Eq. (2-41)

### 2.3.2.2 Arrangement (ii): A Pendant Drop in Contact with a Second Immiscible Liquid

An alternative experimental arrangement to measure line tension involving lowering a pendant drop so that it touches a second liquid in a container, see Fig. 2-3. At the contact rim a three phase contact line is formed between the two liquids and the ambient fluid (e.g.
Fluid Pendant Drop

Second Liquid

Schematic of a pendant drop in contact with a second liquid. $\gamma^{(1)}$ and $\gamma^{(2)}$ are the surface tensions of the pendant liquid and the second liquid; $\gamma^{(3)}$ is the interfacial tension between the two liquids; $\sigma\kappa$ represents the line tension contribution to the quadrilateral relation.
One of the key benefits of using a pendant drop is that the extent of the contact between the two liquids can be fully controlled by adjusting the drop position, providing some ease and flexibility of experimentation. Furthermore, the liquid-liquid engulfing problem is avoided.

If one knows the three surface tensions, then to obtain an estimate of the line tension, one would need to measure two angles. One strategy would be to measure directly the contact angles $\theta_{i2}$ and $\theta_{ki}$ through a physical observation of the slope of the pendant drop at the three phase contact line. Another strategy for evaluating these two contact angles is to apply the Axisymmetric Drop Shape Analysis (ADSA) methodology [105-107]; one would obtain images of a part of the pendant drop profile and of the second liquid surface (which is between the second liquid and the ambient fluid), and then best fit these images (curves) to the Laplace equation of capillarity. The intersection of the two Laplacian curves is the position of the three phase contact line in the cross section of the pendant drop. Once the intersection is found, the slope of the pendant drop profile at the three phase contact line can be determined and with that, the two contact angles $\theta_{i2}$ and $\theta_{ki}$ are obtained. The last parameter to be determined in applying the quadrilateral relation, Eq. (241), is the curvature of the contact line, which, however, can be easily obtained through the distance between the two opposite intersections beside the axisymmetric axis of the pendant drop (the diameter of the contact line). Finally, the line tension can be estimated from Eq. (2-41). It is noted that employing the methodology of ADSA may greatly enhance the accuracy of the experiment with the added potential of automating the experimental procedure.
A cone-shaped capillary system (Fig. 2-4) is another interesting experimental situation that is similar to the sessile drop arrangement for measuring line tension [55-63]. The mechanical boundary conditions at the contact line follow Eqs. (2-32) and (2-33)

\[ \gamma^{(1)} \cos \theta_{12} + \gamma^{(2)} - \gamma^{(3)} - \sigma \kappa \cos \theta_{3k} = 0 \quad (2-43) \]

and

\[ \gamma^{(1)} \sin \theta_{12} + \sigma \kappa \sin \theta_{3k} - P_N = 0 \quad (2-44) \]

where \( \theta_{12} \) is the contact angle of the liquid against the solid surface, \( \theta_{3k} \) is the contact angle which is predetermined through the apex angle \( \theta_A \) of the cone: \( \theta_{3k} = (\pi - \theta_A) / 2 \), and \( P_N \) denotes the solid surface stress component in the normal direction. It is necessary to assume that a surface stress exists at the three phase contact line; otherwise, Eq. (2-44) cannot hold since the left-hand side of the equation is positive definite when \( P_N \) is absent. The same situation exists in the case of a sessile drop where a normal component of the surface stress has to be assumed, to balance the vertical force equation at the contact line.

A relevant question regarding a sessile drop on a solid surface was raised by Bikerman [108,109]. He objected to the Young equation by mentioning that the conventional proof of the equation was incorrect in that the vertical (to the solid surface) component of liquid surface tension \( \gamma^{(1)} \), namely \( \gamma^{(1)} \sin \theta \), was unaccounted for. He indicated that such a tension component had to be balanced by a force not of a surface origin. This force is believed to
Fig. 2-4  Schematic of a cone-shaped capillary. $\gamma^{(1)}$, $\gamma^{(2)}$ and $\gamma^{(3)}$ are the surface tensions of liquid-fluid (air), solid-fluid and solid-liquid; $\sigma\kappa$ represents the line tension contribution to the quadrilateral relation; $P_N$ is the normal stress component of solid surface.
originate from the bulk stress tensor in the solid, manifesting itself as a solid surface stress at the three phase contact line.

Although the solid surface is regarded as flat (in the radial direction for a cone), a small surface strain is likely present, which will induce a finite surface stress. Through a hydrostatic analysis [79,110], the normal stress component can be written as

\[ P_N = P_3 = \int (\sigma_{13} + \sigma_{23} + \sigma_{33}) \, dT \]  

(2-45)

where \( \sigma_j \)'s (i,j=1,2,3) are the components of the stress tensor in the solid, and \( T \) is the integrating path along the solid surface and perpendicular to the three phase contact line. Future work may be to study the stress and strain of the solid in order to verify the assumption of the normal stress component.

In the experiment of the cone-shaped capillary, one has to measure the contact angle \( \theta_{12} \) and the curvature of the contact line \( \kappa \). The contact angle \( \theta_{12} \) may be obtained through a direct optical observation, and \( \kappa \) can be calculated through the diameter of the contact line which is horizontal. By using Eq. (2-43), the line tension can be estimated if the three surface tensions are known. The difficulty in finding the solid surface tensions \( \gamma^{(2)} \) and \( \gamma^{(3)} \) may be resolved by using an equation of state approach [111,112].

One of the benefits of using the cone-shaped capillary is that one can control the size of the three phase contact line by adjusting the amount of the liquid. Also, by varying the radius of the curvature of the three phase line, the curvature dependence of the line tension may be determined.

It is also noted that, by changing the circular shape of the cross-section to a, say,
elliptical shape, and observing the shape of the three phase line, one may study the line tension effect on the wetting and adhesion on the solid surface. It is anticipated that the distortion of the three phase contact line is affected by the magnitude of line tension as well as by the local curvature of the cone shaped capillary.

2.4 Summary

The thermodynamic treatments in the first two sections are Gibbsian in the sense that they are based on his concept of the dividing surface and the dividing line. Line tension is defined from the fundamental equation of a linear phase, which is in complete analogy to the accepted thermodynamic definitions for surface tension and bulk pressure. The treatments are limited to the situations where the radii of curvature of lines as well as surfaces are much larger than the thickness of the surfaces and the width of the multiphase contact lines. As a result, Gibbs' moderate curvature approximation is applicable [2,42,78,80,92].

The grand canonical potential is identified as the appropriate free energy for a capillary system where thermal equilibrium as well as chemical equilibrium are established. The classical Neumann triangle relation is then modified to account for line tension effects, using the free energy minimum principle. The modified Neumann triangle relation represents the proper mechanical equilibrium boundary condition, which converts the triangle of forces to a quadrilateral. From the quadrilateral pictograph, it becomes easy to derive various forms of the mechanical equilibrium conditions at the contact line and to evaluate which form(s) would be appropriate for a particular experimental situation. Several common geometries are
discussed and strategies for determining the line tension are proposed. In all cases involving deformable liquid phases (e.g., a liquid lens system), the line tension may be obtained provided that two contact angles in addition to three surface tensions are determined. For liquids in contact with ideal solid surfaces, the line tension may be measured after measuring one contact angle and three surface tensions or, alternatively, the drop-size dependence of contact angle and the surface tension of the liquid drop.
Chapter 3

Line Tension Measurement I: An Application of the Quadrilateral Relation to Liquid Lens Systems

In this chapter, an application of the Quadrilateral Relation to a liquid lens system is demonstrated. The experimental design presented in this chapter will, however, be valid essentially for all fluid, three-phase systems; it will allow line tension measurement to be performed on both pure liquid lens systems and systems containing surfactant or a monolayer. Here, a system which consists of a dodecane liquid lens floating on an air-water interface is chosen. From the experiment, the line tension value is determined by a straightforward utilization of the Quadrilateral Relation.

3.1 Theoretical Analysis

With the help from the graphical representation of the Quadrilateral Relation (Fig. 2-2), one can easily obtain several scalar forms of the Quadrilateral Relation, such as equations involving cosines of contact angles [101]. Here, only the scalar form of the Quadrilateral Relation that suits the present experimental design (Fig. 3-1) is given. This contact line represents the intersection of three interfaces among the two immiscible liquids and the ambient gaseous phase (air in the present experiment). Such a design avoids the difficulty of liquid-liquid engulfing; it also provides control of the extent of the contact between the two
Schematic of a pendant/floating liquid lens in contact with a second liquid. $\gamma^{(1)}$ and $\gamma^{(2)}$ are the surface tensions of the pendant liquid and the second liquid; $\gamma^{(3)}$ is the interfacial tension between the two liquids; $\sigma_\kappa$ represents the line tension contribution to the quadrilateral relation. Contact angles $\theta_1$ and $\theta_2$ are measured in the experiment, which can be used to calculate necessary contact angles in Eq. (3-1) to obtain line tension: The angles in the quadrilateral relation can be obtained from $\theta_{k1} = \theta_1$, $\theta_{2k} = \pi - \theta_2$, and $\theta_{12} = \pi - \theta_1 + \theta_2$. 

Fig. 3-1
liquids and hence improves the stability of the system. This stability is necessary since an immobile hanging liquid lens is required so that the three-phase contact angles can be detected with high accuracy.

To calculate line tension through the Quadrilateral Relation, three interfacial (surface) tensions are needed. They can be routinely measured to a high degree of accuracy by an appropriate methodology, such as Axisymmetric Drop Shape Analysis (ADSA) [105-107,114-116]. In addition, two contact angles at the three-phase contact line are also required. A convenient way to obtain them is to measure the contact angles $\theta_{12}$ and $\theta_{31}$ directly (Fig. 3-1), through a physical observation of the slopes of the two interfaces between the two liquids and the air.

It is noted that only two contact angles are needed among a total of four angles at the three-phase contact line; the contact angles spanned by the dodecane-water interface (in our present case) need not to be measured. To measure the contact angles spanned by the dodecane-water interface would, on the other hand, pose a great difficulty since such a measurement would have to be made through the liquid phases.

With the parameters chosen above, one can readily write a scalar form of the Quadrilateral Relation in order to calculate line tension. Equation (2-41) presented in the last chapter is quadratic with respect to the line tension $\sigma$, and its solution may be easily obtained once the curvature $\kappa$ of the three-phase line is known. The radius of this curvature may be measured by determining the diameter of the liquid lens. This, along with the detection of the two slopes of the interfaces, may be achieved by acquiring the cross-sectional image of the liquid lens.
Solving Eq. (2-41) for the line tension $\sigma$, one obtains

$$
\sigma \kappa = -\left[ \gamma^{(1)} \cos \theta_{k1} + \gamma^{(2)} \cos \theta_{2\kappa} \right] \\
\pm \sqrt{\left[ \gamma^{(1)} \cos \theta_{k1} + \gamma^{(2)} \cos \theta_{2\kappa} \right]^2 - \left( \gamma^{(1)} \right)^2 + \left( \gamma^{(2)} \right)^2 + 2 \gamma^{(1)} \gamma^{(2)} \cos \theta_{12} \gamma^{(3)} \right]^{2}} (3-1)
$$

Two solutions for the line tension are possible, and it will be shown that one of the solutions can be rejected by comparing contact angles predicted by the classical Neumann triangle relation and those calculated through the Quadrilateral Relation (see below).

It is noted that in the actual experiment, the two contact angles, $\theta_1$ and $\theta_2$, are measured, corresponding to the slopes of the pendant/floating liquid and of the base liquid at the three-phase contact line (Fig. 3-1). These two angles are related to the contact angles in Eq. (3-1) by $\theta_{k1} = \theta_1$, $\theta_{2\kappa} = \pi - \theta_2$, and $\theta_{12} = \pi - \theta_1 + \theta_2$.

3.2 Experimental

3.2.1 Materials

The pair of immiscible liquids used here were dodecane and water. Dodecane with a purity of 99+% was obtained from Aldrich Chemical Company, Inc., USA. Water was distilled; its purity was checked by the surface tension measurement which, at 25°C, resulted in $72.14 \pm 0.04 \text{ mJ/m}^2$ at the 95% confidence level (the experimental method employed is ADSA as described below), comparing well to the standard pure water surface tension. The two liquids were saturated with each other for 24 hours before the experiment.
3.2.2 Interfacial (Surface) Tensions

The surface tensions of the two liquids and the interfacial tension between them were measured by Axisymmetric Drop Shape Analysis (ADSA) [105-107,114-116]. The ADSA technique determines liquid-fluid interfacial tensions and contact angles from the shape of axisymmetric menisci, i.e., from pendant drops and sessile drops. The principle of such a technique is to fit the experimental drop profile to a theoretical one given by the Laplace equation of capillarity, and the interfacial tension is generated as a fitting parameter through a non-linear regression procedure. The ADSA program requires several coordinate points along the drop profile, the value of the density difference across the interface, and the value of the local gravitational constant as input. The details of this methodology and its experimental design can be found elsewhere [105-107,114-116].

To maintain the mutual saturation of the liquids throughout the surface/interfacial tension measurements, an experimental setup similar to that in Ref. [116] was used. Briefly, a quartz cuvette (4.5 × 2.5 × 8 cm) contained the two immiscible liquids (alkane and water in the present case), the heavier one at the bottom (Fig. 3-2). The bubbles or drops were created at the tip of a Teflon tube inserted in the appropriate liquid phase. This setup allowed measurement of surface tensions by creating an air bubble in each of the two liquids. The interfacial tension was measured by forming a water drop inside the dodecane phase. All these measurements were done while the two bulk liquids remained in contact.

Since the density of each of the saturated liquids is likely affected by mutual solubility, an accurate measurement of the density is also required. The density measurement was
Fig. 3-2  Experimental setup for surface tension measurement under mutual saturation condition.
performed on a digital density meter (Anton Paar DMA 45, Austria). The results obtained were 0.7451 g/cm³ for dodecane and 0.9970 g/cm³ for water. With these density values, the interfacial tension between dodecane and water was 52.09 ± 0.04 mJ/m², the surface tension between dodecane and the air was 23.53 ± 0.06 mJ/m², and the surface tension between water and the air was 71.93 ± 0.02 mJ/m². The statistical analysis was based on 10 runs for each interfacial (surface) tension measurement, and the error limits were given at the 95% confidence level. All these measurements were performed at room temperature, 25 °C. The values of these interfacial and surface tensions are comparable to the data published in [116] where both decane and hexadecane saturated with water were used; the values for the dodecane-water system are intermediate between those for decane and hexadecane-water systems.

3.2.3 Experimental design

A schematic of the experimental setup is shown in Fig. 3-3. The dodecane drop was created at the tip of a Teflon needle (capillary) with an outer diameter of 1.6 mm (Chromatographic Specialties, Inc., Canada). (Occasionally a finer stainless steel needle with an outer diameter of 0.3 mm and an inner diameter of 0.15 mm was used.) The needle was connected to a Hamilton gastight syringe (Chromatographic Specialties, Inc., Canada) which was driven by a programmable stepper motor (Model 18705, Oriel Corporation, Stratford, Conn. USA). The syringe was supported by a micromanipulator (Leica, ON, Canada) which could be used to position the pendant/floating dodecane drop with precision. When lowering
Fig. 3-3 Schematic of the experimental setup. The pendant/ floating drop of dodecane is supported by a Teflon capillary (needle). Upon lowering the needle with a stepper motor, a three-phase contact line is formed among dodecane, water and air.
the needle, a dodecane liquid lens was formed on the center of the water surface. The size of the three-phase contact line between dodecane, water and air could be adjusted by raising or lowering the dodecane drop, or by adding or removing liquid from the drop. The typical drop diameter range used in the present experiment was between 1 and 7 mm. The water was contained in a 2 cm in diameter by 2 cm in height Teflon (or glass) cylinder with a circular opening which ensures that the liquid lens formed was also circular. To observe the water-air interface from a side-view of the pendant/floating liquid lens system, the water level in the glass cylinder had to be above the rim of the cylinder, i.e., the cylinder was overfilled with water [117-119]. To prevent possible contamination from airborne impurities, the system was enclosed in a quartz cuvette which was sitting on a leveling stage.

The pendant/floating liquid lens was illuminated with a white light source (Model V-WLP 1000, Newport Corp., Fountain Valley, CA, USA) shining through a heavily frosted glass diffuser. The image of the cross section of the liquid lens was obtained by a microscope (Leitz Apozoom, Leica, ON, Canada) linked to a monochrome charge-coupled device video camera (Cohu 4810, Infrascan, Inc., BC, Canada). The video signal of the drop was transmitted to a digital video processor (Parallax XVideo board) which performed the framegrabbing and digitization of the image to 640 \( \times \) 480 pixels with 256 grey levels. A workstation (Sun SPARCstation 10, Sun Microsystems, ON, Canada) was used to acquire the images from the digitization board. An image analysis scheme was then followed (see below). The entire setup, except for the workstation, was placed on a vibration-free table (Technical Manufacturing Corp., Peabody, MA, USA) to isolate the system from external disturbances. The experiments were performed at room temperature, 25 °C. A typical image
obtained is shown in Fig. 3-4.

With the motorized syringe, both static and dynamic modes were employed in the experiment. In the static mode, the liquid lens maintains its size by fixing the volume of the dodecane drop created at the needle tip. For each static liquid lens, images were captured at 0.5 second intervals initially and progressively less rapidly, up to 1 minute intervals, near the end of the run of 6 minutes. In the dynamic mode, the dodecane drop size is varied by changing the drop volume through the motorized syringe. Within a 1 minute cycle, the diameter of the three-phase contact line changed from 4.5 mm to 7 mm and back. During this size change, images were taken at 0.3 second intervals throughout.

3.2.4 Image analysis

Having acquired the cross-sectional image of the liquid lens system (Fig. 3-4), an image analysis scheme is required to extract the drop profile and to obtain the profile coordinates of interfaces. The goal in this procedure is to obtain the diameter of the three-phase contact line (i.e., the diameter of the liquid lens) and two contact angles ($\theta_1$ and $\theta_2$) at the intersection point of the three interfaces (Fig. 3-1). A program in C language was written to process the digital image of the liquid lens:

First, edge detection was performed to extract the profile coordinates of the interfaces. The Sobel edge detection scheme was chosen because of its relative insensitivity to noise and the ability to detect edges well in situations other than horizontal and vertical
Fig. 3-4  An image acquired for the cross section of a pendant/floating liquid lens of dodecane in contact with water.
[120,121]. After applying the Sobel edge operator, a secondary image called a gradient image was obtained, from which the edges (corresponding to interfaces) were identified as the arrays of pixels with the steepest intensity (grey-level) gradient. A resulting interface (edge) profile is shown in Fig. 3-5 (top picture).

The next step was to find the co-planar points A and A' in Fig. 3-5; these intersection points correspond to the points at the three-phase contact line. The strategy to find the left intersection point A, for instance, was to march along the interface profile from the left side (point C in Fig. 3-5) and search for an abrupt change in the slope of the profile. The monitoring process involved fitting a straight line to the first 10 coordinate points, starting from point C, and then skipping these 10 coordinate points and fitting another line to the next 10 points. If there was a significant difference in the slope between the two fitted lines, say 10 degrees, the intersection point A must be located between these two fitted lines. The coordinate of the intersection between these two fitted lines should give the coordinate for the desired point A with adequate accuracy. The same procedure was repeated for finding the right intersection point A' at the three-phase contact line, but this time starting from the right side of the interface profile (point C' in Fig. 3-5). The distance between the two intersection points A and A' gave the diameter of the liquid lens (i.e., the diameter of the three-phase contact line).

Finally, to find the two contact angles at each of the two intersection points A and A', a straight line was fitted to the first 30 coordinate points, starting from the intersection point A for instance, along each of the two interfaces that are intersecting at A (Fig. 3-5, bottom picture). From the slopes of the fitted lines, the two contact angles $\theta_1$ and $\theta_2$ in Fig. 2 were
Fig. 3-5  A drop profile acquired from an image (as in Fig. 3-4) through an image detection scheme. The distance between A and A' is 6.69 mm, representing the diameter of the liquid lens. The bottom picture is an enlargement of the portion enclosed by a rectangle in the top picture, where 30 pixel points along each of the interfaces AB and AC, starting from the intersection point A, are used in the linear curve-fit.
obtained. The same procedure was repeated for the other intersection point A'. The average values for θ₁ and θ₂ were used in Eq. (3-1) to calculate line tension.

The reasons for using 30 coordinate points in the straight line fit for finding the contact angles at the intersection points are as follows: Ideally, one would wish to find the tangent to the interface at the intersection, and from this tangent the contact angle would be calculated. One of the methods to find the tangent is to fit a few pixel points at or near the intersection to a straight line along the interface; the slope of the fitted line will represent the tangent. However, as can be seen from Fig. 3-5, it is not possible to use only a small number, say 5 or fewer pixel points, because the resolution of the profile is only to the closest pixel. This results in horizontal strings of pixels as shown in Fig. 3-5 (bottom picture), to the left of point A. To obtain adequate averaging a number of pixels significantly larger than five must be used. By inspection of the interface profile in Fig. 3-5, it is also seen that the interfaces are actually curved; hence, using too many pixel points would also lead to errors.

To seek an optimal number of pixel points used in the linear curve-fit, linear curve-fit results are plotted against the number of pixel points for a typical drop profile (Figs. 3-6 and 3-7). Figure 3-6 shows the slope of the fitted straight line to the pixel points along the interface AB, starting from the intersection point A, as in Fig. 3-5. It is seen that error limits are very large when using too few pixel points (less than 10); as more pixel points (more than 40) are used, the slope is decreasing progressively. This latter observation is also perceived in the curvature along the interface AB (Fig. 3-5). Only within the region where between 20 and 40 pixel points are used, are constant slopes, also with relatively small error limits, observed. The contact angle variation corresponding to the slope fluctuation within 20 to 40 pixel point
Fig. 3-6 The slope of the fitted straight line to the interface AB in Fig. 3-5 against the number of pixel points used in the fit, which indicates a steady value of the slope, also with a relatively small fluctuation, in the region of 20 to 40 pixel points. The errors associated with each slope are the standard errors in the linear curve-fit.
Fig. 3-7 The slope of the fitted straight line to the interface AC in Fig. 3-5 against the number of pixel points used in the fit, which indicates a steady value of the slope, also with a relatively small fluctuation, in the region of 20 to 40 pixel points. The errors associated with each slope are the standard errors in the linear curve-fit.
region is found to be less than 0.3 °, after converting the slope to the angle. As will be shown latter, such a small contact angle change does not affect the line tension results drastically. Therefore, 30 pixel points were chosen for the linear curve-fit.

A similar pattern is found in Fig. 3-7, where the slope of the straight line fitted to the pixel points along the interface AC of Fig. 3-5, starting from the point A, is plotted against the number of the pixel points used in the fit. Again, a relatively constant slope is found in the region of 20 to 40 pixel points. When more pixel points are used in the curve-fit, the slope starts to increase progressively; this is also perceived in the curvature along the interface AC (Fig. 3-5). As a consequence from Figs. 3-6 and 3-7, 30 pixel points were chosen in the linear curve-fitting procedure.

Another reason for using a 30 pixel point linear curve-fit is that the 30 pixel point fit provides excellent linear correlation coefficients for each of the two intersecting interfaces (AB and AC in Fig. 3-5), typically, better than 0.995 for the interface AB and 0.9 for the interface AC along with extremely high confidence levels (> 99.9%). It might be suggested to fit a higher order polynomial to the interface profile and then to calculate the slope of the fitted polynomial at the intersection point; however, it was found that the higher order polynomial fit was too sensitive to the pattern and/or noise in the pixels detected for the interface (edge) (see Fig. 3-5). This resulted in contact angle fluctuation of well above 1° when a slightly different number of pixels (say, 32 instead of 30) was used for a third or fourth order polynomial fit. Thus, the linear curve-fit to 30 pixel points along the interface profile seemed optimal. (It should be noted that the above conclusion is based on the analysis on the present liquid lens configuration where the alkane lens size ranges from 1 to 7 mm.)
three surface tensions obtained above, one could calculate the contact angles with the classical Neumann relation and compare the results with those calculated from Eqs. (3-2) and (3-3). The one of the two $\theta_{3k}$'s which significantly differs from the prediction of the classical Neumann triangle relation will be rejected, see below.

3.3 Results

3.3.1 Determination of the Appropriate Sign in Equation (3-1)

To determine the appropriate sign in Eq. (3-1), by using the data extracted from an image as shown in Fig. 3-4 for the dodecane-water-air three-phase contact line system, two line tension values, approximately $-1 \times 10^{-8}$ and $8 \times 10^{-5}$ J/m, were calculated, corresponding to the negative and positive signs preceding the square root term on the right-hand side of Eq. (3-1), respectively. By applying Eqs. (3-2) and (3-3), values of 13° and 167°, corresponding to the minus and plus signs, were obtained for $\theta_{3k}$.

On the other hand, suppose the line tension can be neglected, i.e., the classical Neumann triangle relation can be used. The contact angle $\theta_{13}$ (equal to $\theta_{3k} + \theta_{kl}$ in Fig. 3-1) between the air-dodecane interface and the dodecane-water interface can be calculated, yielding a value of 39°. With the contact angle $\theta_1$ ($= \theta_{kl} \sim 28°$) observed from the slope of the air-dodecane interface, one obtains $\theta_{3k} = 39 - 28 = 11°$, which is close to $\theta_{3k} = 13°$ for the minus sign in Eq. (3-1). Because the contact angle $\theta_{3k} = 167°$ corresponding to the plus sign is drastically different from the prediction from the classical Neumann triangle relation,
3.2.5 Line tension calculation

Having the three interfacial (surface) tensions, the two contact angles and the radius of curvature of the three-phase contact line, the line tension can be calculated by using Eq. (3-1), for each image acquired. In applying Eq. (3-1), $\gamma^{(1)}$, $\gamma^{(2)}$ and $\gamma^{(3)}$ correspond to the interfacial tensions of dodecane-air, water-air and dodecane-water, respectively. It is necessary to make a choice for the sign in front of the square-root on the right-hand side of Eq. (3-1). However, one had no a priori knowledge of line tension. Both of the signs were then used to calculate the line tension value initially. The next step was to determine which one of the two line tension values was reasonable.

Having the line tension value, one could calculate all the contact angles at the three-phase contact line, including $\theta_{3x}$ (Fig. 3-1). Projecting the Quadrilateral Relation into two orthogonal directions, one of which follows the horizontal line tension direction, yields [3]

$$\cos \theta_{3x} = -\frac{1}{\gamma^{(3)}} \left[ \sigma \kappa + \gamma^{(1)} \cos \theta_{x1} + \gamma^{(2)} \cos \theta_{x2} \right]$$

and

$$\sin \theta_{3x} = \frac{1}{\gamma^{(3)}} \left[ \gamma^{(1)} \sin \theta_{x1} - \gamma^{(2)} \sin \theta_{x2} \right]$$

Thus, the contact angle $\theta_{3x}$ can be determined. The resulting contact angle $\theta_{3x}$'s are expected to be drastically different for the two line tension values. On the other hand, it is known that the existence of line tension does not change contact angles by large amounts from those determined from the classical Neumann triangle relation [55,56]. Therefore, by using the
this choice of sign is then rejected. Consequently, the negative sign was used in calculating line tension from Eq. (3-1).

### 3.3.2 Line Tension Results from Static Measurements

It is worth noting again that in using Eq. (3-1) to calculate line tension, only two contact angles $\theta_1$ and $\theta_2$ are required (see also Fig. 3-1). The contact angles spanned by the dodecane-water interface do not have to be measured; hence, the difficulty to determine the position of this interface is avoided.

Figure 3-8 gives the diameter, the two contact angles $\theta_1$ and $\theta_2$ (c.f., Fig. 3-1), and the line tension calculated from Eq. 3-1. The data are shown as a function of time in a static experiment where the dodecane drop volume was kept constant. Within the 6 min span, there is no obvious trend of change in the data. Small fluctuations occur in each of the four graphs in this figure, which correspond to less than 10% error limits at the 95% confidence level. Particularly, the error limits for the two contact angles $\theta_1$ and $\theta_2$ are less than $\pm 0.1^\circ$, based on the analysis of more than 30 images of a static drop and the use of the student $t$-distribution. It is noted that all the line tension values are negative, resulting in an average of $-1.42 \pm 0.11 \times 10^{-6}$ J/m at the 95% confidence level for the liquid lens with a diameter of 6.91 mm. This result is entered into Table 3-1 for comparison with the results from other liquid lenses of different diameters.
Fig. 3-8  The diameter, two contact angles corresponding to the slopes of the air-dodecane interface and air-water interface (relating to the contact angles in Fig. 3-1 by $\theta_1 = \theta_{e1}$ and $\theta_2 = \theta_{e2} + \theta_{12} - \pi$), and line tension plotted as a function of time up to 6 min. The values of the diameter and line tension are entered into Table 3-1.
Table 3-1 Line Tension versus Diameters of the Dodecane Liquid Lens

<table>
<thead>
<tr>
<th>Diameter (mm)</th>
<th>Line Tension (μJ/m)</th>
<th>95% Confidence Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.84</td>
<td>-1.43</td>
<td>± 0.03</td>
</tr>
<tr>
<td>2.31</td>
<td>-1.03</td>
<td>± 0.16</td>
</tr>
<tr>
<td>3.47</td>
<td>-1.39</td>
<td>± 0.05</td>
</tr>
<tr>
<td>4.55</td>
<td>-1.16</td>
<td>± 0.15</td>
</tr>
<tr>
<td>6.91</td>
<td>-1.42</td>
<td>± 0.11</td>
</tr>
<tr>
<td>Overall Average</td>
<td>-1.29</td>
<td></td>
</tr>
<tr>
<td>Overall 95% Confidence Limits</td>
<td>± 0.24</td>
<td></td>
</tr>
</tbody>
</table>

When changing the dodecane drop volume, the diameter (and hence the curvature) of the three-phase contact line changes. In this static mode, line tensions were obtained as shown in Table 3-1. Again, the values of line tension for all five runs, with diameters ranging from 1 to 7 mm, are negative, on the order of $10^{-6}$ J/m. From the table, no apparent trend in line tension is observed with the drop size variation. Averaging these five line tensions results in $-1.29 \pm 0.24 \times 10^{-6}$ J/m at the 95% confidence level (Table 3-1).

It is noted that in Table 3-1 the 95% confidence limits for each run are rather small and do not overlap from run to run. This is believed to be due to the random variation in the initial conditions under which the liquid lenses were formed. As mentioned in Section 3.2.3, a liquid lens was formed by lowering the needle, which supported the pendant drop of the sample liquid (Fig. 3-3), through a manual control over the micromanipulator.
3.3.3 Line Tension Results from Dynamic Measurements

Figure 3-9 illustrates line tension as a function of time in a dynamic experiment, during which the diameter of the three-phase contact line was varied in a periodic mode from 4.5 mm to 7 mm. Each cycle took approximately 1 min, and two cycles are presented in Fig. 3-9. Although the change in the diameter induces a periodic variation in the contact angles, especially for $\theta_1$, the line tension essentially remains constant. The steady, slight decrease in the line tension is attributed to a gradual accumulation of impurities (e.g., from the air) during the experiment. Applying linear regression to the line tension values yields an intercept value for the line tension at $-1.40 \pm 0.05 \times 10^6$ J/m ($0.05$ is the standard error from the linear regression), which is comparable to the line tension value from the static experiment (Table 3-1). This intercept value of line tension represents the value at time zero when the experiment starts, and hence it is assumed to be least subject to impurities.

An interesting feature in Fig. 3-9 is the drop-size (or lens-size) dependence of the contact angle, i.e., the effect of diameter variation on the contact angle. Conceptually, one may adopt a similar analysis as used in the drop-size dependence of contact angle for a sessile drop on a solid surface [55,56], i.e., to use the modified Young equation to analyze the drop-size dependence in Fig. 3-9. The fact that the increase in contact angle ($\theta_1$ in Fig. 3-9) corresponds to the increase in drop size (represented by the diameter in Fig. 3-9) indicates a negative value for the line tension. This confirms that the line tension in the present system is negative.
Fig. 3-9  The diameter, two contact angles corresponding to the slopes of the air-dodecane interface and air-water interface, and line tension versus time in a dynamic mode, where the drop-size is controlled by adjustment of the drop volume of dodecane. The intercept at time zero of the fitted straight line to the line tension values yields a line tension of \(-1.39 \pm 0.05 \times 10^{-6} \text{ J/m}\) (0.05 is the standard error limit in the linear regression), comparable to the values in the static experiment (Table 3-1).
3.4 Discussion

3.4.1 Possible Sources of Error in Line Tension Measurements

By using the automatic image analysis scheme, it is possible to analyze a large amount of data, which all result in a negative line tension of the order of $10^6$ J/m (Table 3-1, Figs. 3-8 and 3-9). To confirm this image analysis scheme, manual digitization for an image as shown in Fig. 3-4 was also performed. In this manual digitization, one first chose ten pixel points along an interface, starting from an intersection point (which could be identified by eye). By linear curve-fitting to these ten points with a least-squares procedure, one then found the slope of the interface, which could be converted into a contact angle. The distance between the two intersection points was also measured, which represents the diameter of the liquid lens. Finally, with the contact angles and the diameter obtained, the line tension was calculated using Eq. (3-1). The resulting values were comparable to the values reported in Table 3-1, except that the scatter in the line tension value was from -1 to $-3 \times 10^6$, which was larger than that of the automatic image analysis scheme (Table 3-1). This indicates that the automatic image analysis scheme can not only process a large amount of data points in a relatively short period of time but also give better precision than a manual digitization scheme.

In Fig. 3-5, which results from the automatic image analysis scheme, one sees that the interface AC contains two steps within the first 30 pixel points from the intersection point A. There are 5, 15 and 9 pixel points in consecutive horizontal sections; the slope of a fitted straight line will then be affected by the positions of these two steps. This is reflected in Fig.
where the scatter in the contact angle is observed. The line tension values show a corresponding scatter. (In Chapter 5, an improved version of the image analysis scheme with subpixel resolution in edge detection will be introduced. The results there will show reduced scatter in the data, but nevertheless confirm the average values of line tension reported here.)

Another possible source of error might be the surface and interfacial tension determination. The ADSA technique is able to determine surface and interfacial tensions typically to ±0.04 mJ/m² at the 95% confidence level, with the present setup. These error limits will translate into an error of the order of 10⁻⁶ J/m in line tension value, which is two orders of magnitude smaller than the values of the line tension found.

Furthermore, the surface/interfacial tension values reported in Ref. [116] for several other alkane-water systems were used to interpolate the values for the dodecane-water system. The resulting surface/interfacial tensions are 23.71, 71.55 and 51.51 mJ/m² for dodecane-air, water-air and dodecane-water interfaces, respectively. With these values, the line tension corresponding to Fig. 3-8 was re-calculated, yielding -1.23 ± 0.29 × 10⁻⁶ J/m instead of -1.42 ± 0.11 × 10⁻⁶ J/m at the 95% confidence level. This indicates that the errors from the surface/interfacial tensions are minimal, not resulting in substantial change in the line tension value.

3.4.2 Impossibility of Zero Line Tension

The line tension obtained in the present experimental design is -1.29 × 10⁻⁶ J/m (Table 3-1, with the diameter of the liquid lens ranging from 1 to 7 mm). This line tension has the
same order of magnitude as that resulting from the drop-size dependence of contact angle measurement on a solid surface, although with the opposite sign [55,56]. However, this value differs from that of other reports [4-34] by orders of magnitude, where an order of 10\(^{-10}\) J/m is typically reported. From the perspective of the results reported here, such a result would mean that line tension would not be detectable, i.e., \(\sigma = 0\).

In order to demonstrate that our observation of the shape of the liquid lens (Fig. 3-4) cannot be explained in the absence of line tension or with line tension only of an order of 10\(^{-10}\) J/m, the following calculations are performed. First, one calculates the contact angle with the classical Neumann triangle relation, i.e., setting the line tension zero in Eq. (2-41). Then, one compares this calculated contact angle with the angle measured in the present experiment. For a typical liquid lens, the classical Neumann relation gives the contact angle \(\theta_{12} = 152.9^\circ\) (c.f., Fig. 3-1), but the experimental value is \(\theta_{12} = \pi -\theta_1 + \theta_2 = 155.7 \pm 0.2^\circ\) (data from Fig. 3-4) at the 95% confidence level. The difference in contact angle of 2.8\(^\circ\) is an order of magnitude larger than the error limits in the experiment; thus, the possibility of zero line tension is ruled out.

The above not only rules out the possibility of zero line tension but also implies that a line tension of the order of 10\(^{-10}\) J/m is incompatible with the data obtained in the present experiment. This is significant since, through a dimensional argument, one may state [4] that line tension should be on the order of magnitude of the product of surface tension and some characteristic length. It has been speculated [4] that such a characteristic length is the width of a contact line region. If one takes the surface tension to be of the order of 100 mJ/m\(^2\) (the common order of magnitude for surface tension) and the width of the contact line to be of the
order of $10^9$ m (one molecular size), then the estimated order of magnitude for the line
tension would be $10^{-10}$ J/m. Thus, the value of the order of $10^{10}$ J/m seems reasonable.
However, such a dimensional argument should be used with caution since there is no proof
for its validity. As mentioned in the Introduction chapter, the current development of
statistical thermodynamics has not been able to resolve the problems in predicting the value
of line tension.

Furthermore, if the above argument can be used for estimating line tension, a similar
argument should be applicable for evaluating the order of magnitude of surface tension; that
is, the surface tension would approximately equal the product of bulk pressure and the
thickness of an interface. When one takes the pressure to be one atmospheric pressure and
the thickness of the interface to be of the order of $10^9$ m, their product would predict the
order of $10^{-1}$ mJ/m$^2$ for the surface tension. However, this prediction is three orders of
magnitude smaller than the surface tension value, which is often of the order of 100 mJ/m$^2$,
such as the water surface tension. One interesting observation is that in both predictions for
line tension and for surface tension, the estimated values are smaller than the experimental
ones, all by three or four orders of magnitude. This discrepancy certainly indicates that the
validity of this dimensional argument is questionable.
3.4.3 Quadrilateral Pictograph of a Negative Line Tension

With the line tension measured, i.e., \(-1.29 \times 10^{-6}\) J/m (Table 3-1), one may draw a quadrilateral with four sides, in proportion, representing the three surface (interfacial) tensions and the one line tension term, and using the contact angles obtained from the actual measurement (Fig. 3-10). As expected, the resulting quadrilateral (top portion of Fig. 3-10) looks essentially the same as a classical Neumann triangle since the line tension value is small and the line tension contribution is negligible relative to the surface tension terms in the quadrilateral. However, with a magnification of 100 times, one can show the contribution of the line tension. While large compared to some published data, this line tension is still small compared to the surface tension contribution. It is seen that the negative line tension contribution to the quadrilateral diagram results in crossing of the two surface tension vectors, although the topology of the quadrilateral remains intact.

3.5 Summary

The Quadrilateral Relation, as a generalization of the classical Neumann triangle relation, was applied to a liquid lens system. The line tension of the three-phase contact line formed by dodecane-water-air three phases was found to be \(-1.29 \pm 0.21 \times 10^{-6}\) J/m at the 95% confidence level, with the diameter of the liquid lens ranging from 1 to 7 mm. This value of line tension is supported by both static and dynamic measurements on the present liquid lens system. In agreement with the formulation of the Quadrilateral Relation (Chapter
Fig. 3-10 Quadrilateral diagram with four sides representing three surface (interfacial) tensions (dodecane-air, water-air and dodecane-water) and a line tension contribution (dodecane-water-air three-phase contact line) in proportion, using the contact angles obtained from the actual experiment (corresponding to Fig. 3-4). Because of the minuteness of the line tension relative to the surface tension, the resulting quadrilateral diagram looks like a classical Neumann triangle (top portion of the figure). With a magnification of 100 times, the contribution of this small, negative line tension can be seen, which constitutes the fourth side of the quadrilateral (bottom portion of the figure). The negative line tension contribution to the quadrilateral diagram results in crossing of the two surface tension sides, although the topology of the quadrilateral remains intact.
2), there is no lens-size dependence of line tension observed with the diameter of the liquid lens ranging from 1 to 7 mm. The experimental design presented is able to provide relatively stable and reproducible line tension measurements, and this design in principle works for all three-phase contact line systems involving only fluid phases.
Chapter 4

Line Tension Measurement II: Lens-Size Dependence of Contact Angles in Liquid Lens Systems

A methodology has been established in the preceding chapter for measuring the line tension in liquid lens systems, where the Quadrilateral Relation has played an essential role. The line tension of the three-phase contact line formed by dodecane-water-air was found to be negative and of the order of \(10^4\) J/m, which is of the same order of magnitude as that from the drop-size dependence of contact angle measurement on a solid surface, although with the opposite sign [55,56]. This result has been confirmed from both static and dynamic measurements (Figs. 3-8 and 3-9). The measurement shown in Fig. 3-9 was in fact a drop-size or, more precisely, a lens-size, dependence of contact angle experiment. This leads to the question whether such information can be used in determining line tension, just as that used in solid-liquid-air systems. This chapter answers this question by exploring the possibilities of using the lens-size dependence of contact angle information to estimate the line tension value.

As pointed out before, compared with those in solid-liquid-fluid systems, the interfaces in liquid-liquid-fluid systems are smooth and homogeneous; hence, zero contact angle hysteresis is expected. That is, the contact angle measured will be independent of whether an advancing or a receding contact angle is used in the experiment. However, there is still a need to support this claim with experimental evidence. Furthermore, the lens-size
dependence of contact angle measurement is dynamic in nature; therefore, it is reasonable to ask whether the rate at which the three-phase contact moves will affect the outcome of contact angle measurements. These questions will be answered in this chapter.

Specifically, to exclude the possibility of any fluid mechanics or other dynamic effects, the change of lens size was performed (in a periodic mode) at three different rates. To confirm and complement the measurements presented in the last chapter, contact angles were determined as a function of lens diameter. In this chapter line tension results as determined by two approaches are presented: One is that presented in the last chapter which uses the quadrilateral formula directly to calculate the line tension from individual floating lenses, and for the sake of distinction this is called Method I. A dodecane liquid lens floating on a water-air surface was formed and the contact line was advanced and receded continuously at a fixed speed in order to study lenses of different sizes. Further, a new scheme (called Method II) is developed to calculate line tension by reformulating the Quadrilateral Relation, where, similar to the application of the modified Young equation to the drop-size dependence of contact angle of a sessile drop on a solid surface, the slope of the cosine of the contact angle against the diameter of contact line is used. The resulting line tension from this new scheme will be compared to that obtained in the last chapter (i.e., with Method I).

4.1 Theoretical Analysis

The main purpose of this section is to generate a theoretical expression which allows for a correlation between line tension and the drop-size dependence of contact angle.
However, this may not be an easy task since, unlike the case in a solid-liquid-fluid system, no interface can be regarded as flat in a liquid-liquid-fluid three-phase contact line system, due to the deformability of liquids and fluids. In the following, the theoretical expression employed for Method I will be briefly reviewed, thereby leading to a development of the necessary theoretical expressions of line tension in relation to the drop-size dependence of contact angles.

The theoretical relation used in calculating line tension in Method I has been presented in the last chapter. The line tension is calculated based on the values of three interfacial (surface) tensions, two contact angles at the three-phase contact line, and the diameter of the liquid lens. The scalar form of the Quadrilateral Relation suitable for the experimental design is Eq. (2-41)

\[
\gamma_{12}^2 = (\sigma \kappa)^2 + \gamma_1^2 + \gamma_2^2 + 2\sigma \kappa \gamma_1 \cos \theta_{k1} + 2\gamma_1 \gamma_2 \cos \theta_{i2} + 2\gamma_2 \sigma \kappa \cos \theta_{2x} \quad (2-41)
\]

where \( \gamma_1 \) and \( \gamma_2 \) are the surface tensions of the pendant liquid and of the base liquid (dodecane and water in the present case), respectively; \( \gamma_{12} \) is the interfacial tension between the two; \( \sigma \) is the line tension of the three phase contact line; the sum of the three contact angles \( \theta_{k1} + \theta_{i2} + \theta_{2x} = 2\pi \).

Solving Eq. (2-41) for the line tension \( \sigma \), one obtains

\[
\sigma \kappa = \frac{-(\gamma_1 \cos \theta_{k1} + \gamma_2 \cos \theta_{2x})}{\pm \sqrt{(\gamma_1 \cos \theta_{k1} + \gamma_2 \cos \theta_{2x})^2 - (\gamma_1^2 + \gamma_2^2 + 2\gamma_1 \gamma_2 \cos \theta_{i2} - \gamma_{12}^2)}} \quad (3-1)
\]

It is noted in Eq. (3-1) that this form of the Quadrilateral Relation resembles the modified
Young equation [55,56] if only the first term on the right-hand side of the equation is retained. The modified Young equation (see also Appendix A) can be written as

$$\sigma \kappa = -\gamma_{lv} \cos \theta + \gamma_{sv} - \gamma_{sl} \quad \text{(4-1)}$$

where \( \kappa \) is the curvature of the three-phase contact line of the sessile drop on a solid surface; \( \gamma_{lv}, \gamma_{sv}, \) and \( \gamma_{sl} \) are the surface tensions between the liquid and the air, the solid and the air, and the solid and the liquid, respectively; \( \theta \) is the liquid contact angle on the solid surface and is the counterpart of \( \theta_{sl} \) in Eq. (3-1). The technique of the drop-size dependence of contact angle determines line tension by finding the slope \((-\sigma/\gamma_{lv}) \cos \theta \) against \( \kappa = 1/R \), where \( R \) is the radius of the contact circle. To find this slope, a series of contact angles is measured within a range of the curvature \( \kappa \) of the three-phase contact line. The benefit of using the slope to determine line tension is that the solid surface tensions are not needed (Appendix A).

The Method II utilizes a similar slope method in conjunction with the Quadrilateral Relation to calculate line tension. However, in Eq. (3-1), the slope of \( \cos \theta_{sl} \) against \( \kappa \) involves not only \(-\sigma/\gamma_{lv}\) but also several other terms. To find out how useful the slope \( d\cos \theta_{sl}/d\kappa \) is in determining the line tension \( \sigma \), Eq. (3-1) is reformulated into [123]

$$\sigma \frac{d\kappa}{d\cos \theta_1} = -(\gamma_1 - \gamma_2) \frac{d\cos \theta_2}{d\cos \theta_1}$$

$$- (\gamma_1 \cos \theta_1 - \gamma_2 \cos \theta_2)(\gamma_1 - \gamma_2) \frac{d\cos \theta_2}{d\cos \theta_1} + \gamma_1 \gamma_2 \frac{d\cos (\theta_1 - \theta_2)}{d\cos \theta_1}$$

$$\frac{\sqrt{(\gamma_1 \cos \theta_1 - \gamma_2 \cos \theta_2)^2 - [\gamma_1^2 + \gamma_2^2 - 2 \gamma_1 \gamma_2 \cos (\theta_1 - \theta_2) - \gamma_{12}^2]}}{\sqrt{(\gamma_1 \cos \theta_1 - \gamma_2 \cos \theta_2)}}$$

where \( \theta_{sl} = \theta_1, \theta_{2x} = \pi - \theta_2, \) and \( \theta_{12} = \pi - \theta_1 + \theta_2 \) are employed. It is apparent that in order
to determine the line tension $\sigma$, three slopes have to be measured: $d\cos\theta_1/d\kappa$, $d\cos\theta_2/d\cos\theta_1$, and $d\cos(\theta_1-\theta_2)/d\cos\theta_1$, in addition to all three surface tensions, and two contact angles $\theta_1$ and $\theta_2$. No computational advantage over Eq. (3-1) seems to be gained. Nevertheless, the input required for Eq. (4-2) is quite different from that for Eq. (3-1). While the latter only requires information about the contact angles at one lens diameter, the former also requires information on the lens size dependence of contact angles. Thus, while Eq. (4-2) is, at face value, less convenient than Eq. (3-1), it provides a test for the internal consistency of the approach.

Furthermore, as will be shown later, for the dodecane-water-air three-phase contact line system in our present experiment, the first term is the dominant one on the right-hand side of Eq. (4-2); hence,

$$\sigma = -\gamma_1 \frac{d\cos\theta_1}{d\kappa} \quad (4-3)$$

The significance of Eq. (4-3) lies in the fact that the line tension can be estimated for the present system—and presumably many similar ones—from a single surface tension and the lens size dependence of a single contact angle. In Eq. (4-3), the surface tension can be in error by a few percent at the most. Hence, the sign and the magnitude of the line tension depend entirely on the lens size dependence of the contact angle $\theta_1$. This is significant since the line tension values of the order of $-10^{-6}$ J/m reported here are separated from a line tension value of 0 (or $10^{-10}$ J/m) only by less than 3 degrees in $\theta_{12}$ (see the last chapter). While the experimental accuracy is indeed an order of magnitude better than this, some concern about
a systematic error, e.g., due to lighting, might remain. But it would seem far less likely that
such a putative error in lighting would also produce a similarly faulty value for the lens-size
dependence of the contact angle.

4.2 Experimental

The materials used, the interfacial (surface) tensions measured, and the image analysis
schemes applied were the same as those presented in the last chapter. The experimental
design was also similar to that of the last chapter, except that the motorized syringe was used
strictly to vary the size of the lens by adding and removing liquid from the lens (c.f., Section
3.2.3).

4.2.1 Experimental Procedure

Lenses were formed by creating an initial dodecane drop at the needle tip then
carefully lowering the needle down until the drop just touched the water surface. The drop
would then spread to form the lens, and the motor could then be used to pump more fluid
in to increase the size of the lens. During the static experiment in which the lens diameter was
held constant, images were captured at 0.5 second intervals initially and progressively less
rapidly, up to 1 minute intervals, near the end of the run of 6 minutes. During the dynamic
experiments the lens size varied by changing the drop volume through the motorized syringe.
Three motor speeds were employed: 20, 5 and 1 step(s) per second, which corresponded to
92.2, 23.2 and 4.75 μm/s for the advancing and receding of the contact line. They also corresponded to approximately 1, 3.5 and 16 minutes per cycle, within which the diameter of the three-phase contact line changed from 4.5 to 7 mm and back. During this size change, images were taken at 0.3 second intervals throughout.

4.2.2 Line Tension Calculation

Having the three interfacial (surface) tensions, the two contact angles and the radius of curvature of the three-phase contact line, the line tension can be calculated by using Eq. (3-1) as well as Eq. (4-2), for each image acquired. In applying Eq. (3-1), \( \gamma_1, \gamma_2 \) and \( \gamma_{12} \) correspond to the surface (interfacial) tensions of dodecane-air, water-air, and dodecane-water interfaces, respectively. As mentioned before, the negative sign in front of the square-root on the right-hand side of Eq. (3-1) was chosen by comparing the experimental contact angles with those predicted by the classical Neumann triangle relation (see Chapter 3). In applying Eq. (4-2), three derivatives have to be determined through the drop-size dependence of contact angles; hence, a linear regression procedure was employed to find the respective slopes (see below).
4.3 Results

4.3.1 Method I: Line Tension from Individual Lenses

Figure 4-1 illustrates the results of diameter, two contact angles $\theta_1$ and $\theta_2$ (c.f., Fig. 3-1), and line tension calculated from Eq. (3-1) for a typical dodecane-water-air lens system. The data are shown as a function of time in the experiment in which the dodecane drop volume was kept constant. This is similar to Fig. 3-8, except with a different lens size. Within the 6 min span, there is no obvious trend in the data. Small fluctuations occur in each of the four graphs, which correspond to less than 10% error limits at the 95% confidence level. All the line tension values are negative, resulting in $-1.2 \pm 0.1 \times 10^{-6}$ J/m at the 95% confidence level for the liquid lens at a diameter of 3.5 mm.

Figures 4-2 to 4-4 illustrate the contact angle and line tension data as a function of time for the case in which the diameter of the three-phase contact line was varied in a periodic mode from 4.5 mm to 7 mm. Each cycle takes approximately 1, 3.5 and 16 min for Figs. 4-2, 4-3 and 4-4, respectively. Although the change in diameter induces a periodic variation in the contact angles, especially in $\theta_1$, the line tension essentially remains unaffected. The steady, slight decrease in the line tension may be attributed to a gradual accumulation of impurities during the experiment (c.f., Section 3.3.3). With the decrease in the rate of the diameter change, the decline in line tension within one cycle increases, from Fig. 4-2 to Fig. 4-4. This is due to the increase in experiment time. By applying linear regression to the line tension
The diameter, two contact angles defining the slopes of the dodecane-air interface and water-air interface (cf. Fig. 3-1), and line tension plotted as a function of time, for individual static lenses.
The diameter, two contact angles defining the slopes of the dodecane-air interface and water-air interface, and line tension versus time. The lens size is varied by adjustment of the drop volume of dodecane at a rate of 1 min per cycle, i.e., 92.2 μm/s of the contact line movement. The intercept at time zero of the fitted straight line yields a line tension of $-1.4 \pm 0.1 \times 10^{-6}$ J/m (0.1 is the standard error limit in the linear regression).
Fig. 4-3  The diameter, two contact angles defining the slopes of the dodecane-air interface and water-air interface, and line tension versus time. The lens size is varied by adjustment of the drop volume of dodecane at a rate of 3.5 min per cycle, i.e., 23.2 \( \mu \text{m/s} \) of the contact line movement. The intercept at time zero of the fitted straight line yields a line tension of \(-1.3 \pm 0.1 \times 10^{-6} \) J/m (0.1 is the standard error limit in the linear regression). The slight decline in line tension is due to gradual accumulation of impurities at the interface and the contact line regions.
Fig. 4-4  The diameter, two contact angles defining the slopes of the dodecane-air interface and water-air interface, and line tension versus time. The lens size is varied by adjustment of the drop volume of dodecane at a rate of 16 min per cycle, i.e., 4.75 \( \mu \)m/s of the contact line movement. The intercept at time zero of the fitted straight line yields a line tension of \(-1.1 \pm 0.1 \times 10^6\) J/m (0.1 is the standard error limit in the linear regression). The slight decline in line tension with time is due to gradual accumulation of impurities at the interface and the contact line regions.
values, the intercept values for the line tension are obtained at $-1.4 \pm 0.1 \times 10^6$, $-1.3 \pm 0.03 \times 10^6$ and $-1.1 \pm 0.02 \times 10^6$ J/m (the error limits are the standard error) from Figs. 4-2, 4-3 and 4-4, respectively. These values compare well with the line tension value from the static lenses (Fig. 4-1) and that presented in the last chapter (Table 3-1). The intercept represents the value of the line tension at time zero when the experiment starts; this value is assumed to be least subject to impurities.

4.3.1.1 Comparison between Advancing and Receding Contact Angles

An interesting feature in Figs. 4-2 to 4-4 is the lens-size dependence of the contact angle, i.e., the effect of diameter variation on the contact angle. Figure 4-5 shows this dependence of the contact angle $\theta_i$ on the diameter of the three-phase contact line for three rates. A significant change in $\theta_i$ is observed with the diameter variation between 4.5 and 7 mm. With the slowest rate of the diameter change (Fig. 4-5c), it is seen that $\theta_i$ corresponding to advancing and receding contact angles branches out markedly. This branching between advancing and receding contact angles is also indicated in Fig. 4-5b for the intermediate rate. However, at the fastest speed of diameter variation (Fig. 4-5a), essentially the same advancing and receding contact angle $\theta_i$ are seen. This indicates that the contact angle hysteresis for the liquid-liquid-fluid system is negligible, contrary to most sessile drops on solid surfaces where imperfection of the solid surfaces always induces a difference between the advancing and receding contact angles.

The most likely explanation for the rate-dependent branching between the advancing
Fig. 4-5 The lens-size dependence of contact angle at three different speeds of advancing and receding the contact line (a) 1 min per cycle, (b) 3.5 min per cycle, and (c) 16 min per cycle. At lower speeds (b) and (c), the difference between the advancing contact angle and the receding contact angle is attributed to gradual accumulation of impurities to the interfaces and the three-phase contact line.
and receding contact angles is the accumulation of impurities at the three-phase contact line and the interfaces; hence, the interfacial tensions as well as line tension can be influenced. With the highest rate, the impurity effects, presumably linked to adsorption processes, do not influence the contact angle significantly due to a short period of time of adsorption [123]. Further comments on the effects of impurity adsorption are given in Section 5.2.1.

4.3.2 Method II: Line Tension Calculations from the Lens-Size Dependence of Contact Angles

As mentioned above, the lens-size dependence of contact angles results from line tension effects. In a manner similar to the practice of the drop size dependence of contact angle on a solid surface [55,56], it is hoped to make use of the lens size dependence of the contact angles through Eq. (4-2). In Fig. 4-2, the first half cycle AB is labelled as Leg 1, the second half cycle CD as Leg 2, the third half cycle EF as Leg 3, and the last half cycle GH as Leg 4. From each of these legs, one finds three derivatives $d\cos\theta_1/d\kappa$, $d\cos\theta_2/d\cos\theta_1$ and $d\cos(\theta_1-\theta_2)/d\cos\theta_1$ by linear curve-fitting, which are required in line tension calculation. Using Leg 3 as an example, typical curve-fitting results are presented in Table 4-1. Using these slopes, representing the necessary derivatives, one calculates the line tension values from Eq. (4-2). The results are shown in Table 4-2, along with the line tension results calculated by Eq. (3-1), for all legs and all runs.

Both equations (3-1) and (4-2) give the same sign and order of magnitude of line tension in Table 4-2. With Eq. (4-2), the mean value of the line tension shows larger variations from one leg to another because the slopes differ from one leg to another; however,
within one leg, the error limits of $\sigma$ are much smaller than those using Eq. (3-1). The considerable difference in error limits from the two types of calculations of $\sigma$ arises from the very different mathematical procedures; the smaller error limits within one leg, calculated from Eq. (4-2), do not necessarily reflect more accurate line tension values.

Table 4-1. Linear Regression Results of the Three Derivatives for Leg 3 in Fig. 4-2.

<table>
<thead>
<tr>
<th></th>
<th>$d\cos\theta_1/d\kappa$ (m)</th>
<th>$d\cos(\theta_1-\theta_2)/d\cos\theta_1$</th>
<th>$d\cos\theta_2/d\cos\theta_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>$1.14 \pm 0.12 \times 10^{-4}$</td>
<td>$0.47 \pm 0.11$</td>
<td>$0.07 \pm 0.02$</td>
</tr>
<tr>
<td>Intercept</td>
<td>$0.84 \pm 0.01$</td>
<td>$0.50 \pm 0.01$</td>
<td>$0.93 \pm 0.01$</td>
</tr>
<tr>
<td>Correlation Coefficient</td>
<td>$0.90$</td>
<td>$0.69$</td>
<td>$0.64$</td>
</tr>
<tr>
<td>No. of Observations</td>
<td>24</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>Degrees of Freedom</td>
<td>22</td>
<td>22</td>
<td>22</td>
</tr>
</tbody>
</table>

Note: The slope and intercept above are given in form of the mean $\pm$ standard error.
Table 4-2. Line Tension $\sigma$ (\(\mu J/m\)) as Calculated by Various Methods.

<table>
<thead>
<tr>
<th>Speed ((\mu m/s))</th>
<th>Leg</th>
<th>Eq. (3-1)</th>
<th>Eq. (4-2)</th>
<th>Eq. (4-3)</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>92.2 (Fig. 5)</td>
<td>1</td>
<td>-1.4 ± 0.3</td>
<td>-1.2 ± 0.002</td>
<td>-2.0</td>
<td>-1.4 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-1.7 ± 0.4</td>
<td>-2.0 ± 0.005</td>
<td>-2.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-1.7 ± 0.3</td>
<td>-1.8 ± 0.003</td>
<td>-2.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>-1.7 ± 0.3</td>
<td>-2.3 ± 0.006</td>
<td>-2.9</td>
<td></td>
</tr>
<tr>
<td>23.2 (Fig. 6)</td>
<td>1</td>
<td>-1.4 ± 0.3</td>
<td>-0.6 ± 0.001</td>
<td>-1.4</td>
<td>-1.3 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-1.7 ± 0.3</td>
<td>-3.0 ± 0.007</td>
<td>-3.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-1.8 ± 0.3</td>
<td>-1.9 ± 0.004</td>
<td>-3.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>-2.1 ± 0.3</td>
<td>-3.7 ± 0.009</td>
<td>-3.8</td>
<td></td>
</tr>
<tr>
<td>4.75 (Fig. 7)</td>
<td>1</td>
<td>-1.1 ± 0.2</td>
<td>-0.3 ± 0.001</td>
<td>-0.8</td>
<td>-1.1 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-2.0 ± 0.3</td>
<td>-4.3 ± 0.006</td>
<td>-4.7</td>
<td></td>
</tr>
</tbody>
</table>

Note: The speed above represents the rate of advancing and receding the contact line. The line tension above is given in form of the mean ± standard deviation. The intercept is the line tension value at time zero as calculated by linear regression.

4.3.2.1 Line Tension Calculation from a Single Surface Tension and Lens-Size Dependence of Contact Angle

Also included in Table 4-2 are the results calculated by Eq. (4-3), where the line tension is approximated by the equation that resembles the modified Young equation for liquids in contact with a flat solid surface. Again, the same negative sign and order of
magnitude of line tension are produced although the values show relatively large variations from one leg to another. The absolute values of the results of Eq. (4-3) tend to be larger by approximately 50% than those obtained from Eq. (4-2). This clearly indicates that for this system and presumably many similar ones, Eq. (4-3) can be expected to give the correct sign and order of magnitude of line tension, all on the basis of essentially a single lens size dependence of contact angle.

If the lower liquid (water in the present case) has a much higher density than both the lens liquid and the ambient (bathing) fluid, then it is unlikely that the liquid lens deforms the interface between the fluid and the lower liquid to a significant extent. In this situation, the liquid lens would be indeed similar to that of a sessile drop on a solid surface. The corresponding mechanical equilibrium condition becomes the modified Young equation (see also Section 2.3.2.1), which is the only balance relation that applies (in the direction that is parallel to the horizontal top of the lower liquid). Thus, following this argument, Eq. (4-3) would provide a much better approximation for line tension than just the sign and the order of magnitude. In fact, Wallace and Schürch [46,47] have used this approach based on Eq. (4-3) to measure line tension; their experiments were performed on a substrate-bathing fluid interface modified by a surfactant monolayer (where an estimate of the monolayer surface tension was required).
4.4 Discussion

4.4.1 Rate Dependence of the Contact Angle and the Line Tension

Within the error limits, there is no considerable rate dependence of the contact angle and subsequently calculated line tension (Figs. 4-2 to 4-4, Fig. 4-5 and Table 4-2) for the range of speeds studied. This is expected because of the high mobility of the fluid phases. In general, a rate-dependence is associated with either hydrodynamics or adsorption at the surface and/or at the contact line. Within our speed range of changing the liquid lens diameter, hydrodynamic effects are unlikely to play a role. On the other hand, since pure, essentially mutually immiscible liquids were used to form the three-phase contact line system, adsorption processes would not occur, except possibly for impurities. This is in contrast to liquid lenses formed by solutions, e.g., surfactant solutions, where the equilibration of the three-phase contact line system is expected to be important due to the adsorption of the solutes at the surfaces and the contact line.

Although the rate of diameter change does not affect the contact angle and the line tension directly, the impurity effects increase with decreasing speed of the lens size variation. The line tension decline becomes more apparent as slower rates are used, see Fig. 4-2 to Fig. 4-4. Furthermore, the difference between the advancing contact angle and the receding contact angle becomes more evident at lower speeds (Fig. 4-5). The impurities tend to reduce the contact angle $\theta_1$, while, on the other hand, the line tension affects the contact angle such that during advancing $\theta_1$ is increased, and subsequently decreased upon receding of the
contact line. Therefore, opposing effects on the contact angle $\theta_1$ from impurity accumulation and the line tension occur during advancing the three-phase contact line (leg AB in Figs. 4-3 and 4-4); in the contact angle receding mode (leg CD in Figs. 4-3 and 4-4), additive effects from both impurity accumulation and the line tension occur. As a result, the receding contact angle shows a larger slope with respect to the diameter of liquid lens, and this is also reflected in the line tension calculation using Eqs. (4-2) and (4-3) (Table 4-2). In Table 4-2, the line tensions calculated by using slopes obtained from the receding contact angles are generally more negative than those from the advancing contact angles.

4.4.2 Lens-Size Dependence of Contact Angles

Using the lens-size dependence of contact angle as input information, which is different from that used in Eq. (3-1), the line tension calculation with Eq. (4-2) provides an independent means and hence confirmation for the results of line tension calculated by Eq. (3-1), at least, to the order of magnitude and the sign. When neglecting the terms on the right-hand side of Eq. (4-2) except the first one, Eq. (4-3) results. The justification for Eq. (4-3) is as follows: The second term on the right-hand side of Eq. (4-2), $\gamma_2(d\cos\theta_2/d\cos\theta_1)$, is small relative to the first term, because the derivative $d\cos\theta_2/d\cos\theta_1$ is close to zero (in Figs. 4-2 to 4-4, $\theta_2$ shows little dependence on the lens-size). The last term on the right-hand side of Eq. (4-2) is complicated, and only through the actual computation within the whole range of contact angles in the experiment can this term be shown to be small relative to the first term. Therefore, Eq. (4-3) allows for an estimate of line tension with only one lens-size dependence.
of contact angle and one surface tension, \( \gamma_1 \).

As stated earlier, the significance of this result lies in the fact that the sign and the order of magnitude of line tension depend, apart from the relatively trivial matter of the surface tension \( \gamma_1 \) of the floating lens, only on the lens-size dependence of the contact angle \( \theta_1 \). It would be very difficult if not impossible to ascribe the lens-size dependence reported here to artefacts, such as imperfection of the lighting in the experiment. Thus, the conclusion seems inevitably that the line tension is negative and of the order of \( 10^{-6} \) J/m in the dodecane-water-air three-phase contact line system.

### 4.5 Summary

Two techniques are used to calculate line tension: Method I utilizes the Quadrilateral Relation directly on individual liquid lenses, and Method II is based on the lens-size dependence of contact angles. The contact angle and the line tension of the dodecane-water-air three-phase contact line system are measured at three speeds of advancing and receding the contact line. With the highest speed, where the impurity influence on the contact angle is minimized, no contact angle hysteresis is observed. No apparent rate dependence of contact angle and line tension can be measured, other than that due to impurity accumulation at lower speeds.

The lens-size dependence of contact angles can be used to calculate line tension. With Eq. (4-2) three derivatives need to be obtained in addition to two contact angles and three surface tensions. No computational advantage can be gained by using Eq. (4-2) over Eq. (3-
1); however, as an independent computation scheme, the resulting line tension values can be used to confirm the results previously obtained with Eq. (3-1) if only the sign and the order of magnitude are the primary concerns.

When simplifying Eq. (4-2) by neglecting less important terms, Eq. (4-3) results, which resembles the modified Young equation for sessile drops on a flat solid surface. For the system studied here, by using Eq. (4-3), an estimate of line tension can be obtained to a factor of two, based only on one slope of the contact angle against the lens-size and one surface tension.

In all situations, the line tension calculated is negative and between -1 to \(-4 \times 10^6\) J/m, and probably nearer \(-1 \times 10^6\) J/m if impurity effects can be avoided. The results agree well with the data calculated using Method I which yielded a line tension value of \(-1.29 \pm 0.21 \times 10^6\) J/m (see also Chapter 3).
Chapter 5

Line Tension Measurement III: Chain-Length Dependence

of Line Tension in the Alkane-Water-Air System

In the preceding two chapters, methodologies have been established for line tension measurement. Using a dodecane-water-air three-phase contact line system, the line tension was determined to be negative and of the order of $10^6$ J/m, based on individual liquid lenses or on the lens-size dependence of contact angles. In this chapter, the line tension measurement will be extended to a series of alkanes. The purpose of this study is twofold: One, it is expected that the line tensions of similar chemical systems would not be significantly different, and hence the same sign and order of magnitude are anticipated for all the alkane-water-air three-phase contact line systems. Two, it is known that the surface tension of alkanes monotonically decreases with decreasing chain-length [90,110,124]. It would be interesting to investigate whether a similar trend in line tension with decreasing alkane chain-length exists.

As demonstrated in Chapter 3, the line tension calculation relies on measurement of two independent contact angles at the three-phase contact line. For the measurement of contact angles, an image analysis scheme is required to generate liquid meniscus profiles after image acquisition, and edge detection is the key for obtaining high quality data. In the previous studies (Chapters 3 and 4), the edge detection scheme had only pixel resolution, which resulted in a certain degree of scatter in contact angle values and hence a scatter in the
line tension value as calculated from the Quadrilateral Relation. In this chapter, a new image analysis scheme is presented in which sub-pixel resolution is achieved in edge detection. It is hoped to demonstrate that, with the improved image analysis scheme, the scatter in contact angles and line tension can be reduced.

Overall, the two objectives of this chapter are: i) to study the hydrocarbon chain-length dependence of the line tension in the alkane-water-air three-phase contact line system; ii) to apply the new image analysis scheme for obtaining accurate contact angle data and hence line tension values.

5.1 Experimental

The basic experimental setup and procedure were the same as that described in Chapter 3; the following only provides the information which was additional to or different from that in Section 3.2.

5.1.1 Materials

The alkanes used in the experiment were hexadecane, tetradecane, dodecane and decane; they were obtained from Aldrich Chemical Company, Inc., USA, with a purity of 99+%.

Water was deionized and glass distilled; its purity was checked by surface tension measurement which, at 25°C, resulted in 72.14 ± 0.04 mJ/m² at the 95% confidence level (the experimental method employed was ADSA as described in Chapter 3), which was in good
agreement with literature values [124]. Each of the alkanes was mutually saturated with the water for at least 12 hours before the experiment.

5.1.2 Interfacial (Surface) Tensions

In order to calculate line tension from the Quadrilateral Relation, surface tensions of water and alkane and interfacial tension of water-alkane are needed. The method employed to obtain these values was the same as that described in Chapter 3. The results of these surface/interfacial tensions are shown in Table 5-1, which are comparable to the data published in Ref. [116]. Also included in the table are the densities of the liquids, measured under the condition of mutual saturation, which are necessary in the surface/interfacial tension measurement (cf. Section 3.2.2).

Table 1. Interfacial or Surface Tensions (mJ/m²) and Mass Densities (g/cm³)
of Alkanes and Water under Mutual Saturation, at 25°C.

<table>
<thead>
<tr>
<th></th>
<th>C₁₆H₃₄</th>
<th>C₁₄H₃₀</th>
<th>C₁₂H₂₆</th>
<th>C₁₀H₂₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkane Surface Tension</td>
<td>26.44</td>
<td>25.64</td>
<td>23.53</td>
<td>22.79</td>
</tr>
<tr>
<td>Water Surface Tension</td>
<td>72.18</td>
<td>72.35</td>
<td>71.93</td>
<td>71.98</td>
</tr>
<tr>
<td>Alkane-Water Interfacial Tension</td>
<td>53.82</td>
<td>52.71</td>
<td>52.09</td>
<td>51.20</td>
</tr>
<tr>
<td>Density of Alkane</td>
<td>0.7689</td>
<td>0.7590</td>
<td>0.7451</td>
<td>0.7262</td>
</tr>
<tr>
<td>Density of Water</td>
<td>0.9970</td>
<td>0.9970</td>
<td>0.9970</td>
<td>0.9969</td>
</tr>
</tbody>
</table>
5.1.3 Image Analysis

Having acquired the drop image (cf. Section 3.2), an image analysis scheme is needed to extract the drop profile and to obtain the profile coordinates of interfaces. The goal in this procedure is to obtain the diameter of the three-phase contact line (i.e., the diameter of the liquid lens) and two contact angles ($\theta_1$ and $\theta_2$) at the intersection point of the three interfaces (Fig. 3-1). A program in C language was written to process the digital image of the liquid lens. As in the previous work (Chapter 3), the Sobel operator was the edge detection technique used to obtain the liquid lens profile from the digital image. The values obtained by applying the Sobel operator to a digital image represent the change in intensity or gray levels at any given pixel of the image with respect to adjacent pixels. Thus, edge points can be found by searching for high Sobel values in the image. As mentioned above, our earlier effort to obtain the liquid lens profile was based on edge detection with pixel resolution, resulting in a certain degree of scatter in contact angles (Chapter 3). In the present study, an edge detection scheme with sub-pixel resolution was adopted. In addition, to enhance the reliability and efficiency of the program, a new strategy was used for finding the intersection point from the extracted profile.

A typical liquid lens image is shown in Fig. 5-1, where the details (see below, Fig. 5-2) in gray level variation across the edge of the lens were removed in order to increase the contrast of the image. The new edge detection scheme works as follows: Three coordinate points are selected by the user, one anywhere inside the needle at the top of the image (point 1 in Fig. 5-1) where the program is going to start searching for the edges (left and right), and
Fig. 5-1  A typical image acquired of the cross section of a pendant/floating liquid lens of alkane on the water surface.
two points near the left and right boundaries of the image (points 2 and 3 in Fig. 5-1) that specify where the program will stop following the edge.

Starting from point 1, the program searches to the left for the point with the maximum Sobel gradient value \([114,115,120,121]\), which determines the location of the first point of the left edge within pixel resolution, i.e., pixel integer coordinate values. Figure 5-2 shows how the intensity or gray level of the pixels change across the edge of the drop from higher values on the bright background of the image to lower values inside the dark drop, and how the Sobel values reach a maximum at the pixel location that corresponds to the edge of the drop \((x = 267\) in Fig. 5-2). This edge detection procedure is essentially the same as the that of the previous method described in Chapter 3.

To refine the location of the edge to sub-pixel resolution (i.e., real or floating-point coordinate values), it is clear that the Sobel gradient values near the edge start increasing gradually a few pixels away from the edge and decrease as one moves past the edge. Therefore, one can get a more accurate location of the edge by fitting a quadratic polynomial to the Sobel gradient values of a few pixels in the directions normal to the edge (to the left and to the right directions in this case for the first point) and finding the maximum Sobel value of the fitted polynomial [122]. In Fig. 5-2, this corresponds to the edge location at \(x = 266.9\).

To determine the number of pixels to use for the polynomial fit, one notices that the number of pixels contained between the points where the Sobel gradient values start to increase on both sides of the edge varies depending on the sharpness and contrast of the image. For sharp and bright images, this "band" was usually found to be five pixels wide (the pixel with the maximum Sobel value and two pixels on each side), and wider for images
The intensity or graylevel of the pixel change across the edge of the liquid lens from higher values on the bright background of the image to lower values inside the dark image. The Sobel values reach a maximum at the pixel location that corresponds to the edge of the lens at $x = 267$. After refining the location of the edge to sub-pixel resolution, $x = 266.9$. 
with less contrast. To automate the procedure, the program selects the pixels on both sides of the edge that have Sobel values greater than 50% of the maximum value, or 5 pixels, whichever is larger. The quadratic polynomial fit is then performed on these pixels and the location of its maximum value is computed to obtain the edge location with sub-pixel resolution. If the sub-pixel edge location is more than one pixel away from the original pixel value, the sub-pixel value is rejected and only the pixel resolution point is used.

Once an edge point has been found, only adjacent pixels in the direction of the edge are scanned for the next edge point (the edge is assumed to be continuous) and the sub-pixel algorithm is applied until the specified end points are reached (points 2 and 3). To determine the direction of search and to avoid sudden change of direction due to noise in the data, the width of the Sobel band (see above) is computed in all directions (vertical, horizontal and diagonal) at the edge point. Since this bandwidth is minimum in the direction normal to the edge, the search direction is set to the direction normal to the minimum bandwidth. For instance, at the first edge point near point 1, the light intensity gradient is larger in the horizontal direction which is reflected by a narrower Sobel band in the same direction. This means that at this point the edge is vertical, and one searches for the next edge point in the vertical direction.

The outcome of this algorithm is shown in Fig. 5-3 (top), with the enclosed rectangular area enlarged in the bottom figure. From this figure, it can be seen that, with sub-pixel resolution edge detection, rather smooth interfaces (edges) are obtained, in particular for the lower part of the curve corresponding to the air-water interface. In comparison, Fig. 5-4 shows the profile of the same liquid lens system when using the edge detection with pixel
Fig. 5-3 A drop profile (top) acquired from the image in Fig. 5-1 through the edge detection scheme with sub-pixel resolution. The distance between A and A' is 6.8 mm, representing the diameter of the liquid lens. The bottom picture is an enlargement of the portion enclosed by the rectangle in the top picture, where 30 pixel points along each of the interfaces AB and AC, starting from the intersection point A, are used in the linear curve-fit (see text).
Fig. 5-4  A drop profile (top) acquired from the image in Fig.5-1 through the edge detection scheme with pixel resolution. The distance between A and A' is 6.7 mm, representing the diameter of the liquid lens. The bottom picture is an enlargement of the portion enclosed by the rectangle in the top picture, where 30 pixel points along each of the interfaces AB and AC, starting from the intersection point A, are included. Note that two steps occur in the lower portion of the curve (bottom picture) because of the limitation of pixel resolution in edge detection.
resolution (see also Section 3.2.4 and Fig. 3-5). It is seen that several steps occur in the lower part of the curve in Fig. 5-4; this will result in uncertainty in the slope of the straight line that is fitted to this portion of the profile (see below), i.e., the slope will fluctuate depending on the number of fitted points.

The next step of the image analysis is to find the two intersection points from the profile, i.e., the coplanar points A and A' in Fig. 5-3. The strategy used in this chapter for finding A is different from that in Chapters 3, and is described as follows: First, locate two points B and C on the edge, far away from the intersection A (Fig. 5-5); this can be done by choosing B and C anywhere near the syringe needle and the left boundary of the profile, respectively (see also Fig. 5-3). Then, B and C are connected with a straight line, and the distance, \(d\), of each point on the edge (between B and C) to the line BC is computed. The point corresponding to the maximum distance represents the intersection point A, whose coordinates are recorded. The location of this intersection point may be refined by image analysis means:

For each (sub-)pixel point on the edge (interface), one can fit two straight lines to a few pixels of the edge: one to the left and the other to the right of this chosen point. The number of pixels used in the linear curve fitting was selected to be 30 (see below). If this chosen point is not at the intersection, then one of the two fitted lines will go over the intersection point. For instance, if this chosen point is on the edge AC (Fig. 5-5), then the right fitted line will go over the intersection point A, and some pixels on the edge AB will have been used for the linear curve fitting. Between the two fitted straight lines, an angle is formed at this chosen point. It may be seen that this angle will not be minimum unless this
Illustration of the procedure for locating the intersection point A: 1) finding the maximum distance, $d$, of a point on the interfaces to the straight line BC, and 2) finding the smallest angle, $\theta$, between the two fitted straight lines, one to the left and the other to the right of a point which is within the range of ten pixel points away from the point A.
chosen point is at the intersection. Therefore, the minimum angle between the two fitted straight lines may be used for locating the intersection point, as an alternative to the method based on the maximum distance $d$ to the line BC described above (Fig. 5-5).

A program in C language was written for this purpose (Appendix C), the strategy of which is as follows: First, one chooses 20 consecutive pixels, centered around the point A which may be predetermined by the maximum distance method. Then, for each of these 20 pixels, starting from the left end, one computes the angle formed at this chosen pixel point by the two straight lines which are fitted to 30 pixels each: one to the left and the other to the right of this chosen point. The point corresponding to the minimum angle will be located as the intersection. The least squares method was used in the linear curve-fit.

Once the two intersection points (A and A' in Fig. 5-3) were located, two contact angles required in line tension calculation $\theta_1$ and $\theta_2$ (Fig. 3-1) were then obtained in the same manner as that described in Section 3.2.4, where 30 pixels were also used in the least squares linear curve-fit.

The rationale for using 30 (sub-)pixel points to perform the linear curve-fit is similar to that described in Section 3.2.4 where edge detection is of pixel resolution. Briefly, when a small number of points, say five or fewer, were used, the error associated with the curve-fit would be large and hence result in a large scatter in the contact angles determined from the slopes of the fitted lines. On the other hand, if a large number of points, say forty or more, were chosen for the curve-fit, the curving of the interfaces would influence the results, causing a deviation from the tangents at the intersection point (Fig. 5-5). Therefore, an optimal number of points must be sought. Figure 5-6 shows the contact angles $\theta_1$ and $\theta_2$. 
Fig. 5-6 The contact angles $\theta_1$ and $\theta_2$ obtained from a linear curve-fit as a function of the number of the points used in the fitting procedure, which indicates a steady value, also with a relatively small fluctuation, in the region of 20 to 40 points. The errors associated with each slope are the standard errors in the linear curve-fit. In addition, the correlation coefficients associated with the curve-fits appear to reach the plateau when using 20 points in the fitting procedure, and a further increase in the number of the points does not result in a significant increase in the correlation coefficient value.
determined from the slopes, as a function of the number of points used in the linear curve-fit. As expected, large errors are associated with using small numbers of the points, and a progressive decrease in $\theta _1$ and increase in $\theta _2$ occur when too large a number of points are used in the curve-fit. Only in the region of 20 to 35 points, can both small errors and relatively constant contact angles be found (Fig. 5-6). In addition, in the same region, the correlation coefficient reaches a plateau; a further increase in the number of fitting points does not improve the correlation coefficient significantly. Therefore, 30 points were selected for the linear curve-fit (c.f., Section 3.2.4).

It is worth noting that choosing 30 (sub-) pixel points to perform the linear curve-fit, instead of other numbers of points between 20 and 35, e.g., 25 points, is somewhat arbitrary. As shown in Fig. 5-6, the error limits of the contact angles within the region of 20 to 35 points are overlapping; the difference in the average contact angle is generally less than 1°. Furthermore, it was demonstrated in Section 3.4.2 that the line tension does not change its sign or order of magnitude unless the contact angle is varied by 3°. Therefore, the choice of 30 points used in the curve-fit will not affect the line tension result that this thesis concerns.

5.2 Results and Discussion

5.2.1 Improvement from the Edge Detection and Image Analysis Scheme

Figure 5-7 illustrates line tension as a function of time in a dynamic experiment for a dodecane liquid lens on the water surface, during which the diameter of the three-phase contact line was varied in a periodic mode from 4.5 to 7.0 mm. Each cycle takes
The diameter, two contact angles, and line tension versus time in a dynamic experiment for a dodecane liquid lens on the water surface. The results are obtained from the image analysis scheme described in the text. Compared with the results in Fig. 5-8 (see below), which are obtained from the original image analysis scheme used in Chapter 3, this present version of image analysis, including edge detection with sub-pixel resolution, significantly reduces the scatter in the contact angles and hence in the line tension.
Fig. 5-8  The diameter, two contact angles, and line tension versus time in a dynamic experiment for a dodecane liquid lens on the water surface. The results are obtained from the original image analysis scheme used in Chapter 3 with pixel resolution in edge detection. Note that the data show a relatively large scatter, compared with those in Fig. 5-7.
approximately one minute, and two cycles are shown. It is seen that both contact angles $\theta_1$ and $\theta_2$ vary smoothly with the diameter of the contact line, and the line tension calculated from Eq. (3-1) is consistently negative and of the order of $10^{-6} \text{ J/m}$. To compare the present image analysis scheme with the previous one (Chapter 3), the same liquid lens images were re-analyzed using the image analysis scheme used previously where edge detection is of pixel resolution (Chapter 3). The result is shown in Fig. 5-8, from which one can see that, as the diameter of the dodecane liquid lens varies, the corresponding contact angles $\theta_1$ and $\theta_2$ change with a relatively large fluctuation. As a result, the line tension shows a larger fluctuation, as compared with that in Fig. 5-7.

Although the present image analysis scheme provides a more precise determination of contact angles and line tension, both the present and the previous schemes result in a negative line tension, of the order of $10^{-6} \text{ J/m}$. Another common feature in Figs. 5-7 and 5-8 is that there is a slightly downward trend in line tension with time once the diameter starts varying. This is, as explained before, possibly due to the gradual accumulation of impurities at the three-phase contact line and at the interfaces, since there may be a small amount of impurities originally contained in the sample liquids. However, it is observed that, in static experiments (see below), such a downward trend in line tension is not apparent. The difference between the results of the two types of experiments may be due to the movement of the three-phase contact line in the dynamic experiments. Such movement may accelerate the accumulation of impurities at the contact line and the interfaces. On the other hand, in static experiments, the accumulation may not be sufficiently fast so that its effects on line tension are not detected.
Furthermore, the difference between the dynamic and the static experiments in the observation of a downward trend in line tension might be explained in terms of the rate constants for adsorption and desorption. It is generally believed that for many molecules the rate constant for adsorption is higher than that for desorption. In dynamic experiments, the surface area of interfaces is varied continuously in association with the movement of the three-phase contact line. When the surface area is increased, impurity molecules adsorb at the interfaces due to the availability of additional adsorption sites. When the surface area is decreased, impurity molecules do not desorb from the interfaces as fast as they adsorb, because of a lower rate constant for desorption. As a result, the cycling of the surface area generates a net adsorption of impurity molecules at the interfaces, and hence accelerates the accumulation of impurities at the interfaces. Similarly, for the three-phase contact line, the back and forth movement of the contact line would generate a net adsorption of impurity molecules and accelerate the accumulation of impurities. Therefore, the downward trend in line tension with time is more noticeable in dynamic experiments than in static experiments.

5.2.2 Line Tension as a Function of the Alkane Chain-Length

For the four alkane systems studied: hexadecane, tetradecane, dodecane and decane, Fig. 5-9 shows representative results for each alkane liquid lens on the water surface. In Fig. 5-9a, the results of diameter, two contact angles $\theta_1$ and $\theta_2$, and line tension calculated from Eq. (3-1) are illustrated as a function of time for the hexadecane-water-air three-phase contact
The diameter, two contact angles, and line tension plotted as a function of time up to 60 s in the static mode of the experiment for hexadecane. The errors are all at the 95% confidence level. The scatter in the data appears to increase with decreasing alkane chain-length (from Figs. 5-9a to 5-9d).
Fig. 5-9b  The diameter, two contact angles, and line tension plotted as a function of time up to 60 s in the static mode of the experiment for tetradecane. The errors are all at the 95% confidence level. The scatter in the data appears to increase with decreasing alkane chain-length.
Fig. 5-9c The diameter, two contact angles, and line tension plotted as a function of time up to 60 s in the static mode of the experiment for dodecane. The errors are all at the 95% confidence level. The scatter in the data appears to increase with decreasing alkane chain-length.
Fig. 5-9d  The diameter, two contact angles, and line tension plotted as a function of time up to 60 s in the static mode of the experiment for decane. The errors are all at the 95% confidence level. The scatter in the data appears to increase with decreasing alkane chain-length.
line system. It is seen that the line tension obtained shows little fluctuation, with an average value of $-2.16 \pm 0.05 \, \mu J/m$ at the 95% confidence level. Similar results are shown in Fig. 5-9b, 5-9c and 5-9d for the tetradecane, dodecane, and decane-water-air three-phase contact line systems, respectively. With the decrease in alkane chain-length, a decrease in the absolute value of line tension is observed: $-2.16 \pm 0.05$, $-1.59 \pm 0.03$, $-1.13 \pm 0.03$, and $-0.79 \pm 0.09 \, \mu J/m$ for hexadecane, tetradecane, dodecane, and decane, respectively. The results are summarized in Table 5-2; the value for hexadecane is an average over three independent runs (data not shown), and that for dodecane is an average over five independent runs (see Table 5-3).

<table>
<thead>
<tr>
<th></th>
<th>Hexadecane</th>
<th>Tetradecane</th>
<th>Dodecane</th>
<th>Decane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line Tension ((\mu J/m))</td>
<td>-1.98</td>
<td>-1.59</td>
<td>-1.09</td>
<td>-0.79</td>
</tr>
<tr>
<td>95% Conf. Limits</td>
<td>(\pm 0.06)</td>
<td>(\pm 0.05)</td>
<td>(\pm 0.24)</td>
<td>(\pm 0.09)</td>
</tr>
</tbody>
</table>

From Table 5-2, it is inferred that the line tension is negative, and the absolute value of line tension increases with alkane chain length.

The fluctuation in the data tends to increase with the decrease in alkane chain-length, see Figs. 5-9a to 5-9d. With the decane-water-air system, the scatter in line tension is 10% (Fig. 5-9d). In the actual experimentation, it was found that it was more difficult to form and maintain a decane liquid lens than a hexadecane lens. Eventually, the lens detached from the needle and floated down the curved water surface. The hexadecane-water-air system was the
most stable and could be maintained statically up to half an hour, while the decane-water-air system could only be maintained for ten minutes or less. This observation also indicates the limitation of the current technique for measuring line tension; i.e., formation and some stability of a liquid lens are necessary.

5.2.3 Lens-Size Dependence of Line Tension

It is noted that in Table 5-2, the error limits of the line tension for the dodecane system are larger than those for the other systems. This is due to the fact that the range of diameter of the dodecane liquid lens used in the experiment was much larger than those of the other alkane systems, and hence a larger amount of randomness, due to the change in lens size, might occur in the measurement. However, on the other hand, the question arises whether a drop-size dependence of line tension exists. Table 5-3 shows the line tension as a function of lens size for the dodecane-water-air three-phase contact line system. The images used are the same as those of Table 3-1, but the image analysis given here is of subpixel resolution.

It is observed that the line tension value fluctuates as the lens size varies, but there is no obvious trend as the diameter of the liquid lens changes from about 1.8 to 6.8 mm. The resulting average of line tensions is $-1.09 \pm 0.24 \mu J/m$ at the 95% confidence level, comparable to that in Table 3-1.
Table 5-3. Line Tension versus the Diameter of a Dodecane Liquid Lens on the Air-Water Surface

<table>
<thead>
<tr>
<th>Diameter (mm)</th>
<th>Line Tension (μJ/m)</th>
<th>95% C.L.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.84</td>
<td>- 1.44</td>
<td>± 0.03</td>
</tr>
<tr>
<td>2.31</td>
<td>- 0.97</td>
<td>± 0.09</td>
</tr>
<tr>
<td>3.48</td>
<td>- 1.13</td>
<td>± 0.03</td>
</tr>
<tr>
<td>4.50</td>
<td>- 0.91</td>
<td>± 0.03</td>
</tr>
<tr>
<td>6.84</td>
<td>- 1.00</td>
<td>± 0.07</td>
</tr>
</tbody>
</table>

Overall Average: - 1.09
Overall 95% Confidence Limits: ± 0.24

In the formulation of the Quadrilateral Relation for three-phase contact lines, line tension is tacitly assumed to be independent of the size of the three-phase contact line, i.e., the curvature of the system [?]. This assumption is consistent with the fact that line tension, in a proper thermodynamic analysis, appears in both the Quadrilateral Relation and the modified Young equation [78] (i.e., the mechanical equilibrium condition for dividing lines) at the lowest level of generality, i.e., the same level in the hierarchy at which the classical Laplace equation is the appropriate equilibrium condition between bulk phases. All these relations follow from the general analysis only under the assumption that all tensions are independent of curvature [78]. The results in Table 5-3 are in agreement with these theoretical assumptions.
5.3 Summary

The newly-developed image analysis scheme with sub-pixel resolution [122] for edge detection not only confirms the line tension results obtained previously (Chapters 3 and 4) but also proves to be more precise, as reflected in the reduced scatter in contact angles and line tension. For the four alkanes: hexadecane, tetradecane, dodecane and decane, the absolute value of line tension increases with increasing alkane chain-length. The value of line tension of the dodecane-water-air three-phase contact line is shown to be independent of the lens size, i.e., the curvature of the three-phase contact line, which is in agreement with the theoretical considerations presented in the present thesis (Chapter 2).
Chapter 6

Summary and Conclusions

The concept of line tension arises as a natural and necessary extension of the requirements of a fundamental equation when applied to systems with multiphase boundary curves. Line tension is defined in complete analogy to the accepted thermodynamic definitions for bulk pressure and surface tension; it represents the excess free energy per unit length of a multi-phase boundary curve. Despite being a well-defined thermodynamic quantity, line tension had not been quantified satisfactorily. The major problems associated with the experiments reported in the literature, before this thesis, are: (i) the chosen three-phase contact line systems in which necessary contact angles can be readily measured are often complicated, leading to difficulties in experimental control; (ii) the theoretical models used in data analysis are not always straightforward, resulting in significant errors in calculating line tension (e.g., for methods based on heterogeneous nucleation).

In view of these difficulties, study of a simple three-phase contact line system, i.e., a liquid lens, was chosen in this thesis. In order to determine line tension, a new theoretical framework was generated, which provides a straightforward correlation between line tension and measurable quantities. Subsequently, a new experimental strategy was developed, which allows determination of line tension through the application of this theoretical framework to liquid lens systems. An initial demonstration of this experimental strategy was conducted on a dodecane-water-air three-phase contact line system, where a negative line tension of the
order of $10^{-6}$ J/m was obtained.

To confirm this line tension value, two additional computational schemes for calculating line tension were developed; the required input is the lens-size dependence of contact angles. These two schemes not only provide a test for the internal consistency of the approach, but also eliminate the concern about a systematic error, e.g., due to lighting in the experimental design.

In the third stage of the experimental work, a series of alkanes was used to form three-phase contact line systems, and line tensions were determined in order to investigate the dependence of line tension on hydrocarbon chain-length. In addition, an improved image analysis scheme was developed, where an edge detection with subpixel resolution [122] was adapted. This resulted in a re-confirmation of the line tension value obtained, with higher accuracy.

Specifically, the following conclusions may be drawn:

1. The contact line Quadrilateral Relation was derived using the free energy minimum principle. This relation generalizes the classical Neumann triangle relation by including line tension effects into the mechanical equilibrium condition of three-phase contact lines.

2. A graphical representation of the Quadrilateral Relation was developed, which consists of three surface (interfacial) tension quantities and a line tension term ($\sigma k$). From the quadrilateral pictograph, it becomes easy to derive various forms of the
Quadrilateral Relation and to evaluate which form(s) would be appropriate for a particular experimental situation.

3. Several common geometries were discussed and strategies for determining the line tension are proposed. In all cases involving deformable liquid phases, the line tension may be obtained from two contact angles in addition to three surface tensions.

4. An experimental strategy for measuring line tension was developed, where the Quadrilateral Relation was applied to liquid lens systems. The experimental procedure consists of (i) image acquisition (to obtain the cross-sectional image of liquid lenses), (ii) image analysis (to perform edge detection and extract the coordinates of the lens profile), (iii) numerical analysis (to compute experimental data and generate line tension values according to the properly formulated theoretical expression).

5. The line tension of the three-phase contact line formed by dodecane, water, and air three phases was found to be negative and of the order of $10^{-6}$ J/m at 25°C. This result is supported by both static and dynamic measurements.

6. The line tension value obtained was found to be independent of the lens size, i.e., there was no curvature dependence of line tension, when the diameter of the liquid lens varied from 1 to 7 mm. This is in agreement with the theoretical formulation of
the Quadrilateral Relation.

7. Two additional computational schemes were developed by reformulating the Quadrilateral Relation, which allow line tension estimation from the lens-size dependence of contact angles in liquid lens systems. The outcome of these methods agreed with the line tension value obtained with the original method based on individual lenses.

8. The absolute value of line tensions was found to increase with increasing alkane chain-length, based on the experiments with four alkanes: hexadecane, tetradecane, dodecane and decane. The line tension values, being all negative, ranged from $-1.98$ to $-0.79 \times 10^4$ J/m at 25°C.
Chapter 7

Future Work

To extend the research presented in this thesis, the following topics may be studied:

7.1 Other Three-Phase Contact Line Systems

The establishment of the methodology for line tension measurement provides an opportunity to study many other three-phase contact line systems. So far only alkane lenses at the air-water interface have been investigated. Other liquid systems can be studied with the same methodology, as long as a three-phase contact line can be constructed, i.e., two liquid phases are immiscible. The first step may be to use some slightly polar liquids to form lenses on the water surface. Since it is known that molecular polarity has effects on surface tension, it would be interesting to see if line tension is influenced by the polarity in a similar manner.

Another interesting system is a three-phase contact line system containing surfactant. Because of its strong adsorption at interfaces, surfactant can drastically change interfacial (surface) tension. It is expected that surfactant would have a similar impact on the three-phase contact line; thus, line tension would likely be altered significantly by the presence of surfactant.

However, due to its high affinity to interfaces (surfaces) and lines, surfactant starts
adsorbing at the phase boundaries once a three-phase contact line is constructed; then, the system will undergo an equilibration process. Therefore, line tension measurement may be conducted only after equilibrium or quasi-equilibrium is reached.

There are at least two reasons for studying surfactant-containing three-phase contact line systems: (i) The results will provide information about the (surfactant) concentration-dependence of line tension. This information will be important not only in practical situations but also in theoretical considerations. In surface systems, the concentration-dependence of surface tension is described by the Gibbs adsorption equation [90]. In line systems, a similar line adsorption equation is expected. Thus, the experimental data obtained in the proposed study could be used for verifying such a line adsorption equation. (ii) The outcome of this experiment could be used to compare with those previously published in the literature, thereby leading to a better understanding of line tension and its role in the three-phase contact line construction.

7.2 Combination of Line Tension and Film Tension Measurements

Recently, a new methodology for measuring film tension has been found (see Appendix D). It has been demonstrated that the film tension and film rupture of alkanes at the air-water interface can be determined [125]. It is possible to form a three-phase contact line system in which one of the three intersecting interfaces may be coated with a film. In this case, the graphical representation of the Quadrilateral Relation, which was composed of three surface tensions and one line tension term, will be modified by replacing one of the surface
tensions with the film tension. A simultaneous measurement of the film tension and the two contact angles at the three-phase contact line will permit line tension determination. This is significant because (i) such a measurement would allow for the study of the correlation between line tension and film tension, two thermodynamic quantities which are both fundamentally important but difficult to measure with the previously existing techniques [3,125], and (ii) the outcome of this measurement would be used to compare with the results published previously in the literature, in order to understand the line tension effects in thin film systems better.

7.3 New Strategy to Determine Contact Angles

The current strategy in determining the two contact angles for line tension calculation using the Quadrilateral Relation is to measure the slopes of the two interfaces at the three-phase contact line. The precision in such measurements is a few tenth of a degree. This may be improved by using an approach that has been adopted for Axisymmetric Drop Shape Analysis-Profile (ADSA-P) in contact angle determination. Since the governing equation for the profile of interfaces is alway the Laplace equation of capillarity, fitting the Laplacian curve to the experimentally obtained profile of the interface would generate contact angle information as well as surface tension if it is not known \textit{a priori}. However, if surface tension can be determined beforehand, the contact angle would be determined more easily and robustly since fewer fitting parameters are needed. This work can be interesting as it may lead to development of a technique that is capable of measuring line tension, contact angle,
and surface tension all at the same time.
Appendix A. The Modified Young Equation of Capillarity in Line Tension Measurement

This appendix contains the modified Young equation of capillarity and explains how it is applied for line tension measurement. The modified Young equation of capillarity \[78\] is the mechanical equilibrium condition for a sessile drop on an ideal solid surface and may be written as follows:

\[
\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} - \sigma \kappa
\]  

(A-1)

where \(\gamma_{lv}, \gamma_{sv}, \) and \(\gamma_{sl}\) are the surface (interfacial) tensions of the liquid-vapour interface, the solid-vapour interface, and the solid-liquid interface, respectively; \(\theta\) is the local equilibrium contact angle; \(\sigma\) is the line tension; and \(\kappa\) is the local curvature of the three-phase contact line. If the substrate is a horizontal, planar, smooth, homogeneous, and rigid surface, the sessile drop will be axisymmetric and the three-phase contact line will be a circle. The curvature \(\kappa\) will become

\[
\kappa = \frac{1}{R}
\]  

(A-2)

where \(R\) is the radius of curvature of the three-phase contact circle. Equation (A-1) can be reduced to

\[
\cos \theta = \cos \theta_0 - \frac{\sigma}{\gamma_{lv}} \cdot \frac{1}{R}
\]  

(A-3)
where $\theta$ is the contact angle corresponding to a finite contact radius $R$, and $\theta_\infty$ is the contact angle corresponding to an infinitely large drop, i.e., $R = \infty$. Equation (A-4) is the well-known classical Young equation of capillarity. The modified Young equation (A-3) relates line tension to contact angles and the radius of curvature of a contact line. As seen from Eq. (A-4), $\theta_\infty$ is constant for a given solid-liquid system. Equation (A-3) predicts that $\cos \theta$ should be a linear function of $1/R$, provided that line tension is constant. Thus, the line tension can be obtained through the slope of $\cos \theta$ vs. $1/R$, which in turn can be obtained by measurement of the drop-size dependence of contact angles [46,47,55,56].

\[
\cos \theta_\infty = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (A-4)
\]
Appendix B. Heterogeneous Nucleation Theory and its Application to Line Tension Measurement

This appendix contains a review of heterogeneous nucleation theory and its application to line tension measurement. The existing theoretical analysis for heterogeneous nucleation [6-8, 18-30] starts out with an expression of the free energy of formation for a cap-shaped nucleus on a planar solid substrate (Fig. B-1)

\[ \Delta \Omega = \Omega_f - \Omega_i \]  
(B-1)

where \( \Omega_f \) and \( \Omega_i \) represent the grand canonical potentials [1] for the final state of the system (after the appearance of the little droplet) and for the initial state of the system. \( \Omega_f \) contains three types of free energy terms

\[ \Omega_f = \Omega_f^{(V)} + \Omega_f^{(A)} + \Omega_f^{(L)} \]  
(B-2)

where \( \Omega_f^{(V)} \) is the grand canonical potential for the two bulk fluid phases, \( \Omega_f^{(A)} \) for the three interfaces between the two fluid phases and between the solid substrate and the two fluid phases, and \( \Omega_f^{(L)} \) for the three-phase contact line. \( \Omega_i \) contains two types of free energy terms

\[ \Omega_i = \Omega_i^{(V)} + \Omega_i^{(A)} \]  
(B-3)

where \( \Omega_i^{(V)} \) is the grand canonical potential for one bulk fluid phase (i.e., vapour), and \( \Omega_i^{(A)} \)
Fig. B-1  Cap-shaped nucleus situated on the surface of a planar substrate.
for the interface between the vapour and the solid substrate. According to the thermodynamic definition of the grand canonical free energy [1], these $\Omega$'s can be expressed as

$$
\Omega_i^{(v)} = -P_v V_v = -P_v V_t \\
\Omega_i^{(A)} = (A_{sv})_i \gamma_{sv} \\
\Omega_f^{(v)} = -P_l V_l - P_v (V_t - V_l) \\
\Omega_f^{(A)} = A_{lv} \gamma_{lv} + (A_{sv})_f \gamma_{sv} + A_{sl} \gamma_{sl} \\
\Omega_f^{(L)} = L \sigma
$$

where $P_v$ is the vapour pressure

$P_l$ is the liquid nucleus pressure

$\gamma_n$ is the solid-vapour surface tension

$\gamma_l$ is the liquid-vapour surface tension

$\gamma_{sl}$ is the solid-liquid interfacial tension

$V_v = V_t$ is the total volume of the vapour before the nucleus formation

$V_l$ is the volume of the liquid nucleus

$(A_{sv})_i$ is the initial interfacial area between the solid and the vapour

$(A_{sv})_f$ is the final interfacial area between the solid and the vapour

$A_{lv}$ is the initial interfacial area between the liquid and the vapour

$A_{sl}$ is the initial interfacial area between the solid and the liquid

$L$ is the perimeter length of the three-phase contact line

$\sigma$ is the line tension

To obtain explicit expressions for these individual free energy terms, the geometry of the nucleus droplet is idealized as a portion of a sphere (Fig. B-1). Relevant mathematical
relations are as follows:

$$V_L = \frac{4\pi r^3 \phi(\theta)}{3}$$

$$A_{SL} = \pi r^2 (1 - \cos^2 \theta)$$

$$A_{LV} = 2\pi r^2 (1 - \cos \theta)$$

$$L = 2\pi r \sin \theta$$

$$\phi(\theta) = \frac{2 - 3\cos \theta + \cos^3 \theta}{4}$$

Finally, combining Eqs. (B-1) - (B-4), the free energy of nucleus formation can be written as [6-8,18-30]

$$\Omega = -\frac{4\pi r^3}{3} \phi(\theta) (P_L - P_v) - \pi r^2 \sin^2 \theta (\gamma_{lv} - \gamma_{sl}) + 2\pi r^2 (1 - \cos \theta) \gamma_{lv} + 2\pi r \sin \theta \quad (B-5)$$

where $r$ is the radius of curvature of the spherical surface of the nucleus, $\theta$ is the contact angle of the nucleus on the solid substrate, and $\phi(\theta)$ is a special function of the contact angle, defined as

$$\phi(\theta) = \frac{2 - 3\cos \theta + \cos^3 \theta}{4} \quad (B-6)$$

With the free energy expression, Eq. (B-5), the equilibrium stability conditions for the critical nucleus droplet can be analysed to generate the critical contact angle $\theta$ and radius of curvature $r$ [6-8,18-30]. These critical values are then related to the supersaturation $P_v / P_\infty$ ($P_v$ is the vapour pressure of a supersaturation system, and $P_\infty$ that of a saturated one) through the Gibbs-Thomson equation.
where \( y \) is the molecular volume of the liquid and \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature.

The nucleation rate is given by the Volmer equation [88]

\[
J = A \exp \left( -\frac{\Delta \Omega}{kT} \right)
\]  

where \( \Delta \Omega \) is the work of formation of a critical nucleus or the energy barrier and can be calculated from Eq. (B-1), and \( A \) is the pre-exponential factor.

By analysing the above Eqs. (B-1)-(B-8), the line tension effects on heterogeneous nucleation can be predicted as follows [6-8, 17-21]: (i) the nucleation barrier will be modified by the presence of line tension; (ii) the nucleation contact angle will be smaller if \( \sigma \) is negative, and the nucleation contact angle will be larger if \( \sigma \) is positive; (iii) there is a limit to the minimum size of the nucleus when line tension is positive; (iv) spontaneous (i.e., barrierless) nucleation of cap-shaped droplets is possible when line tension is negative; (v) homogeneous nucleation will be more favourable than heterogeneous nucleation when positive line tension becomes sufficiently large.
Appendix C. Programs for Analysing the Liquid Lens Profile and Computing Line Tension

This appendix provides four programs for analysing the liquid lens profile and computing line tension. The first two programs are used to determine the trend of contact angle and line tension change with respect to the number of the fitting points used for finding the tangents at the intersection points; therefore, from these programs the optimum number of the fitting points is generated. The last two programs are used to analyse multiple images for computing contact angles, a lens diameter and line tension through the Quadrilateral Relation.

C.1 Program I: TLT.MinA

*Background:* This program is used to determine the trend of contact angle and line tension change with respect to the number of the fitting points used for finding the tangents at the intersection points, from which two angles $\theta_1$ and $\theta_2$ are calculated (Fig. 3-1). This program has three main functions: (i) locating the two intersection points, one on the left side of the lens profile and the other on the right side of the lens profile, by the maximum distance method (see below); (ii) finetuning the location of the intersection points with the minimum angle method (see below); (iii) determining the optimum number of the fitting points from the trend of contact angle and line tension change with respect to the number of the fitting points.
(i) The program starts by locating two points on the edge, far from the intersection. Considering the left side of the lens profile (the procedure is the same for the right side), one point is located near the syringe needle, the other is located at the left boundary of the lens profile. These two points, referred to as points B and C, respectively (Figure 5-5), are joined by a straight line BC. For each point on the edge bounded by B and C, the distance, \( d \), to the line BC is computed. The point, A, corresponding to the maximum distance, is recorded. Ideally, this should be the intersection point among the three phases on the left side of the lens profile.

(ii) However, the intersection point determined above may be deviated from the true intersection point due to noise and artifacts near the intersection points. (It was found that the subpixel points detected for the edge near the intersection were noisier than those far away from the intersection.) Thus, a finetuning process is employed: First, a number of (sub-)pixel points (specified by the user, e.g., 20) are selected centered around the intersection point A as detected above. Starting at one end, for each point selected, two straight lines are fitted to pixel points, one to the left and the other to the right of this point. Once fitted, the angle between the two lines is calculated. The point corresponding to the minimum angle is then located as the intersection. This new point is taken to be the more "correct" intersection.

Furthermore, to avoid the effect of noise and artifacts near the intersection of the three phases, a certain small number of points (to be specified by the user) surrounding the intersection point can be removed, or taken off. Then, two new straight lines are fitted to the profiles, one to the left and the other to the right of the intersection point. From the slopes
of these two straight lines, two angles \( \theta_1 \) and \( \theta_2 \) are obtained (Fig. 3-1).

(iii) Once the intersection points are located, the trend of contact angle and line tension change with respect to the number of fitting points used in the linear fit can be studied. The number of points used in the fit may influence the angle. The linear fits should approximate real tangents to the intersection point of the three phases. By using more points to fit, the correlation may be greater, but the line deviates from the true tangent. On the other hand, using fewer points may allow the line to model the tangent better, but the error associated with the fit would be unacceptable (see also Sections 3.2.4 and 5.1.3). This program tests the optimum number of fitting points to use. Hence, the prefix TLT, or Test Line Tension, is used in the program name.

It was also seen that the diameter of the liquid lens determined from the distance between the two intersection points is influence by the method used to locate the intersection points. The diameter determined through the maximum distance algorithm, denoted as \( D_{\text{max}} \), was different from that obtained through the minimum angle approach, denoted as \( D_{\text{min}} \). This program uses \( D_{\text{min}} \) to calculate the radius of curvature, \( \kappa \), which is required in line tension calculation. Hence the suffix MinA, or minimum angle, is used in the program name.

As an example, a typical image was analysed. The profile was obtained as outlined in Section 5.1.3, and this program was run. The image, the profile file, and the input and output files of this program are shown in Figs. C-1, C-2, C-3 and C-4, respectively.
### File Name: 02.02 pt

The file has been truncated to fit onto one page. These are the edge coordinates of File C-1. The file has been

<table>
<thead>
<tr>
<th>000000</th>
<th>15.6</th>
<th>000000</th>
<th>21.4</th>
<th>000000</th>
<th>27.2</th>
<th>000000</th>
<th>33.0</th>
<th>000000</th>
<th>38.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>000000</td>
<td>11.4</td>
<td>000000</td>
<td>17.2</td>
<td>000000</td>
<td>23.0</td>
<td>000000</td>
<td>28.8</td>
<td>000000</td>
<td>34.6</td>
</tr>
<tr>
<td>000000</td>
<td>7.2</td>
<td>000000</td>
<td>13.0</td>
<td>000000</td>
<td>18.8</td>
<td>000000</td>
<td>24.6</td>
<td>000000</td>
<td>30.4</td>
</tr>
<tr>
<td>000000</td>
<td>3.0</td>
<td>000000</td>
<td>8.8</td>
<td>000000</td>
<td>14.6</td>
<td>000000</td>
<td>20.4</td>
<td>000000</td>
<td>26.2</td>
</tr>
</tbody>
</table>

**Supplemental information**

- Extent: 000000 to 000000
- Dimensions: 000000 x 000000
- Page count: 1
- Date: 000000

---

**Sample profile data:** These are the edge coordinates of File C-1. The file has been

<table>
<thead>
<tr>
<th>000000</th>
<th>15.6</th>
<th>000000</th>
<th>21.4</th>
<th>000000</th>
<th>27.2</th>
<th>000000</th>
<th>33.0</th>
<th>000000</th>
<th>38.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>000000</td>
<td>11.4</td>
<td>000000</td>
<td>17.2</td>
<td>000000</td>
<td>23.0</td>
<td>000000</td>
<td>28.8</td>
<td>000000</td>
<td>34.6</td>
</tr>
<tr>
<td>000000</td>
<td>7.2</td>
<td>000000</td>
<td>13.0</td>
<td>000000</td>
<td>18.8</td>
<td>000000</td>
<td>24.6</td>
<td>000000</td>
<td>30.4</td>
</tr>
<tr>
<td>000000</td>
<td>3.0</td>
<td>000000</td>
<td>8.8</td>
<td>000000</td>
<td>14.6</td>
<td>000000</td>
<td>20.4</td>
<td>000000</td>
<td>26.2</td>
</tr>
</tbody>
</table>

**Supplemental information**

- Extent: 000000 to 000000
- Dimensions: 000000 x 000000
- Page count: 1
- Date: 000000
Fig. C-3  Example of a typical input file for TLT.MinA or TLT.MaxD.

Filename:  input

23.5286
71.9283
52.09
0.00001923076923
245
245
20
5
20
5
0
1
60
s055.02.plt
<table>
<thead>
<tr>
<th>Fit/Fine</th>
<th>Left</th>
<th>Right</th>
</tr>
</thead>
<tbody>
<tr>
<td>005</td>
<td>020</td>
<td>005</td>
</tr>
<tr>
<td>006</td>
<td>020</td>
<td>006</td>
</tr>
<tr>
<td>007</td>
<td>020</td>
<td>007</td>
</tr>
<tr>
<td>008</td>
<td>020</td>
<td>008</td>
</tr>
<tr>
<td>009</td>
<td>020</td>
<td>009</td>
</tr>
<tr>
<td>010</td>
<td>020</td>
<td>010</td>
</tr>
<tr>
<td>011</td>
<td>020</td>
<td>011</td>
</tr>
<tr>
<td>012</td>
<td>020</td>
<td>012</td>
</tr>
<tr>
<td>013</td>
<td>020</td>
<td>013</td>
</tr>
<tr>
<td>014</td>
<td>020</td>
<td>014</td>
</tr>
<tr>
<td>015</td>
<td>020</td>
<td>015</td>
</tr>
<tr>
<td>016</td>
<td>020</td>
<td>016</td>
</tr>
<tr>
<td>017</td>
<td>020</td>
<td>017</td>
</tr>
<tr>
<td>018</td>
<td>020</td>
<td>018</td>
</tr>
<tr>
<td>019</td>
<td>020</td>
<td>019</td>
</tr>
<tr>
<td>020</td>
<td>020</td>
<td>020</td>
</tr>
<tr>
<td>021</td>
<td>020</td>
<td>021</td>
</tr>
<tr>
<td>022</td>
<td>020</td>
<td>022</td>
</tr>
<tr>
<td>023</td>
<td>020</td>
<td>023</td>
</tr>
<tr>
<td>024</td>
<td>020</td>
<td>024</td>
</tr>
<tr>
<td>025</td>
<td>020</td>
<td>025</td>
</tr>
<tr>
<td>026</td>
<td>020</td>
<td>026</td>
</tr>
<tr>
<td>027</td>
<td>020</td>
<td>027</td>
</tr>
<tr>
<td>028</td>
<td>020</td>
<td>028</td>
</tr>
<tr>
<td>029</td>
<td>020</td>
<td>029</td>
</tr>
<tr>
<td>030</td>
<td>020</td>
<td>030</td>
</tr>
<tr>
<td>031</td>
<td>020</td>
<td>031</td>
</tr>
<tr>
<td>032</td>
<td>020</td>
<td>032</td>
</tr>
<tr>
<td>033</td>
<td>020</td>
<td>033</td>
</tr>
<tr>
<td>034</td>
<td>020</td>
<td>034</td>
</tr>
<tr>
<td>035</td>
<td>020</td>
<td>035</td>
</tr>
<tr>
<td>036</td>
<td>020</td>
<td>036</td>
</tr>
<tr>
<td>037</td>
<td>020</td>
<td>037</td>
</tr>
<tr>
<td>038</td>
<td>020</td>
<td>038</td>
</tr>
<tr>
<td>039</td>
<td>020</td>
<td>039</td>
</tr>
<tr>
<td>040</td>
<td>020</td>
<td>040</td>
</tr>
<tr>
<td>041</td>
<td>020</td>
<td>041</td>
</tr>
<tr>
<td>042</td>
<td>020</td>
<td>042</td>
</tr>
<tr>
<td>043</td>
<td>020</td>
<td>043</td>
</tr>
<tr>
<td>044</td>
<td>020</td>
<td>044</td>
</tr>
<tr>
<td>045</td>
<td>020</td>
<td>045</td>
</tr>
<tr>
<td>046</td>
<td>020</td>
<td>046</td>
</tr>
<tr>
<td>047</td>
<td>020</td>
<td>047</td>
</tr>
<tr>
<td>048</td>
<td>020</td>
<td>048</td>
</tr>
<tr>
<td>049</td>
<td>020</td>
<td>049</td>
</tr>
<tr>
<td>050</td>
<td>020</td>
<td>050</td>
</tr>
<tr>
<td>051</td>
<td>020</td>
<td>051</td>
</tr>
<tr>
<td>052</td>
<td>020</td>
<td>052</td>
</tr>
<tr>
<td>053</td>
<td>020</td>
<td>053</td>
</tr>
<tr>
<td>054</td>
<td>020</td>
<td>054</td>
</tr>
<tr>
<td>055</td>
<td>020</td>
<td>055</td>
</tr>
<tr>
<td>056</td>
<td>020</td>
<td>056</td>
</tr>
<tr>
<td>057</td>
<td>020</td>
<td>057</td>
</tr>
<tr>
<td>058</td>
<td>020</td>
<td>058</td>
</tr>
<tr>
<td>059</td>
<td>020</td>
<td>059</td>
</tr>
<tr>
<td>060</td>
<td>020</td>
<td>060</td>
</tr>
<tr>
<td>061</td>
<td>020</td>
<td>061</td>
</tr>
<tr>
<td>062</td>
<td>020</td>
<td>062</td>
</tr>
<tr>
<td>063</td>
<td>020</td>
<td>063</td>
</tr>
<tr>
<td>064</td>
<td>020</td>
<td>064</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sigma (micro/m)</th>
<th>Diameter (mm)</th>
<th>Theta1 (deg)</th>
<th>Error1 (deg)</th>
<th>r1</th>
<th>Theta2 (deg)</th>
<th>Error2 (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.33801</td>
<td>7.11527</td>
<td>29.47323</td>
<td>4.91644</td>
<td>0.984950</td>
<td>3.84782</td>
<td>5.41793</td>
</tr>
<tr>
<td>1.33802</td>
<td>7.11527</td>
<td>29.47323</td>
<td>4.91644</td>
<td>0.984950</td>
<td>3.84782</td>
<td>5.41793</td>
</tr>
<tr>
<td>1.33803</td>
<td>7.11527</td>
<td>29.47323</td>
<td>4.91644</td>
<td>0.984950</td>
<td>3.84782</td>
<td>5.41793</td>
</tr>
<tr>
<td>1.33804</td>
<td>7.11527</td>
<td>29.47323</td>
<td>4.91644</td>
<td>0.984950</td>
<td>3.84782</td>
<td>5.41793</td>
</tr>
<tr>
<td>1.33805</td>
<td>7.11527</td>
<td>29.47323</td>
<td>4.91644</td>
<td>0.984950</td>
<td>3.84782</td>
<td>5.41793</td>
</tr>
</tbody>
</table>

Fig. C-4 Example of a typical output file for TLTMinA.

Filename: output
**Usage:** In order to run TLT.MinA, an input file containing a number of parameters and the name of the profile to be analysed must be created. Figure C-3 shows an example of a typical input file, and an explanation of each of the parameters is given below. To run the program, enter:

\[
tension\% \rightarrow \text{tlt.mina}
\]

at the prompt. The program will then prompt the user for the input file:

*Enter input file name: input*

followed by the number of points to remove around the intersection, in order to reduce the effect of noise around the intersection:

*Enter no. of takeoff points: 3*

Finally the program will prompt the user for the name of the file to write the output to:

*Enter output file name: output*
The Input File: The input file (Fig. C-3) consists of the parameters that the program needs for the calculation of line tension. The layout is shown below:

line 1: surface tension of liquid 1 (lens), \( \gamma_1 \) (mJ/m\(^2\))
line 2: surface tension of liquid 2 (surface), \( \gamma_2 \) (mJ/m\(^2\))
line 3: interfacial tension between liquids 1 and 2, \( \gamma_{12} \) (mJ/m\(^2\))
line 4: scaling or magnification factor, (m/pixel)
line 5: y-coordinate of left cut-off point
line 6: y-coordinate of right cut-off point
line 7: # of finetuning points for the left side of the lens profile
line 8: # of linear fitting points to use initially for the left side of the lens profile
line 9: # of finetuning points for the right side of the lens profile
line 10: # of linear fitting points to use initially for the right side of the lens profile
line 11: the increment of increase of the # of finetuning points for each run
line 12: the increment of increase of the # of linear fitting points for each run
line 13: the range of linear fitting points, i.e., # of iterations
line 14: filename of the image profile to be analysed

This program allows one to perform an analysis of the dependence of the slope of the "tangent" on the number of fitting points used. Lines 1, 2 and 3 are the surface tensions needed by the Quadrilateral Relation. Line 4 relates the pixel size to the lens' real size and is obtained through calibration of the microscope and the CCD camera used in the experiment. Lines 5 and 6 specify the upper extent of the lens for the left and right sides, respectively; any part of the profile above this cutoff is considered as part of the needle and is not used. Line 7 specifies the number of points used to finetune the location of the left intersection point, or
the range which the finetuning test sweeps through to determine the point associated with the minimum angle (see above). Line 8 specifies the initial number of fitting points to be used in order to obtain the “tangent” angles $\theta_1$ and $\theta_2$ on the left side of the lens profile. Lines 9 and 10 are the same as lines 7 and 8, but are for the right side. Line 11 specifies the increment of increase of the finetuning points to be used in each run, and hence it increases the range of points to test. Usually it is kept as 0. Line 12 specifies the increment of increase of the fitting points for each run. Line 13 specifies the range of increase of the fitting points. Hence, as seen in Figs. C-3 and C-4, the range of fitting points used would be 60, with an initial value of 5 points, increasing to a final value of 64, with an incremental increase of 1. Line 14 specifies the image profile on which the analysis will be performed.

**The Output File:** The output file (Fig. C-4) is a table of information. Columns 1 and 2 show the numbers of the fitting and finetuning points for the left side of the lens profile, respectively. Columns 3 and 4 show the same information for the right side. Columns 5 and 6 display the line tension ($\mu J/m$) and the diameter (mm), respectively. Columns 7, 8, and 9 show $\theta_1$ (deg), the error of $\theta_1$ (deg), and the correlation coefficient in the linear curve-fit for finding $\theta_1$, respectively. Columns 10, 11, and 12 display the same information for $\theta_2$.

**The Computer Codes in C Language:**
typedef double * float_array;

/* INPUT DATA */
int fitNumP_L, fineNumP_L, fitNumP_R, fineNumP_R;
int takeoff_point;
double gamma1, gamma2, gamma12;
double factor;
double cut_left_y, cut_right_y;

/* OUTPUT DATA */
double theta1, theta2, theta12;
double sigma, lensDia;
double deltaL, deltaR, delta, rL, rR, r;

/* INPUT FILE VARIABLES */
int count, i;
char plotFile[20];
FILE *inFile;

/* FUNCTIONS */
double calSigma ( double t2L, double t1L, double t2R, double t1R, double lensDia,
                 double t12L, double t12R);
double linear_fit ( int point_number, double *x, double *y);
double linear_fit2 ( int point_number, double *x, double *y);

void detect_point ( char plotFile[20], int direction ) {

    FILE *data;
    char temp2;
    int numPoints = 0;
    int max_i = 0, left_max_i = 0, right_max_i = 0;
    int count = 0, temp = 0;
    int i = 0, j = 0, j1, j2, end = 0;
    int cut_left_index, cut_right_index, check = 0, point_begin;
    int min_left_i, min_right_i, down_begin, up_begin, center_point;
    double rLineX1 = 0, rLineY1 = 0, rLineX2 = 0, rLineY2 = 0;
    double X = 0, Y = 0;
    double tg_slope = 0, sin_slope = 0, cos_slope = 0;
    double L_down_up = 0, distance = 0;
double left_max_x = 0, left_max_y = 0, right_max_x = 0, right_max_y = 0, max = 0;
double t12Lmin, t12Rmin;
double xconPointL, yconPointL, xconPointR, yconPointR;
double t12L, t12R;
double lensTilt;
double down_beta, up_beta, down_beta_0, up_beta_0;
double t12L, t12R, t1R;
double fit_rLineX1[150], fit_rLineY1[150];
double fit_rLineX2[150], fit_rLineY2[150];
double temp_change;
float_array x_coord, y_coord;

numPoints = 0;
data = fopen( plotFile, "rt" );

if ( data == NULL ) {
    printf ( "Failure to open:\n", plotFile );
    exit ( 1 );
}

if ( direction == 0 ) {
    do {
        fscanf ( data, "%c", &temp2 );
        if ( temp2 == '#')
            count = count + 1;
    } while ( count < 3 );

    fscanf ( data, "%d", &numPoints );

    do {
        fscanf ( data, "%c", &temp2 );
    } while ( temp2 != '\n' );

    temp = 0;
    x_coord = ( double * ) calloc ( numPoints, sizeof ( double ) );
    y_coord = ( double * ) calloc ( numPoints, sizeof ( double ) );
    fscanf ( data, "%lf%lf", &x_coord[temp], &y_coord[temp] );
    check = 1;
do {
    temp = temp + 1;
    fscanf ( data, "%lf%lf", &x_coord[temp], &y_coord[temp] );
    if (y_coord[temp] > cut_left_y) {
        if (check == 1) {
            cut_left_index = temp;
            check = -1;
        }
    }
} while (temp <= (numPoints - 1));

point_begin = cut_left_index;
fclose (data);
}
else if (direction == 1) {
    do {
        fscanf ( data, "%c", &temp2 );
        if (temp2 == '#')
            count = count + 1;
    } while (count < 5);

tscanf ( data, "%d", &numPoints );
temp = 0;

do {
    fscanf ( data, "%c", &temp2 );
} while (temp2 != 'n');

x_coord = (double *) calloc (numPoints, sizeof(double));
y_coord = (double *) calloc (numPoints, sizeof(double));
fscanf ( data, "%lf%lf", &x_coord[temp], &y_coord[temp] );
check = 1;

do {
    temp = temp + 1;
    fscanf ( data, "%lf%lf", &x_coord[temp], &y_coord[temp] );

    if (y_coord[temp] > cut_right_y) {
        if (check == 1) {
            cut_right_index = temp;
        }
    }
} while (temp <= (numPoints - 1));
cut_right_index = temp;
    check = -1;
}
}
} while ( temp <= ( numPoints - 1 ) );

point_begin = cut_right_index;
fclose ( data );
}

/* FIND MAXIMUM DISTANCE POINT */
 rLineY1 = y_coord[numPoints - 1];
 rLineX1 = x_coord[numPoints - 1];
 rLineY2 = y_coord[point_begin];
 rLineX2 = x_coord[point_begin];
 L_down_up = sqrt ( pow ( ( rLineY1 - rLineY2 ), 2 ) +
                   pow ( ( rLineX1 - rLineX2 ), 2 ) );
 tg_slope = ( rLineY1 - rLineY2 ) / ( rLineX1 - rLineX2 );
 sin_slope = fabs ( ( rLineY1 - rLineY2 ) / L_down_up; 
 cos_slope = fabs ( ( rLineX1 - rLineX2 ) / L_down_up;
 max = 0;
 max_i = 0;
 distance = 0;

for ( i = point_begin; i < numPoints; i++ ) {
    X = fabs ( x_coord[i] - rLineX1 );
    Y = fabs ( y_coord[i] - rLineY1 );
    distance = ( X + ( Y * tg_slope ) ) * sin_slope - Y / cos_slope;

    if ( distance > max ) {
        max = distance;
        max_i = i;
    }
}

if ( direction == 0 ) {
    left_max_x = x_coord[max_i];
    left_max_y = y_coord[max_i];
    left_max_i = max_i;
}

if ( direction == 1 ) {
    right_max_x = x_coord[max_i];
right_max_y = y_coord[max_i];
right_max_i = max_i;
}

;/*  FIND LEFT SIDE MINIMUM ANGLE  */
if ( direction == 0 ) {
    t12Lmin = 3.1415926;
    center_point = left_max_i;

    for ( i = 0; i <= fineNumP_L; i++) {
        down_begin = center_point + fineNumP_L / 2 - i;
        up_begin = down_begin;

        for ( j = 0; j < fitNumP_L; j++) {
            j1 = down_begin + j;
            j2 = up_begin - j;
            fit_rLineX1[j] = x_coord[j1];
            fit_rLineY1[j] = y_coord[j1];
            fit_rLineX2[j] = x_coord[j2];
            fit_rLineY2[j] = y_coord[j2];
        }

        down_beta = linear_fit (fitNumP_L, fit_rLineX1, fit_rLineY1);
        up_beta = linear_fit (fitNumP_L, fit_rLineX2, fit_rLineY2);
        t12L = fabs ( atan ( down_beta ) ) + 3.1415926 - fabs ( atan ( up_beta ) );

        if ( t12L < t12Lmin ) {
            t12Lmin = t12L;
            min_left_i = down_begin;
        }
    }
}

;/*  FIND LEFT CONTACT POINT  */
for ( j = 0; j < fitNumP_L; j++) {
    j1 = min_left_i + j + takeoff_point;
    j2 = min_left_i - j - takeoff_point;
    fit_rLineX1[j] = x_coord[j1];
    fit_rLineY1[j] = y_coord[j1];
    fit_rLineX2[j] = x_coord[j2];
fit_rLineY2[j] = y_coord[j2];
}

t2L = linear_fit ( fitNumP_L, fit_rLineX1, fit_rLineY1 );
temp_change = t2L;
t1L = linear_fit ( fitNumP_L, fit_rLineX2, fit_rLineY2 );
down_beta_0 = linear_fit2 ( fitNumP_L, fit_rLineX1, fit_rLineY1 );
up_beta_0 = linear_fit2 ( fitNumP_L, fit_rLineX2, fit_rLineY2 );
xconPointL = ( down_beta_0 - up_beta_0 ) / ( t1L - t2L );
yconPointL = down_beta_0 + t2L * xconPointL;

t12L = fabs( atan( t2L ) ) + 3.1415926 - fabs( atan( t1L ) );
deltaL = delta;
rL = r;

/* FIND RIGHT SIDE MINIMUM ANGLE */
if ( direction == 1 ) {
    t12Rmin = 3.14159;
    center_point = right_max_i;

    for ( i = 0; i <= fineNumP_R; i++ ) {
        down_begin = center_point + fineNumP_R / 2 - i;
        up_begin = down_begin;

        for ( j = 0; j < fitNumP_R; j++ ) {
            j1 = down_begin + j;
            j2 = up_begin - j;
            fit_rLineX1[j] = x_coord[j1];
            fit_rLineY1[j] = y_coord[j1];
            fit_rLineX2[j] = x_coord[j2];
            fit_rLineY2[j] = y_coord[j2];
        }

        down_beta = linear_fit ( fitNumP_R, fit_rLineX1, fit_rLineY1 );
        up_beta = linear_fit ( fitNumP_R, fit_rLineX2, fit_rLineY2 );
        t12R = fabs( atan( down_beta ) ) + 3.1415926 - fabs( atan( up_beta ) );

        if ( t12R < t12Rmin ) {
            t12Rmin = t12R;
            min_right_i = down_begin;
        }
    }
}
/ * FIND RIGHT CONTACT POINT  */
for (j = 0; j < fitNumP_R; j++) {
    j1 = min_right_i + j + takeoff_point;
    j2 = min_right_i - j - takeoff_point;
    fit_rLineX1[j] = x_coord[j1];
    fit_rLineY1[j] = y_coord[j1];
    fit_rLineX2[j] = x_coord[j2];
    fit_rLineY2[j] = y_coord[j2];
}

t2R = linear_fit (fitNumP_R, fit_rLineX1, fit_rLineY1);
t1R = linear_fit (fitNumP_R, fit_rLineX2, fit_rLineY2);
down_beta_0 = linear_fit2 (fitNumP_R, fit_rLineX1, fit_rLineY1);
up_beta_0 = linear_fit2 (fitNumP_R, fit_rLineX2, fit_rLineY2);
xconPointR = (down_beta_0 - up_beta_0) / (t1R - t2R);
yconPointR = down_beta_0 + t2R * xconPointR;
t12R = fabs (atan (t2R)) + 3.1415926 - fabs (atan (t1R));
deltaR = delta;
rR = r;

/*/ CALCULATE LENS DIAMETER  */
if (direction == 1) {
    lensDia = sqrt (pow ((xconPointL - xconPointR), 2) +
                    pow ( (yconPointL - yconPointR), 2 ));
    lensTilt = (yconPointL - yconPointR) / (xconPointL - xconPointR);
}

/*/ CALCULATE LINE TENSION  */
if (direction == 1) {
    if (fabs (t12L - t12R) < 5.*3.1415926/180. ) {
        sigma = calSigma (temp_change, t1L, t2R, t1R, lensDia, t12L, t12R);
    }
    else {
        fprintf (inFile, "ABS(Theta12_L - Theta12_R) > 5 deg.");
        fprintf (inFile, " The run is ignored.
");
    }
}

free (x_coord);
free (y_coord);
double linear_fit ( int point_number, double *x, double *y ) {

    int i = 0;
    double SS_xx = 0, SS_xy = 0, SS_yy = 0, SSE = 0;
    double sum_xx = 0, sum_xy = 0, sum_x = 0, sum_y = 0, sum_yy = 0;
    double beta_0 = 0, beta_1 = 0;
    double s = 0, s_beta = 0, t_a = 0;

    for ( i = 0; i < point_number; i++ ) {
        sum_x = sum_x + x[i];
        sum_y = sum_y + y[i];
        sum_xy = sum_xy + x[i] * y[i];
        sum_xx = sum_xx + x[i] * x[i];
        sum_yy = sum_yy + y[i] * y[i];
    }

    SS_xy = sum_xy - ( sum_x * sum_y ) / point_number;
    SS_xx = sum_xx - ( sum_x * sum_x ) / point_number;
    SS_yy = sum_yy - ( sum_y * sum_y ) / point_number;
    beta_1 = SS_xy / SS_xx;
    SSE = SS_yy - beta_1 * SS_xy;
    s = sqrt( SSE / ( point_number - 2 ) );
    s_beta = s / sqrt( SS_xx );
    t_a = 1.96;
    delta = t_a * s_beta * cos( fabs( atan( beta_1 ) ) ) * cos( fabs( atan( beta_1 ) ) );
    r = fabs( SS_xy / sqrt( SS_xx * SS_yy ) );
    return ( beta_1 );
}

double linear_fit2 ( int point_number, double *x, double *y ) {

    int i = 0;
    double SS_xx = 0, SS_xy = 0;
    double sum_xx = 0, sum_xy = 0, sum_x = 0, sum_y = 0;
    double beta_0 = 0, beta_1 = 0;

    for ( i = 0; i < point_number; i++ ) {
    ...
\[ \text{sum}_x = \text{sum}_x + x[i]; \]
\[ \text{sum}_y = \text{sum}_y + y[i]; \]
\[ \text{sum}_xy = \text{sum}_xy + x[i] \times y[i]; \]
\[ \text{sum}_xx = \text{sum}_xx + x[i] \times x[i]; \]

\[
\text{SS}_xy = \text{sum}_xy - (\text{sum}_x \times \text{sum}_y) / \text{point}\_\text{number}; \\
\text{SS}_xx = \text{sum}_xx - (\text{sum}_x \times \text{sum}_x) / \text{point}\_\text{number}; \\
\beta_1 = \text{SS}_xy / \text{SS}_xx; \\
\beta_0 = \text{sum}_y / \text{point}\_\text{number} - \beta_1 \times \text{sum}_x / \text{point}\_\text{number}; \\
\text{return} (\beta_0); 
\]

double calSigma ( double t2L, double t1L, double t2R, double t1R, double lensDia, 
               double t12L, double t12R ) 
{
    double k;
    double pi = 3.1415926;

    theta1 = (fabs(atan(t1L)) + fabs(atan(t1R))) / 2.;
    theta2 = pi - (fabs(atan(t2R)) + fabs(atan(t2L))) / 2.;
    theta12 = (t12L + t12R) / 2.;
    k = 2. / (lensDia * factor);

    sigma = -(gamma1 * cos(theta1) + gamma2 * cos(theta2)) - sqrt((gamma1 * 
        cos(theta1) + gamma2 * cos(theta2)) * (gamma1 * cos(theta1) + 
        gamma2 * cos(theta2)) - (gamma1 * gamma1 + gamma2 * gamma2 
        + 2. * 
        gamma1 * gamma2 * cos(theta12) - gamma12 * gamma12));
    sigma = sigma / k;
    return (sigma);
}
#include <stdio.h>
#include <stdlib.h>
#include <ctype.h>
#include <math.h>
#include "t1t.rnina.h"

void printHeads ( FILE *outFile, char *plotFile );

void main ( int argc, char *argv[] ) {
    int direction = 0; /*direction = 0 for left side, = 1 for right side*/
    int j;
    int fineNumP_L_ini, fitNumP_L_ini;
    int fineNumP_R_ini, fitNumP_R_ini;
    int fitNumP_delta, fineNumP_delta;
    int maxRuns;
    char out[50], in[50];
    FILE *outFile;

    if ( ( inFile = fopen( argv[1], "r" ) ) == NULL ) {
        printf ( "Enter input file name:
" );
        scanf ( "%s", in );
        inFile = fopen ( in, "r" );
    }

    printf ( "Enter no. of takeoff points:
" );
    scanf ( "%d", &takeoff_point );

    printf ( "Enter output file name:
" );
    scanf ( "%s", out );
    outFile = fopen ( out, "w+" );
    rewind ( outFile );

    fscanf ( inFile, "%lf%lf%lf%lf", &gamma1, &gamma2, &gamma12, &factor );
    fscanf ( inFile, "%lf%lf", &cut_left_y, &cut_right_y );
    fscanf ( inFile, "%d%d", &fineNumP_L_ini, &fitNumP_L_ini );
    fscanf ( inFile, "%d%d", &fineNumP_R_ini, &fitNumP_R_ini );
    fscanf ( inFile, "%d%d", &fineNumP_delta, &fitNumP_delta );
    fscanf ( inFile, "%d", &maxRuns );
    fscanf ( inFile, "%s", plotFile );
while (!feof ( inFile )) {
    for ( j = 0; j < maxRuns; j++ ) {
        fitNumP_L = fitNumP_L_ini + fitNumP_delta * j;
        fineNumP_L = fineNumP_L_ini + fineNumP_delta * j;
        fitNumP_R = fitNumP_R_ini + fitNumP_delta * j;
        fineNumP_R = fineNumP_R_ini + fineNumP_delta * j;
        direction = 0;
        detect_point ( plotFile, direction );
        direction = 1;
        detect_point ( plotFile, direction );
        printf ( "run\nstep %d\n", plotFile, j);

        fprintf ( outFile, "%.3d %.3d %.3d %.3d ", fitNumP_L, fineNumP_L,
                 fitNumP_R, fineNumP_R );
        fprintf ( outFile, "%lf ", sigma * 1000 );
        fprintf ( outFile, "%lf ", lensDia * factor * 1000. );
        fprintf ( outFile, "%lf ", theta1 * 180. / 3.1415926 );
        fprintf ( outFile, "%lf ", deltaL * 180. / 3.1415926 );
        fprintf ( outFile, "%lf ", rL );
        fprintf ( outFile, "%lf ", 180. - theta2 * 180. / 3.1415926 );
        fprintf ( outFile, "%lf ", deltaR * 180. / 3.1415926 );
        fprintf ( outFile, "%lf\n", rR );
    }
}

fclose ( inFile );
fclose ( outFile );
}

void printHeads ( FILE *outFile, char *plotFile ) {
    fprintf ( outFile, "Using:\n", plotFile );
    fprintf ( outFile, "Fit/Fine Sigma Diameter" );
    fprintf ( outFile, "Theta1 Error1 r1 Theta2" );
    fprintf ( outFile, "Error2 r2\n" );
    fprintf ( outFile, "Left Right (microJ/m) (mm)" );
    fprintf ( outFile, " (deg) (deg) (deg)" );
    fprintf ( outFile, "\n" );
    fprintf ( outFile, "--------------------------" );
}
fprintf ( outFile, "--------------------------" );
fprintf ( outFile, "------------------\n" );
}
C.2 Program II: TLT.MaxD

**Background:** This program is similar to TLT.MinA except that instead of using $D_{\text{min}}$, the distance between the two intersection points detected using the minimum angle approach, it uses $D_{\text{max}}$, the points detected using the maximum diameter approach (see Section C.1). Otherwise the purposes and structure are the same.

This program tests the optimum number of fitting points to use, and hence the prefix TLT, or Test Line Tension, is used in the program name. Since this program uses $D_{\text{max}}$, the intersection points obtained by the maximum distance approach, in calculating the radius of curvature $\kappa$, the suffix MaxD, or maximum distance, is used in the program name.

As an example, the same image used in TLT.MinA was analysed in this program. The profile was obtained as outline in Section 5.1.3, and this program was run. The image, the detected profile points and the input file used are the same as in TLT.MinA and are shown in Figs. C-1, C-2 and C-3. The output file is shown in Fig. C-5.

**Usage:** In order to run TLT.MaxD, an input file containing a number of parameters and the name of the profile to be analysed must be created. The input file used is the same as that used for TLT.MinA (Fig. C-3). To run the program, enter:

```
tension% /> tlt.maxd
```

at the prompt. The rest of the procedure is the same as TLT.MinA.
F ic/Fine
Riqht

Left

----------------

005
006
007
008
009
010
Oli

020
O20
020
020
020
020
020

005
006
O07
O?!
009
010
O11

O20
020
023
O20
020
020
020

Thetal

Oiamecer
(mm)

(deq)

Errorl
ide91

t1

4 .9l6445
5.636975
4.157221
3.142'32
2.968440
2.407088
2.281921
2.322464
1.626927
1.722768
1.236261
1.127061
1.245369
1.115577
1.004291
O .O03093
O .89447O
O -871746
O .8283L8
0.773346
0.723025
0.718701
0.642011
O .6l4482
O .506251
0.592513
O .563793
O -586471
0.550130
0.558793
O .5338S3
O .S2432l
0.512269
0.522602
0 .Sl7275
0.504827
0.505253
0.5117t2
O .Si7872
9 .SL56SZ
O.5LÎOl4
0.51C732
O .523646

O .98dqSO
O .97678O
O .984O48
0.989191
0.988155
0.991126
0,990690
0.989662
0.994123
0.993020
0.995932
0.996315
0.395293
0.995982
0.995908
O .99756l
O . 996862
O .99689l
O .996982
0.997229
0.997456
0.997399
0.997802
O .997894
O .99eooo
0.997898
0.998022
0.997765
0.997929
0.997811
0.997933
0 -997935
0.997929
0.997800
0.997772
0.997811
0.997735
0.997601
0.997464
O .99744O
O .997348
0 -397338
0.997117
9.997143
0.99697'
3.997078
0.996935
7.397072

----------------------------------------7 .OS7989
7 .O57989
7 .O57989
7.057989
7.057989
7 .CS7989
7.057989
7.057989
7 .OS7989
7.057989
7 .O57989
7.057989
7,057989
7.057989
7.057989
7 .O57989
7.057989
7,057989
7.057989
7.057989
7.057989
7.057969
7.057989
7,057989
7.057989
7.057969
7 .O57989
7 .OS7989
7.057989
7,057989
7 .O57989
7 .O57989
7.057989
7.057989
7 .OS7989
7.057989
7.057909
7.057989
7 .O57989
7 .O57989
7.057989
7 .O57989
7.957999
7.957387
7.357397
7.?5708?
7.957393
7.55ÏqRQ

7 . ;5t?9!
7 .O57389
7.057989
7.957399
7.057989
7 .OS7989
7.057989
7.057989
7.057989
7 .O57999
7.957939
7.057909

29.473233
32 .O83849
32.605332
32.669436
32.310962
32.064558
31.627793
32.111874
31.303603
31.853388
31.238304
30.928900
3 1 .O13034
30.944573
30.967925
30.617808
30 , 5 0 4 O i l
30.568302
30.434379
30.303603
30.183200
30.223221
29.951409
29.813350
29.693631
29.716977
29.611817
29.433236
29.153646
29.183783
29 .lO4628
28.939499
28.652706
28.675628
28.720098
26.627642
28.495940
28.174273
28.199974
28.197294
20.204179
27.946606
27.791254
27.420495
27.678444
27.652CO4
27.464975
27.438799
2 7 .:07132:
27 .O78SZO
27.369259
27 .O52265
26.953906
26.038671
26.7145L5
26 -597970
26,570661
26.547579
26.367061
25.255733

9.514194

C.521555

g.5092?2
9.507626
9.496i5?
J.j i ; 1 3 :

9. Si4?:q

3.396771

O. 9 9 6 6 5 3

9.513555

3.996579

4.504296
0.500467
0.500102
O . 502782
9.503347
0.491118
0.590556
9.387210
2.487525

O . 396653

0.996625
0.996549
O . 996428
0. 996335
0.996461
Q.996389
9.996361
9.996216

Fig. C-5 Example of a typical output file for TLT.MaxD

Filename:

output


**The Input File:** The input file is the same in structure as that used in TLT.MinA. An example is provided in Fig. C-3.

**The Output File:** The output file is a tabulation of information and is the same in structure as that produced by TLT.MinA. However, since the detected intersection points will be different, the line tension values calculated will be different as well. Figure C-5 shows the a typical output from TLT.MaxD using the same image and profile for analysis as TLT.MinA. Note the differences between Figs. C-4 and C-5.

**The Computer Codes in C Language:**
typedef double * float_array;

/* INPUT DATA */
int fitNumP_L, fineNumP_L, fitNumP_R, fineNumP_R;
int takeoff_point;
double gamma1, gamma2, gamma12;
double factor;
double cut_left_y, cut_right_y;

/* OUTPUT DATA */
double theta1, theta2, theta12;
double sigma, lensDia;
double deltaL, deltaR, delta, rL, rR, r;

/* INPUT FILE VARIABLES */
int count, i;
char plotFile[20];
FILE *inFile;

/* FUNCTIONS */
double calSigma ( double t2L, double t1L, double t2R, double t1R, double lensDia,
                 double t12L, double t12R );  
double linear_fit ( int point_number, double *x, double *y );
double linear_fit2 ( int point_number, double *x, double *y );

/**************************TLT.MaxD***************************/
void detect_point ( char plotFile[20], int direction ) {
    FILE *data;
    char temp2;
    int numPoints = 0;
    int max_i = 0, left_max_i = 0, right_max_i = 0;
    int count = 0, temp = 0;
    int i = 0, j = 0, j1, j2, end = 0;
    int cut_left_index, cut_right_index, check = 0, point_begin;
    int min_left_i, min_right_i, down_begin, up_begin, center_point;
    double rLineX1 = 0, rLineY1 = 0, rLineX2 = 0, rLineY2 = 0;
    double X = 0, Y = 0;
    double tg_slope = 0, sin_slope = 0, cos_slope = 0;
    double L_down_up = 0, distance = 0;
double left_max_x = 0, left_max_y = 0, right_max_x = 0, right_max_y = 0, max = 0;
double t12Lmin, t12Rmin;
double xconPointL, yconPointL, xconPointR, yconPointR;
double t12L, t12R;
double lensTilt;
double down_beta, up_beta, down_beta_0, up_beta_0;
double t2L, t1L, t2R, t1R;
double fit_rLineX[150], fit_down_y[150], fit_up_x[150], fit_up_y[150];
double temp_change;
float_array x_coord, y_coord;

numPoints = 0;
data = fopen ( plotFile, "rt" );

if ( data == NULL ) {
    printf ( "Failure to open:\n %s\n", plotFile );
    exit ( 1 );
}

if ( direction == 0 ) {
    do {
        fscanf ( data, "%c", &temp2 );
        if ( temp2 == '#' )
            count = count + 1;
    } while ( count < 3 );

    fscanf ( data, "%d", &numPoints );

do {
    fscanf ( data, "%c", &temp2 );
} while ( temp2 != '\n' );

    temp = 0;
    x_coord = ( double * ) calloc ( numPoints, sizeof ( double ) );
    y_coord = ( double * ) calloc ( numPoints, sizeof ( double ) );
    fscanf ( data, "%lf%lf", &x_coord[temp], &y_coord[temp] );
    check = 1;
do {
    temp = temp + 1;
    fscanf ( data, "%lf%lf", &x_coord[temp], &y_coord[temp] );

    if ( y_coord[temp] > cut_left_y ) {
        if ( check == 1 ) {
            cut_left_index = temp;
            check = -1;
        }
    }
} while ( temp <= ( numPoints - 1 ) );

point_begin = cut_left_index;
fclose ( data );
}
else if ( direction == 1 ) {
    do {
        fscanf ( data, "%c", &temp2 );
        if ( temp2 == '#' )
            count = count + 1;
    } while ( count < 5 );

    fscanf ( data, "%d", &numPoints );
    temp = 0;

    do {
        fscanf ( data, "%c", &temp2 );
    } while ( temp2 != '\n' );

    x_coord = ( double * ) calloc ( numPoints, sizeof ( double ) );
    y_coord = ( double * ) calloc ( numPoints, sizeof ( double ) );
    fscanf ( data, "%lf%lf", &x_coord[temp], &y_coord[temp] );
    check = 1;

    do {
        temp = temp + 1;
        fscanf ( data, "%lf%lf", &x_coord[temp], &y_coord[temp] );

        if ( y_coord[temp] > cut_right_y ) {
if ( check == 1 ) {
    cut_right_index = temp;
    check = -1;
}
} while ( temp <= ( numPoints - 1 ) );

point_begin = cut_right_index;
fclose ( data );

/* FIND MAXIMUM DISTANCE POINT */
rLineY1 = y_coord[numPoints - 1];
rLineX1 = x_coord[numPoints - 1];
rLineY2 = y_coord[point_begin];
rLineX2 = x_coord[point_begin];
L_down_up = sqrt ( pow ( ( rLineY1 - rLineY2 ), 2 ) +
    pow ( ( rLineX1 - rLineX2 ), 2 ) );
tg_slope = ( rLineY1 - rLineY2 ) / ( rLineX1 - rLineX2 );
sin_slope = fabs ( ( rLineY1 - rLineY2 ) ) / L_down_up;
cos_slope = fabs ( ( rLineX1 - rLineX2 ) ) / L_down_up;
max = 0;
max_i = 0;
distance = 0;

for ( i = point_begin; i < numPoints; i++ ) {
    X = fabs ( x_coord[i] - rLineX1 );
    Y = fabs ( y_coord[i] - rLineY1 );
    distance = ( X + ( Y * tg_slope ) ) * sin_slope - Y / cos_slope;
    if ( distance > max ) {
        max = distance;
        max_i = i;
    }
}

if ( direction == 0 ) {
    left_max_x = x_coord[max_i];
    left_max_y = y_coord[max_i];
    left_max_i = max_i;
}

if ( direction == 1 ) {
*/ FIND LEFT SIDE MINIMUM ANGLE /*
if ( direction == 0 ) {
    t12Lmin = 3.1415926;
    center_point = left_max_i;

    for ( i = 0; i <= fineNumP_L; i++ ) {
        down_begin = center_point + fineNumP_L / 2 - i;
        up_begin = down_begin;

        for ( j = 0; j < fitNumP_L; j++ ) {
            j1 = down_begin + j;
            j2 = up_begin - j;
            fit_rLineX1[j] = x_coord[j1];
            fit_down_y[j] = y_coord[j1];
            fit_up_x[j] = x_coord[j2];
            fit_up_y[j] = y_coord[j2];
        }

        down_beta = linear_fit ( fitNumP_L, fit_rLineX1, fit_down_y );
        up_beta = linear_fit ( fitNumP_L, fit_up_x, fit_up_y );
        t12L = fabs ( atan ( down_beta ) ) + 3.1415926 - fabs ( atan ( up_beta ) );

        if ( t12L < t12Lmin ) {
            t12Lmin = t12L;
            min_left_i = down_begin;
        }
    }
}

/*/ FIND LEFT CONTACT POINT */
for ( j = 0; j < fitNumP_L; j++ ) {
    j1 = min_left_i + j + takeoff_point;
    j2 = min_left_i - j - takeoff_point;
    fit_rLineX1[j] = x_coord[j1];
    fit_down_y[j] = y_coord[j1];
fit_up_x[j] = x_coord[j2];
f_up_y[j] = y_coord[j2];
}

t2L = linear_fit ( fitNumP_L, fit_rLineX1, fit_down_y );
temp_change = t2L;
t1L = linear_fit ( fitNumP_L, fit_up_x, fit_up_y );
down_beta_0 = linear_fit2 ( fitNumP_L, fit_rLineX1, fit_down_y );
up_beta_0 = linear_fit2 ( fitNumP_L, fit_up_x, fit_up_y );
xconPointL = x_coord[left_max_i];
yconPointL = y_coord[left_max_i];
t12L = fabs ( atan ( t2L ) ) + 3.1415926 - fabs ( atan ( t1L ) );
deltal = delta;
rL = r;

/* FIND RIGHT SIDE MINIMUM ANGLE */
if ( direction == 1 ) {

t12Rmin = 3.14159;
center_point = right_max_i;

for ( i = 0; i <= fineNumP_R; i++ ) {
    down_begin = center_point + fineNumP_R / 2 - i;
    up_begin = down_begin;

    for ( j = 0; j < fitNumP_R; j++ ) {
        j1 = down_begin + j;
        j2 = up_begin - j;
        fit_rLineX1[j] = x_coord[j1];
        fit_down_y[j] = y_coord[j1];
        fit_up_x[j] = x_coord[j2];
        fit_up_y[j] = y_coord[j2];
    }

    down_beta = linear_fit ( fitNumP_R, fit_rLineX1, fit_down_y );
    up_beta = linear_fit ( fitNumP_R, fit_up_x, fit_up_y );
    t12R = fabs ( atan ( down_beta ) ) + 3.1415926 - fabs ( atan ( up_beta ) );

    if ( t12R < t12Rmin ) {
        t12Rmin = t12R;
        min_right_i = down_begin;
    }
}
/* FIND RIGHT CONTACT POINT */
for ( j = 0; j < fitNumP_R; j++ ) {
    j1 = min_right_i + j + takeoff_point;
    j2 = min_right_i - j - takeoff_point;
    fit_rLineX1[j] = x_coord[j1];
    fit_down_y[j] = y_coord[j1];
    fit_up_x[j] = x_coord[j2];
    fit_up_y[j] = y_coord[j2];
}

t2R = linear_fit ( fitNumP_R, fit_rLineX1, fit_down_y );
t1R = linear_fit ( fitNumP_R, fit_up_x, fit_up_y );
down_beta_0 = linear_fit2 ( fitNumP_R, fit_rLineX1, fit_down_y );
up_beta_0 = linear_fit2 ( fitNumP_R, fit_up_x, fit_up_y );
xconPointR = x_coord[right_max_i];
yconPointR = y_coord[right_max_i];
t12R = fabs ( atan ( t2R ) ) + 3.1415926 - fabs ( atan ( t1R ) );
deltaR = delta;
rR = r;
}

/* CALCULATE LENS DIAMETER */
if ( direction == 1 ) {
    lensDia = sqrt ( pow ( ( xconPointL - xconPointR ), 2 ) +
                    pow ( ( yconPointL - yconPointR ), 2 ) );
    lensTilt = ( yconPointL - yconPointR ) / ( xconPointL - xconPointR );
}

/* CALCULATE LINE TENSION */
if ( direction == 1 ) {
    if ( fabs ( t12L - t12R ) < 5. * 3.1415926 / 180. ) {
        sigma = calSigma ( temp_change, t1L, t2R, t1R, lensDia, t12L, t12R );
    }
    else {
        fprintf ( inFile, "\n% image includes some large noise points"
        fprintf ( inFile, "or the program isn't be able to detect it, so quit\n", plotFile );
    }
}
free ( x_coord );
free ( y_coord );
double linear_fit ( int point_number, double *x, double *y ) {

    int i = 0;
    double SS_xx = 0, SS_xy = 0, SS_yy = 0, SSE = 0;
    double sum_xx = 0, sum_xy = 0, sum_x = 0, sum_y = 0, sum_yy = 0;
    double beta_0 = 0, beta_1 = 0;
    double s = 0, s_beta = 0, ta = 0;

    for ( i = 0; i < point_number; i++ ) {
        sum_x = sum_x + x[i];
        sum_y = sum_y + y[i];
        sum_xy = sum_xy + x[i] * y[i];
        sum_xx = sum_xx + x[i] * x[i];
        sum_yy = sum_yy + y[i] * y[i];
    }

    SS_xy = sum_xy - ( sum_x * sum_y ) / point_number;
    SS_xx = sum_xx - ( sum_x * sum_x ) / point_number;
    SS_yy = sum_yy - ( sum_y * sum_y ) / point_number;
    beta_1 = SS_xy / SS_xx;
    SSE = SS_yy - beta_1 * SS_xy;
    s = sqrt ( SSE / ( point_number - 2 ) );
    s_beta = s / sqrt ( SS_xx );
    ta = 1.96;
    delta = ta * s_beta * cos ( fabs ( atan ( beta_1 ))) * cos ( fabs ( atan ( beta_1 ))) * cos ( fabs ( atan ( beta_1 ))) * cos ( fabs ( atan ( beta_1 )));
    r = fabs ( SS_xy / sqrt ( SS_xx * SS_yy ) ) ;
    return ( beta_1 );
}

double linear_fit2 ( int point_number, double *x, double *y ) {
    int i = 0;
    double SS_xx = 0, SS_xy = 0;
    double sum_xx = 0, sum_xy = 0, sum_x = 0, sum_y = 0;
    double beta_0 = 0, beta_1 = 0;

    for ( i = 0; i < point_number; i++ ) {
        sum_x = sum_x + x[i];
    }
sum_y = sum_y + y[i];
sum_xy = sum_xy + x[i] * y[i];
sum_xx = sum_xx + x[i] * x[i];

SS_xy = sum_xy - (sum_x * sum_y) / point_number;
SS_xx = sum_xx - (sum_x * sum_x) / point_number;
beta_1 = SS_xy / SS_xx;
beta_0 = sum_y / point_number - beta_1 * sum_x / point_number;
return (beta_0);

double calSigma (double t2L, double t1L, double t2R, double t1R, double lensDia, double t12L, double t12R) {

double k;
double pi = 3.1415926;

theta1 = (fabs(atan(t1L)) + fabs(atan(t1R))) / 2.;
theta2 = pi - (fabs(atan(t2R)) + fabs(atan(t2L))) / 2.;
theta12 = (t12L + t12R) / 2.;
k = 2. / (lensDia * factor);
sigma = -(gamma1 * cos(theta1) + gamma2 * cos(theta2)) - sqrt((gamma1 * cos(theta1) + gamma2 * cos(theta2)) *(gamma1 * cos(theta1) + gamma2 * cos(theta2)) - (gamma1 + gamma2) * gamma2 + 2. * gamma1 * gamma2 * cos(theta12) - gamma12 * gamma12);  
sigma = sigma / k;
return (sigma);
}
#include <stdio.h>
#include <stdlib.h>
#include <ctype.h>
#include <math.h>
#include "flt.maxd.h"

void printHeads ( FILE *outFile, char *plotFile );

void main ( int argc, char *argv[] ) {

    int direction = 0; /*direction = 0 for left side, = 1 for right side*/
    int j;
    int fineNumP_L_init, fitNumP_L_init;
    int fineNumP_R_init, fitNumP_R_init;
    int fitNumP_delta, fineNumP_delta;
    int maxRuns;
    char out[50], in[50];
    FILE *outFile;

    if ( inFile = fopen ( argv[1], "r" ) ) == NULL ) {
        printf ( "\nEnter input file name:\n" );
        scanf ( "%s", in );
        inFile = fopen ( in, "r" );
    }

    printf ( "Enter no. of takeoff points:\n" );
    scanf ( "%d", &takeoff_point );

    printf ( "Enter output file name:\n" );
    scanf ( "%s", out );
    outFile = fopen ( out, "w+" );

    rewind ( outFile );

    fscanf ( inFile, "%lf%lf%lf%lf", &gamma1, &gamma2, &gamma12, &factor );
    fscanf ( inFile, "%lf%lf", &cut_left_y, &cut_right_y );
    fscanf ( inFile, "%d%d", &fineNumP_L_init, &fitNumP_L_init );
    fscanf ( inFile, "%d%d", &fineNumP_R_init, &fitNumP_R_init );
    fscanf ( inFile, "%d%d", &fineNumP_delta, &fitNumP_delta );
    fscanf ( inFile, "%d", &maxRuns );
    fscanf ( inFile, "%s", plotFile );
printHeads ( outFile, plotFile );
while ( !feof ( inFile ) ) {
    for ( j = 0; j < maxRuns; j++ ) {
        fitNumP_L = fitNumP_L_ini + fitNumP_delta * j;
        fineNumP_L = fineNumP_L_ini + fineNumP_delta * j;
        fitNumP_R = fitNumP_R_ini + fitNumP_delta * j;
        fineNumP_R = fineNumP_R_ini + fineNumP_delta * j;
        direction = 0;
        detect_point ( plotFile, direction );
        direction = 1;
        detect_point ( plotFile, direction );
        printf ( "run\%s\step \%d\n", plotFile, j );

        fprintf ( outFile, "%.3d %.3d %.3d %.3d ", fitNumP_L, fineNumP_L,
        fitNumP_R, fineNumP_R );
        fprintf ( outFile, "%lf ", sigma * 1000. );
        fprintf ( outFile, "%lf ", lensDia * factor * 1000. );
        fprintf ( outFile, "%lf ", theta1 * 180. / 3.1415926 );
        fprintf ( outFile, "%lf ", deltaL * 180. / 3.1415926 );
        fprintf ( outFile, "%lf ", rL );
        fprintf ( outFile, "%lf ", 180. - theta2 * 180. / 3.1415926 );
        fprintf ( outFile, "%lf ", deltaR * 180. / 3.1415926 );
        fprintf ( outFile, "%lf\n", rR );
    }

    fscanf ( inFile, "%s", plotFile );
}

fclose ( inFile );
fclose ( outFile );

void printHeads ( FILE *outFile, char *plotFile ) {

    fprintf ( outFile, "Using:\%s\n", plotFile );
    fprintf ( outFile, "Fit/Fine Sigma Diameter" );
    fprintf ( outFile, " Theta1 Error1 r1 Theta2" );
    fprintf ( outFile, " Error2 r2\n" );
    fprintf ( outFile, "Left Right (micro/m) (mm)" );
    fprintf ( outFile, " (deg) (deg) (deg)" );
    fprintf ( outFile, " (deg)\n" );
    fprintf ( outFile, "------------------------" );
    fprintf ( outFile, "------------------------" );
}
fprintf ( outFile, "------------------\n" );
C.3 Program III: LT.MinA

**Background:** This program is designed for analysing a series of images after the optimum number of fitting points is determined from Sections C.1 and C.2. This program outputs line tension, diameter and contact angle values for the liquid lens system under study. Hence, the prefix LT, or Line Tension, is used in the program name. Since the program uses $D_{\text{min}}$, the lens size (distance between the intersection points) obtained by the minimum angle approach, the suffix MinA, or Minimum Angle, is used. The previous two programs, TLT.MinA and TLT.MaxD, were designed only for testing of the linear curve-fitting and hence used only one image profile when varying the number of fitting points. This program is the full-fledged version and is used to analyse multiple images with a fixed number of fitting points.

As an example, a typical series of images were analysed. The profiles were obtained as outlined in Section 5.1.3, and this program was run. A typical image from the series, a truncated profile file of that image, and the input and output files are shown in Figs. C-1, C-2, C-6 and C-7, respectively.

**Usage:** In order to run TLT.MinA, an input file containing a number of parameters and the name of the profile to be analysed must be created. Figure C-6 shows an example of a typical input file, and an explanation of each of the parameters is given below. To run the program, enter:

```
tension% ~> lt.mina
```
Fig. C-6  Example of a typical input file for LT.MinA or LT.MaxD. This is the input file used in the sample analysis.

Filename:  input
Fig. C-7  Example of a typical output file for LT.MinA. These are the results of the sample analysis.

Filename: output
at the prompt. The program will then prompt the user for the input file:

\[\text{Enter input file name: input}\]

followed by the number of points to remove around the intersection, in order to reduce the effect of noise around the intersection:

\[\text{Enter no. of takeoff points: 3}\]

Finally the program will prompt the user for the name of the file to write the output to:

\[\text{Enter output file name: output}\]

**The Input File:** The input file (Fig. C-6) consists of the parameters that the program needs for the calculation of line tension. The layout is shown below:

- **line 1:** surface tension of liquid 1 (lens), \(\gamma_1\) (mJ/m\(^2\))
- **line 2:** surface tension of liquid 2 (surface), \(\gamma_2\) (mJ/m\(^2\))
- **line 3:** interfacial tension of liquids 1 and 2, \(\gamma_{12}\) (mJ/m\(^2\))
- **line 4:** scaling or magnification factor, (m/pixel)
- **line 5:** y-coordinate of left cut-off point
- **line 6:** y-coordinate of right cut-off point
Line 7: # of finetuning points on the left side of the lens profile
Line 8: # of linear fitting points on the left side of the lens profile
Line 9: # of finetuning points on the right side of the lens profile
Line 10: # of linear fitting points on the right side of the lens profile
Line 11: filename of the image profile to be analysed
Line 12: filename of next image

Lines 1, 2 and 3 are the surface tension values needed by the Quadrilateral Relation. Line 4 relates the pixel size to the lens' real size and is obtained through calibration of the microscope and the CCD camera used in the experiment. Lines 5 and 6 specify the upper extent of the lens for the left and right sides, respectively; any part of the profile above this cutoff is considered as part of the needle and is not analysed. Line 7 specifies the number of points used to finetune the location of the left intersection point, or the range which the finetuning test sweeps through to determine the point associated with the minimum angle. Line 8 specifies the number of fitting points to be used in order to obtain the "tangent" angles $\theta_1$ and $\theta_2$ on the left side of the lens. Lines 9 and 10 are the same as lines 7 and 8, but for the right side. Lines 11, 12, and higher are used to specify the image profiles to be analysed.

**The Output File:** The output file (Fig. C-7) is a table of information. Columns 1 shows the image profile name. Columns 2 and 3 display the line tension ($\mu$J/m) and the diameter (mm), respectively. Columns 4, 5 and 6 show $\theta_1$ (deg), the error of $\theta_1$ (deg) and the corresponding correlation coefficient in the linear curve fit for finding $\theta_1$, respectively. Columns 7, 8, and 9
display the same information for $\theta_2$.

The chart at the top of the table (Fig. C-7) shows the number of points used in the fitting and finetuning processes for the left and right sides. The finetuning numbers show the range, through which the minimum angle test was applied, centering on the intersection point as determined initially by the maximum distance approach. Hence, for both the left and right sides, a point, $A$, was chosen using the maximum distance test. Then, 10 points each flanking that determined point (Fig. 5-5) were selected. The minimum angle test was then applied, sweeping through all the points in that range.

*The Computer Codes in C Language:*
typedef double * float_array;

/* INPUT DATA */
int fitNumP_L, fineNumP_L, fitNumP_R, fineNumP_R;
int takeoff_point;
double gamma1, gamma2, gamma12;
double factor;
double cut_left_y, cut_right_y;

/* OUTPUT DATA */
double theta1, theta2, theta12;
double sigma, lensDia;
double deltaL, deltaR, delta, rL, rR, r;

/* INPUT FILE VARIABLES */
int count, i;
char plotFile[20];
FILE *inFile;

/* FUNCTIONS */
double calSigma ( double t2L, double t1L, double t2R, double t1R, double lensDia,
                 double t12L, double t12R );
double linear_fit ( int point_number, double *x, double *y );
double linear_fit2 ( int point_number, double *x, double *y );

void detect_point ( char plotFile[20], int direction ) {

    FILE *data;
    char temp2;
    int numPoints = 0;
    int max_i = 0, left_max_i = 0, right_max_i = 0;
    int count = 0, temp = 0;
    int i = 0, j = 0, j1, j2, end = 0;
    int cut_left_index, cut_right_index, check = 0, point_begin;
    int min_left_i, min_right_i, down_begin, up_begin, center_point;
    double rLineX1 = 0, rLineY1 = 0, rLineX2 = 0, rLineY2 = 0;
    double X = 0, Y = 0;
    double tg_slope = 0, sin_slope = 0, cos_slope = 0;
    double L_down_up = 0, distance = 0;
double left_max_x = 0, left_max_y = 0, right_max_x = 0, right_max_y = 0, max = 0;
double t12Lmin, t12Rmin;
double xconPointL, yconPointL, xconPointR, yconPointR;
double t12L, t12R;
double lensTilt;
double down_beta, up_beta, down_beta_0, up_beta_0;
double t2L, t1L, t2R, t1R;
double fit_rLineX1[50], fit_rLineY1[50], fit_rLineX2[50], fit_rLineY2[50];
float_array x_coord, y_coord;

numPoints = 0;
data = fopen (plotFile, "rt");

if (data == NULL) {
    printf ("Failure to open: %s\n", plotFile);
    exit (1);
};

if (direction == 0) {
    do {
        fscanf (data, "%c", &temp2);
        if (temp2 == '#')
            count = count + 1;
    } while (count < 3);

    fscanf (data, "%d", &numPoints);

    do {
        fscanf (data, "%c", &temp2);
    } while (temp2 != '\n');

    temp = 0;
    x_coord = (double *) malloc (numPoints, sizeof (double));
    y_coord = (double *) malloc (numPoints, sizeof (double));
    fscanf (data, "%lf%lf", &x_coord[temp], &y_coord[temp]);
    check = 1;
do {
    temp = temp + 1;
    fscanf ( data, "%lf%lf", &x_coord[temp], &y_coord[temp] );
    if ( y_coord[temp] > cut_left_y ) {
        if ( check == 1 ) {
            cut_left_index = temp;
            check = -1;
        }
    }
} while ( temp <= ( numPoints - 1 ) );

point_begin = cut_left_index;
fclose ( data );
} else if ( direction == 1 ) {
    do {
        fscanf ( data, "%c", &temp2 );
        if ( temp2 == '#' )
            count = count + 1;
    } while ( count < 5 );

    fscanf ( data, "%d", &numPoints );
    temp = 0;

do {
    fscanf ( data, "%c", &temp2 );
} while ( temp2 != '\n' );

x_coord = ( double * ) calloc ( numPoints, sizeof ( double ) );
y_coord = ( double * ) calloc ( numPoints, sizeof ( double ) );
fscanf ( data, "%lf%lf", &x_coord[temp], &y_coord[temp] );
check = 1;

do {
    temp = temp + 1;
    fscanf ( data, "%lf%lf", &x_coord[temp], &y_coord[temp] );

    if ( y_coord[temp] > cut_right_y ) {
        if ( check == 1 ) {
cut_right_index = temp;
check = -1;
}
}
} while ( temp <= ( numPoints - 1 ) );

point_begin = cut_right_index;
fclose ( data );

/* FIND MAXIMUM DISTANCE POINT */
rLineY1 = y_coord[numPoints - 1];
rLineX1 = x_coord[numPoints - 1];
rLineY2 = y_coord[point_begin];
rLineX2 = x_coord[point_begin];
L_down_up = sqrt ( pow ( ( rLineY1 - rLineY2 ), 2 ) +
               pow ( ( rLineX1 - rLineX2 ), 2 ) );
tg_slope = ( rLineY1 - rLineY2 ) / ( rLineX1 - rLineX2 );
sin_slope = fabs ( ( rLineY1 - rLineY2 ) ) / L_down_up;
cos_slope = fabs ( ( rLineX1 - rLineX2 ) ) / L_down_up;
max = 0;
max_i = 0;
distance = 0;

for ( i = point_begin; i < numPoints; i++ ) {
    X = fabs ( x_coord[i] - rLineX1 );
    Y = fabs ( y_coord[i] - rLineY1 );
    distance = ( X + ( Y * tg_slope ) ) * sin_slope - Y / cos_slope;

    if ( distance > max ) {
        max = distance;
        max_i = i;
    }
}

if ( direction == 0 ) {
    left_max_x = x_coord[max_i];
    left_max_y = y_coord[max_i];
    left_max_i = max_i;
}

if ( direction == 1 ) {
    right_max_x = x_coord[max_i];
right_max_y = y_coord[max_i];
right_max_i = max_i;

/* FIND LEFT SIDE MINIMUM ANGLE */
if ( direction == 0 ) {
    t12Lmin = 3.1415926;
    center_point = left_max_i;

    for ( i = 0; i <= fineNumP_L; i++ ) {
        down_begin = center_point + fineNumP_L / 2 - i;
        up_begin = down_begin;

        for ( j = 0; j < fitNumP_L; j++ ) {
            j1 = down_begin + j;
            j2 = up_begin - j;
            fit_rLineX1[j] = x_coord[j1];
            fit_rLineY1[j] = y_coord[j1];
            fit_rLineX2[j] = x_coord[j2];
            fit_rLineY2[j] = y_coord[j2];
        }
    }

    down_beta = linear_fit ( fitNumP_L, fit_rLineX1, fit_rLineY1 );
    up_beta = linear_fit ( fitNumP_L, fit_rLineX2, fit_rLineY2 );
    t12L = fabs ( atan ( down_beta ) ) + 3.1415926 - fabs ( atan ( up_beta ) );

    if ( t12L < t12Lmin ) {
        t12Lmin = t12L;
        min_left_i = down_begin;
    }
}

/* FIND LEFT CONTACT POINT */
for ( j = 0; j < fitNumP_L; j++ ) {
    j1 = min_left_i + j + takeoff_point;
    j2 = min_left_i - j - takeoff_point;
    fit_rLineX1[j] = x_coord[j1];
    fit_rLineY1[j] = y_coord[j1];
    fit_rLineX2[j] = x_coord[j2];
fit_rLineY2[j] = y_coord[j2];
}

t2L = linear_fit ( fitNumP_L, fit_rLineX1, fit_rLineY1 );
t1L = linear_fit ( fitNumP_L, fit_rLineX2, fit_rLineY2 );
down_beta_0 = linear_fit2 ( fitNumP_L, fit_rLineX1, fit_rLineY1 );
up_beta_0 = linear_fit2 ( fitNumP_L, fit_rLineX2, fit_rLineY2 );
xconPointL = ( down_beta_0 - up_beta_0 ) / ( t1L - t2L );
yconPointL = down_beta_0 + t2L * xconPointL;
t12L = fabs ( atan ( t2L ) ) + 3.1415926 - fabs ( atan ( t1L ) );
deltaL = delta;
rL = r;
}

/* FIND RIGHT SIDE MINIMUM ANGLE */
if ( direction == 1 ) {
    t12Rmin = 3.14159;
    center_point = right_max_i;

    for ( i = 0; i <= fineNumP_R; i++ ) {
        down_begin = center_point + fineNumP_R / 2 - i;
        up_begin = down_begin;

        for ( j = 0; j < fitNumP_R; j++ ) {
            j1 = down_begin + j;
            j2 = up_begin - j;
            fit_rLineX1[j] = x_coord[j1];
            fit_rLineY1[j] = y_coord[j1];
            fit_rLineX2[j] = x_coord[j2];
            fit_rLineY2[j] = y_coord[j2];
        }

        down_beta = linear_fit ( fitNumP_R, fit_rLineX1, fit_rLineY1 );
        up_beta = linear_fit ( fitNumP_R, fit_rLineX2, fit_rLineY2 );
        t12R = fabs ( atan ( down_beta ) ) + 3.1415926 - fabs ( atan ( up_beta ) );

        if ( t12R < t12Rmin ) {
            t12Rmin = t12R;
            min_right_i = down_begin;
        }
    }
}

/* FIND RIGHT CONTACT POINT */
for ( j = 0; j < fitNumP_R; j++ ) {
    j1 = min_right_i + j + takeoff_point;
    j2 = min_right_i - j - takeoff_point;
    fit_rLineX1[j] = x_coord[j1];
    fit_rLineY1[j] = y_coord[j1];
    fit_rLineX2[j] = x_coord[j2];
    fit_rLineY2[j] = y_coord[j2];
}

\[ t2R = \text{linear}\_\text{fit}( \text{fitNumP}\_R, \text{fit}\_\text{rLineX1}, \text{fit}\_\text{rLineY1} ) ; \]
\[ t1R = \text{linear}\_\text{fit}( \text{fitNumP}\_R, \text{fit}\_\text{rLineX2}, \text{fit}\_\text{rLineY2} ) ; \]
\[ \text{down}_\beta_0 = \text{linear}\_\text{fit2}( \text{fitNumP}\_R, \text{fit}\_\text{rLineX1}, \text{fit}\_\text{rLineY1} ) ; \]
\[ \text{up}_\beta_0 = \text{linear}\_\text{fit2}( \text{fitNumP}\_R, \text{fit}\_\text{rLineX2}, \text{fit}\_\text{rLineY2} ) ; \]
\[ \text{xconPointR} = ( \text{down}_\beta_0 - \text{up}_\beta_0 ) / ( t1R - t2R ) ; \]
\[ \text{yconPointR} = \text{down}_\beta_0 + t2R * \text{xconPointR} ; \]
\[ t12R = \text{fabs}( \text{atan}( t2R ) ) + 3.1415926 - \text{fabs}( \text{atan}( t1R ) ) ; \]

\[ \text{deltaR} = \text{delta} ; \]
\[ rR = r; \]

/* CALCULATE LENS DIAMETER */
if ( \text{direction} == 1 ) {
    \text{lensDia} = \sqrt( \text{pow}( ( \text{xconPointL} - \text{xconPointR} ), 2 ) + \text{pow}( ( \text{yconPointL} - \text{yconPointR} ), 2 ) ) ; \]
    \text{lensTilt} = ( \text{yconPointL} - \text{yconPointR} ) / ( \text{xconPointL} - \text{xconPointR} ) ;
}

/* CALCULATE LINE TENSION */
if ( \text{direction} == 1 ) {
    \text{if} ( \text{fabs}( t12L - t12R ) < 5. * 3.1415926/180. ) { \text{sigma} = \text{calSigma}( \text{t2L}, \text{t1L}, \text{t2R}, \text{t1R}, \text{lensDia}, \text{t12L}, \text{t12R} ) ; \}
    \text{else} { \text{fprintf}( \text{inFile}, "\text{ABS}(\text{Theta}12\_L - \text{Theta}12\_R) > 5 \text{ deg.}" ); \text{fprintf}( \text{inFile}, "\text{The image is ignored.\n"}, \text{plotFile} ); \}
}

\text{free}( \text{x\_coord} );
\text{free}( \text{y\_coord} );
double Linearfit (int point_number, double *x, double *y) {
    int i = 0;
    double SS_xx = 0, SS_xy = 0, SS_yy = 0, SSE;
    double sum_xx = 0, sum_xy = 0, sum_x = 0, sum_y = 0, sum_yy = 0;
    double beta_0 = 0, beta_1 = 0;
    double s, s_beta, ta;

    for (i = 0; i < point_number; i++) {
        sum_x = sum_x + x[i];
        sum_y = sum_y + y[i];
        sum_xy = sum_xy + x[i] * y[i];
        sum_xx = sum_xx + x[i] * x[i];
        sum_yy = sum_yy + y[i] * y[i];
    }

    SS_xy = sum_xy - (sum_x * sum_y) / point_number;
    SS_xx = sum_xx - (sum_x * sum_x) / point_number;
    SS_yy = sum_yy - (sum_y * sum_y) / point_number;
    beta_1 = SS_yy / SS_xx;
    SSE = SS_yy - beta_1 * SS_xy;
    s = sqrt (SSE / (point_number - 2));
    s_beta = s / sqrt (SS_xx);
    ta = 1.96;
    delta = ta * s_beta * cos (fabs (atan (beta_1))) * cos (fabs (atan (beta_1)));
    r = fabs (SS_xy / sqrt (SS_xx * SS_yy));
    return (beta_1);
}

double linear_fit2 (int point_number, double *x, double *y) {
    int i = 0;
    double SS_xx = 0, SS_xy = 0;
    double sum_xx = 0, sum_xy = 0, sum_x = 0, sum_y = 0;
    double beta_0 = 0, beta_1 = 0;

    for (i = 0; i < point_number; i++) {
        sum_x = sum_x + x[i];
        sum_y = sum_y + y[i];
        sum_xy = sum_xy + x[i] * y[i];
        sum_xx = sum_xx + x[i] * x[i];
    }
\[
SS_{xy} = \sum_{xy} - \left( \sum_x \times \sum_y \right) / \text{point\_number};
\]
\[
SS_{xx} = \sum_{xx} - \left( \sum_x \times \sum_x \right) / \text{point\_number};
\]
\[
\beta_1 = SS_{xy} / SS_{xx};
\]
\[
\beta_0 = \sum_y / \text{point\_number} - \beta_1 \times \sum_x / \text{point\_number};
\]
return ( \beta_0 );

double calSigma ( double t2L, double t1L, double t2R, double t1R, double lensDia, double t12L, double t12R ) {

double k;

double pi = 3.1415926;

theta1 = ( fabs ( atan ( t1L ) ) + fabs ( atan ( t1R ) ) ) / 2.;
theta2 = pi - ( fabs ( atan ( t2R ) ) + fabs ( atan ( t2L ) ) ) / 2.;
theta12 = ( t12L + t12R ) / 2.;
k = 2. / ( lensDia * factor );

sigma = - ( gamma1 * cos ( theta1 ) + gamma2 * cos ( theta2 ) ) - sqrt ( ( gamma1 * cos ( theta1 ) + gamma2 * cos ( theta2 ) ) * ( gamma1 * cos ( theta1 ) + gamma2 * cos ( theta2 ) ) - ( gamma1 * gamma1 + gamma2 * gamma2 + 2. * gamma1 * gamma2 * cos ( theta12 ) - gamma12 * gamma12 ) );

sigma = sigma / k;
return ( sigma );
}
#include <stdio.h>
#include <stdlib.h>
#include <string.h>
#include <ctype.h>
#include <math.h>
#include "lt.mina.h"

void printHeads ( FILE *outFile, char *plotFile );

void main( int argc, char *argv[] ) { 

    int direction = 0; /*direction = 0 for left side, = 1 for right side*/ 
    char out[50], in[50]; 
    FILE *outFile;

    if ( ( inFile = fopen ( argv[1], "r" ) ) == NULL ) { 
        printf ( "Enter input file name:  
        scanf ( "%s", in ); 
        inFile = fopen ( in, "r" ); 
    }

    printf ( "Enter no. of takeoff points:  
    scanf ( "%d", &takeoff_point );

    printf ( "Enter output file name:  
    scanf ( "%s", out ); 
    outFile = fopen ( out, "w+" );

    rewind ( outFile );

    fscanf ( inFile, "%lf%lf%lf%lf", &gammal, &gamma2, &gammal2, &factor );
    fscanf ( inFile, "%lf%lf", &cut_left_y, &cut_right_y );
    fscanf ( inFile, "%d%d", &fineNumP_L, &fitNumP_L );
    fscanf ( inFile, "%d%d", &fineNumP_R, &fitNumP_R );
    fscanf ( inFile, "%s", plotFile );

    printHeads ( outFile, plotFile );

    while ( !feof ( inFile ) ) { 
        printf ( "Analysing:  
        direction = 0;
        detect_point ( plotFile, direction );
        direction = 1;
        detect_point ( plotFile, direction );
fprintf ( outFile, "\s", plotFile );
fprintf ( outFile, "\f", sigma * 1000 );
fprintf ( outFile, "\lf", lensDia * factor * 1000. );
fprintf ( outFile, "\lf", theta1 * 180. / 3.1415926 );
fprintf ( outFile, "\lf", deltaL * 180. / 3.1415926 );
fprintf ( outFile, "\lf", rL );
fprintf ( outFile, "\lf", 180. - theta2 * 180. / 3.1415926 );
fprintf ( outFile, "\lf", deltaR * 180. / 3.1415926 );
fprintf ( outFile, "\lf", rR );
fclose ( inFile );
fclose ( outFile );
}

void printHeads ( FILE *outFile, char *plotFile ) {

    fprintf ( outFile, "\s\n" );
    fprintf ( outFile, "\f\n" );
    fprintf ( outFile, "-------------------\n" );
    fprintf ( outFile, "Left\%d\%d\%d\n", fitNumP_L, fineNumP_L );
    fprintf ( outFile, "Right\%d\%d\%d\n", fitNumP_R, fineNumP_R );
    fprintf ( outFile, "Filename Sigma Diameter\n" );
    fprintf ( outFile, "Theta1 Error1 r1 Theta2\n" );
    fprintf ( outFile, "Error2 r2\n" );
    fprintf ( outFile, "(microJ/m) (mm)\n" );
    fprintf ( outFile, "(deg) (deg) (deg)\n" );
    fprintf ( outFile, "\n" );
    fprintf ( outFile, "\n" );
    fprintf ( outFile, "-------------------\n" );
    fprintf ( outFile, "-------------------\n" );
    fprintf ( outFile, "-------------------------------\n" );
    fprintf ( outFile, "-------------------------------\n" );
    fprintf ( outFile, "------------------\n" );
    fprintf ( outFile, "\n" );
}
C.4 Program IV: LT.MaxD

**Background:** This program is similar to LT.MinA, except that instead of using $D_{\text{min}}$, the distance between the two intersection points detected using the minimum angle approach, it uses $D_{\text{max}}$, the points detected using the maximum diameter approach. Otherwise, the purposes and structure are the same as those in Section C.3.

This program, like LT.MinA, is the full-fledged version used in line tension analysis, and hence the prefix LT, or Line Tension, is used in the program name. Since this program uses $D_{\text{max}}$, the intersection points obtained by the maximum distance approach, in calculating the radius of curvature $\kappa$, the suffix MaxD, or maximum distance, is used in the program name.

As an example, a typical series of images were analysed. The profiles was obtained as outlined in Section 5.1.3, and this program was run. A typical image from the series, a truncated profile file of that image, and the input and output files, all needed to run the program, are shown in Figs. C-1, C-2, C-6 and C-8, respectively.

**Usage:** In order to run LT.MaxD, an input file containing a number of parameters and the name of the profile to be analysed must be created. The input file used is the same as that used for LT.MinA (Fig. C-7). To run the program, enter:

```
tension% -> lt.maxd
```
### Fig. C-8  Example of a typical output file for LT.MaxD

**Filename:** output
at the prompt. The rest of the procedure is the same as LT.MinA.

The Input File: The input file is the same in structure as that used in LT.MinA. An example is provided in Fig. C-6.

The Output File: The output file is a tabulation of information and is the same in structure as that produced by LT.MinA. However, since the detected intersection points will be different, the line tension values calculated will be different as well. Figure C-8 shows a typical output file from LT.MaxD using the same image and profile for analysis as LT.MinA. Note the differences between Figs. C-7 and C-8.

The Computer Codes in C Language:
typedef double * float_array;

/* INPUT DATA */
int fitNumP_L, fineNumP_L, fitNumP_R, fineNumP_R;
int takeoff_point;
double gamma1, gamma2, gamma12;
double factor;
double cut_left_y, cut_right_y;

/* OUTPUT DATA */
double theta1, theta2, theta12;
double sigma, lensDia;
double deltaL, deltaR, delta, rL, rR, r;

/* INPUT FILE VARIABLES */
int count, i;
char plotFile[20];
FILE *inFile;

/* FUNCTIONS */
double calSigma ( double t2L, double t1L, double t2R, double t1R, double lensDia,
                 double t12L, double t12R );
double linear_fit ( int point_number, double *x, double *y );
double linear_fit2 ( int point_number, double *x, double *y );

/****************************LT.MaxD*************************************************************/

void detect_point ( char plotFile[20], int direction ) {

    FILE *data;
    char temp2;
    int numPoints = 0;
    int max_i = 0, left_max_i = 0, right_max_i = 0;
    int count = 0, temp = 0;
    int i = 0, j = 0, j1, j2, end = 0;
    int cut_left_index, cut_right_index, check = 0, point_begin;
    int min_left_i, min_right_i, down_begin, up_begin, center_point;
    double rLineX1 = 0, rLineY1 = 0, rLineX2 = 0, rLineY2 = 0;
    double X = 0, Y = 0;
    double tg_slope = 0, sin_slope = 0, cos_slope = 0;
    double L_down_up = 0, distance = 0;
double left_max_x = 0, left_max_y = 0, right_max_x = 0, right_max_y = 0, max = 0;
double t12Lmin, t12Rmin;
double xconPointL, yconPointL, xconPointR, yconPointR;
double t12L, t12R;
double lensTilt;
double down_beta, up_beta, down_beta_0, up_beta_0;
double t2L, t1L, t2R, t1R;
double fit_rLineX1[150], fit_down_y[150], fit_up_x[150], fit_up_y[150];
double temp_change;
float_array x_coord, y_coord;

numPoints = 0;
data = fopen ( plotFile, "rt" );

if ( data == NULL ) {
    printf ( "Failure to open:\ %s\n", plotFile );
    exit ( 1 );
}

if ( direction == 0 ) {
    do {
        fscanf ( data, "%c", &temp2 );
        if ( temp2 == '#' )
            count = count + 1;
    } while ( count < 3 );

    fscanf ( data, "%d", &numPoints );

    do {
        fscanf ( data, "%c", &temp2 );
    } while ( temp2 != '\n' );

    temp = 0;
    x_coord = ( double * ) calloc ( numPoints, sizeof ( double ) );
    y_coord = ( double * ) calloc ( numPoints, sizeof ( double ) );
    fscanf ( data, "%lf%lf", &x_coord[temp], &y_coord[temp] );
    check = 1;
do {
    temp = temp + 1;
    fscanf ( data, "%lf%lf", &x_coord[temp], &y_coord[temp] );

    if ( y_coord[temp] > cut_left_y ) {
        if ( check == 1 ) {
            cut_left_index = temp;
            check = -1;
        }
    }
} while ( temp <= (numPoints - 1) );

point_begin = cut_left_index;
fclose ( data );
} else if ( direction == 1 ) {
    do {
        fscanf ( data, "%c", &temp2 );
        if ( temp2 == '#' )
            count = count + 1;
    } while ( count < 5 );

    fscanf ( data, "%d", &numPoints );
    temp = 0;

    do {
        fscanf ( data, "%c", &temp2 );
    } while ( temp2 != 'n' );

    x_coord = ( double * ) calloc ( numPoints, sizeof ( double ) );
    y_coord = ( double * ) calloc ( numPoints, sizeof ( double ) );
    fscanf ( data, "%lf%lf", &x_coord[temp], &y_coord[temp] );
    check = 1;

    do {
        temp = temp + 1;
        fscanf ( data, "%lf%lf", &x_coord[temp], &y_coord[temp] );

        if ( y_coord[temp] > cut_right_y ) {
            }
if ( check == 1 ) {
    cut_right_index = temp;
    check = -1;
}
}
} while ( temp <= ( numPoints - 1 ) );

point_begin = cut_right_index;
fclose ( data );
}

/* FIND MAXIMUM DISTANCE POINT */

rLineY1 = y_coord[numPoints - 1];
rLineX1 = x_coord[numPoints - 1];
rLineY2 = y_coord[point_begin];
rLineX2 = x_coord[point_begin];
L_down_up = sqrt ( pow ( ( rLineY1 - rLineY2 ), 2 ) +
        pow ( ( rLineX1 - rLineX2 ), 2 ) );
tg_slope = ( rLineY1 - rLineY2 ) / ( rLineX1 - rLineX2 );
sin_slope = fabs ( ( rLineY1 - rLineY2 ) ) / L_down_up;
cos_slope = fabs ( ( rLineX1 - rLineX2 ) ) / L_down_up;
max = 0;
max_i = 0;
distance = 0;

for ( i = point_begin; i < numPoints; i++ ) {
    X = fabs ( x_coord[i] - rLineX1 );
    Y = fabs ( y_coord[i] - rLineY1 );
    distance = ( X + ( Y * tg_slope ) ) * sin_slope - Y / cos_slope;

    if ( distance > max ) {
        max = distance;
        max_i = i;
    }
}

if ( direction == 0 ) {
    left_max_x = x_coord[max_i];
    left_max_y = y_coord[max_i];
    left_max_i = max_i;
}

if ( direction == 1 ) {
right_max_x = x_coord[max_i];
right_max_y = y_coord[max_i];
right_max_i = max_i;
}

/* FIND LEFT SIDE MINIMUM ANGLE */
if ( direction == 0 ) {
t12Lmin = 3.1415926;
center_point = left_max_i;

for ( i = 0; i <= fineNumP_L; i++ ) {
down_begin = center_point + fineNumP_L / 2 - i;
up_begin = down_begin;

for ( j = 0; j < fitNumP_L; j++ ) {
j1 = down_begin + j;
j2 = up_begin - j;
fit_rLineX1[j] = x_coord[j1];
fit_down_y[j] = y_coord[j1];
fit_up_x[j] = x_coord[j2];
fit_up_y[j] = y_coord[j2];
}
down_beta = linear_fit ( fitNumP_L, fit_rLineX1, fit_down_y );
up_beta = linear_fit ( fitNumP_L, fit_up_x, fit_up_y );
t12L = fabs ( atan ( down_beta ) ) + 3.1415926 - fabs ( atan ( up_beta ) );

if ( t12L < t12Lmin ) {
t12Lmin = t12L;
min_left_i = down_begin;
}
}

/* FIND LEFT CONTACT POINT */
for ( j = 0; j < fitNumP_L; j++ ) {
j1 = min_left_i + j + takeoff_point;
j2 = min_left_i - j - takeoff_point;
fit_rLineX1[j] = x_coord[j1];
fit_down_y[j] = y_coord[j1];
fit_up_x[j] = x_coord[j2];
fit_up_y[j] = y_coord[j2];
}

t2L = linear_fit ( fitNumP_L, fit_rLineX1, fit_down_y );
temp_change = t2L;
t1L = linear_fit ( fitNumP_L, fit_up_x, fit_up_y );
down_beta_0 = linear_fit2 ( fitNumP_L, fit_rLineX1, fit_down_y );
up_beta_0 = linear_fit2 ( fitNumP_L, fit_up_x, fit_up_y );
xconPointL = x_coord[left_max_i];
yconPointL = y_coord[left_max_i];
t12L = fabs ( atan ( t2L ) ) + 3.1415926 - fabs ( atan ( t1L ) );
deltaL = delta;
rL = r;
}

/* FIND RIGHT SIDE MINIMUM ANGLE */
if ( direction == 1 ) {
  t12Rmin = 3.14159;
  center_point = right_max_i;
  for ( i = 0; i <= fineNumP_R; i++ ) {
    down_begin = center_point + fineNumP_R / 2 - i;
    up_begin = down_begin;
    for ( j = 0; j < fitNumP_R; j++ ) {
      j1 = down_begin + j;
      j2 = up_begin - j;
      fit_rLineX1[j] = x_coord[j1];
      fit_down_y[j] = y_coord[j1];
      fit_up_x[j] = x_coord[j2];
      fit_up_y[j] = y_coord[j2];
    }
    down_beta = linear_fit ( fitNumP_R, fit_rLineX1, fit_down_y );
    up_beta = linear_fit ( fitNumP_R, fit_up_x, fit_up_y );
    t12R = fabs ( atan ( down_beta ) ) + 3.1415926 - fabs ( atan ( up_beta ) );
    if ( t12R < t12Rmin ) {
      t12Rmin = t12R;
      min_right_i = down_begin;
    }
  }
}
/* FIND RIGHT CONTACT POINT */
for ( j = 0; j < fitNumP_R; j++ ) {
    j1 = min_right_i + j + takeoff_point;
    j2 = min_right_i - j - takeoff_point;
    fit_rLineX1[j] = x_coord[j1];
    fit_down_y[j] = y_coord[j1];
    fit_up_x[j] = x_coord[j2];
    fit_up_y[j] = y_coord[j2];
}

t2R = linear_fit ( fitNumP_R, fit_rLineX1, fit_down_y );
t1R = linear_fit ( fitNumP_R, fit_up_x, fit_up_y );
down_beta_0 = linear_fit2 ( fitNumP_R, fit_rLineX1, fit_down_y );
up_beta_0 = linear_fit2 ( fitNumP_R, fit_up_x, fit_up_y );
xconPointR = x_coord[right_max_i];
yconPointR = y_coord[right_max_i];
t12R = fabs ( atan ( t2R ) ) + 3.1415926 - fabs ( atan ( t1R ) );
deltaR = delta;
rR = r;
}

/* CALCULATE LENS DIAMETER */
if ( direction == 1 ) {
    lensDia = sqrt ( pow ( ( xconPointL - xconPointR ), 2 ) +
                    pow ( ( yconPointL - yconPointR ), 2 ) );
    lensTilt = ( yconPointL - yconPointR ) / ( xconPointL - xconPointR );
}

/* CALCULATE LINE TENSION */
if ( direction == 1 ) {
    if ( fabs ( t12L - t12R ) < 5. * 3.1415926 / 180. ) {
        sigma = calSigma ( temp_change, t1L, t2R, t1R, lensDia, t12L, t12R );
    }
    else {
        fprintf ( inFile, "ABS(Theta12_L - Theta12_R) > 5 deg." );
        fprintf ( inFile, " The run is ignored.
" );
    }
}
free ( x_coord );
free ( y_coord );
int i = 0;
double SS_xx = 0, SS_xy = 0, SS_yy = 0, SSE = 0;
double sum_xx = 0, sum_xy = 0, sum_x = 0, sum_y = 0, sum_yy = 0;
double beta_0 = 0, beta_1 = 0;
double s = 0, s_beta = 0, ta = 0;

for ( i = 0; i < point_number; i++ ) {
    sum_x = sum_x + x[i];
    sum_y = sum_y + y[i];
    sum_xy = sum_xy + x[i] * y[i];
    sum_xx = sum_xx + x[i] * x[i];
    sum_yy = sum_yy + y[i] * y[i];
}

SS_xy = sum_xy - ( sum_x * sum_y ) / point_number;
SS_xx = sum_xx - ( sum_x * sum_x ) / point_number;
SS_yy = sum_yy - ( sum_y * sum_y ) / point_number;
beta_1 = SS_xy / SS_xx;
SSE = SS_yy - beta_1 * SS_xy;
s = sqrt(SSE / ( point_number - 2 ));
s_beta = s / sqrt(SS_xx);
ta = 1.96;
delta = ta * s_beta * cos(fabs(atan(beta_1))) * cos(fabs(atan(beta_1)));
r = fabs(SS_xy / sqrt(SS_xx * SS_yy));
return (beta_1);

double linear_fit2 ( int point_number, double *x, double *y ) {
    int i = 0;
    double SS_xx = 0, SS_xy = 0;
    double sum_xx = 0, sum_xy = 0, sum_x = 0, sum_y = 0;
    double beta_0 = 0, beta_1 = 0;

    for ( i = 0; i < point_number; i++ ) {
        sum_x = sum_x + x[i];
    }
sum_y = sum_y + y[i];
sum_xy = sum_xy + x[i] * y[i];
sum_xx = sum_xx + x[i] * x[i];
}

SS_xy = sum_xy - ( sum_x * sum_y )/ point_number;
SS_xx = sum_xx - ( sum_x * sum_x )/ point_number;
beta_1 = SS_xy / SS_xx;
beta_0 = sum_y / point_number - beta_1 * sum_x / point_number;
return ( beta_0 );
}

double calSigma ( double t2L, double t1L, double t2R, double t1R, double lensDia, double t12L, double t12R) {

double k;
double pi = 3.1415926;

theta1 = ( fabs ( atan ( t1L ) ) + fabs ( atan ( t1R ) ) ) / 2.;
theta2 = pi - ( fabs ( atan ( t2R ) ) + fabs ( atan ( t2L ) ) ) / 2.;
theta12 = ( t12L + t12R ) / 2.;
k = 2. / ( lensDia * factor );
sigma = - ( gamma1 * cos ( theta1 ) + gamma2 * cos ( theta2 ) ) - sqrt ( ( gamma1 * cos ( theta1 ) + gamma2 * cos ( theta2 ) ) * ( gamma1 * cos ( theta1 ) + gamma2 * cos ( theta2 ) ) - ( gamma1 * gamma1 + gamma2 * gamma2 ) - 2. * gamma1 * gamma2 * cos ( theta12 ) - gamma12 * gamma12 ) );
sigma = sigma / k;
return ( sigma );
}
#include <stdio.h>
#include <stdlib.h>
#include <ctype.h>
#include <math.h>
#include "lt.maxd.h"

void printHeads ( FILE *outFile, char *plotFile );

void main( int argc, char *argv[] ) {

    int direction = 0; /*direction = 0 for left side, = 1 for right side*/
    char out[50], in[50];
    FILE *outFile;

    if ( ( inFile = fopen ( argv[1], "r" ) ) == NULL ) {
        printf ( "Enter input file name:\n" );
        scanf ( "%s", in );
        inFile = fopen ( in, "r" );
    }

    printf ( "Enter no. of takeoff points:\n" );
    scanf ( "%d", &takeoff_point );

    printf ( "Enter output file name:\n" );
    scanf ( "%s", out );
    outFile = fopen ( out, "w+" );

    rewind ( outFile );

    fscanf ( inFile, "%lf%lf%lf%lf", &gamma1, &gamma2, &gamma12, &factor );
    fscanf ( inFile, "%lf%lf", &cut_left_y, &cut_right_y );
    fscanf ( inFile, "%d%d", &fineNumP_L, &fitNumP_L );
    fscanf ( inFile, "%d%d", &fineNumP_R, &fitNumP_R );
    fscanf ( inFile, "%s", plotFile );

    printHeads ( outFile, plotFile );

    while ( !feof ( inFile ) ) {
        printf ( "Analysing:\n", plotFile );
        direction = 0;
        detect_point ( plotFile, direction );
        direction = 1;
        detect_point ( plotFile, direction );
    }

}
void printHeads ( FILE *outFile, char *plotFile ) {

    fprintf ( outFile, "Points\n" );
    fprintf ( outFile, "\tFitting\tFinetuning\n" );
    fprintf ( outFile, "------------------\n" );
    fprintf ( outFile, "Left\%.3f\%.3d\n", fitNumP_L, fineNumP_L );
    fprintf ( outFile, "Right\%.3f\%.3d\n", fitNumP_R, fineNumP_R );
    fprintf ( outFile, "Filename Sigma Diameter" );
    fprintf ( outFile, "Theta 1  Error 1  r 1  Theta 2" );
    fprintf ( outFile, " Error 2  r 2\n" );
    fprintf ( outFile, " (microJ/m)  (mm)" );
    fprintf ( outFile, " (deg)  (deg)  (deg)" );
    fprintf ( outFile, " (deg)\n" );
    fprintf ( outFile, "------------------------" );
    fprintf ( outFile, "------------------------" );
    fprintf ( outFile, "\n" );
}

fprintf ( outFile, "%s \", plotFile );
fprintf ( outFile, "%lf \", sigma * 1000 );
fprintf ( outFile, "%.lf \", lensDia * factor * 1000. );
fprintf ( outFile, "%.lf \", theta1 * 180. / 3.1415926 );
fprintf ( outFile, "%.lf \", deltaL * 180. / 3.1415926 );
fprintf ( outFile, "%.lf \", rL );
fprintf ( outFile, "%lf\n", rR );
fclose ( inFile );
fclose ( outFile );

Appendix D. Film Tension Measurements

This appendix reviews experimental techniques for measuring film tension; in particular, Axisymmetric Drop Shape Analysis - Profile (ADSA-P) is introduced. ADSA-P is the only existing technique which is not restricted to spherical drops or bubbles for measuring film tension. With ADSA-P, film tension can be measured under both static and dynamic conditions. As a demonstration of ADSA-P, film tension and film rupture of alkanes (hexadecane, tetradecane, and dodecane) at the air-water interface are presented. The film tension measured is found to be equal to the sum of alkane-water interfacial tension and alkane surface tension for hexadecane and tetradecane films. In the case of dodecane films, a slight difference between the film tension and the sum of two surface (interfacial) tensions is observed and can be attributed to the interactions between the two surfaces of the film, which may be quantified by disjoining pressure. An important three-phase contact line configuration is observed after “film rupture.” This may allow for a new line tension measurement.

D.1 Background

Compared to the number of techniques for measuring interfacial tension [90], only a small number of methods [126-135] have been developed for measuring film tension. All of these approaches make use of a spherical drop or bubble and relate the simple geometric
parameters of the sphere to the Laplace equation of capillarity to calculate film tension. Platikanov et al. [131,133] reported an experimental method for direct measurement of the film tension of black foam films. Their foam films are obtained in the form of a spherical semi-bubble, whose radius of curvature is determined from microphotographs and the capillary pressure is measured by a manometer. The film tension is calculated from the data obtained by using the Laplace equation of capillarity. This method is applied only to foam films which are bounded by two adjacent gaseous phases. When one of the two bounding phases is liquid, the assumption of the spherical semi-bubble may not be valid because of the effect of gravity.

Another method for measuring film tension that has since emerged is that of Wasan et al. [134-136]. This method is not restricted to foam films; the bounding phases can also be liquid. In the experiment, a single liquid drop coated with a film is formed at the tip of a capillary, and the capillary pressure in the drop is measured. The film tension is calculated from the capillary pressure and the film radius of curvature by using the Laplace equation of capillarity. A necessary condition for use of this method is that the drop supporting the film be spherical in shape. This requires the Eötvös number [134,137,138] to be below 0.02, which may be accomplished by using a narrow capillary so that the effect of gravity will be negligible. In addition, to obtain sufficient stability of the film with this method, special care has to be taken in the capillary design [134,135].

Recently, a new method [125] was developed, which is based on Axisymmetric Drop Shape Analysis (ADSA) [105,114,115] for measuring film tension. This technique only requires that the drop shape be axisymmetric, while the bounding phase may be either liquid
or gas. In addition to film tension, drop or bubble volume, surface area and the radius of curvature at the drop apex are also obtained as the output of ADSA. It has been demonstrated that this method can be used for measuring film tension under both static and dynamic experimental conditions. The following sections describe this technique with an example of application to alkane films at the air-water interface.

D.2 Experimental

The hardware design for film tension measurement is identical to that for interfacial tension [105,114,115]. The only difference is in the procedure of sample arrangement. The liquid films used to demonstrate the measurement are those of alkanes at the air-water interface.

D.2.1 Materials

The three alkanes used were hexadecane, tetradecane, and dodecane, all of which were obtained from Aldrich Chemical Company, Inc., USA, with a purity of 99+. The water used was distilled; its purity was checked by the surface tension measurement which, at 25 ± 0.2°C, resulted in 72.14 ± 0.04 mJ/m² at the 95% confidence level, compared well to the standard water surface tension reported in the literature. In the film tension experiment, an alkane film was formed at the air-water interface (see below); therefore, slight mutual dissolution would necessarily occur between the contacting alkane and water. To eliminate
such a non-equilibrium process during the measurement, the alkane and water were pre-saturated with each other for at least 12 hours.

D.2.2 Sample Preparation and Experimental Procedure

To maintain mutual saturation between alkane and water during the experiment, a special set-up was used in the sample arrangement (Fig. D-1). Both alkane and water were contained in a quartz cuvette (Hellma 330984, 20×50×80 mm³), where a Teflon tube (capillary) of circular cross-section (outer diameter 1.6 mm, inner diameter 1.0 mm) held inside a “J”-shaped stainless steel tube was inserted into the water phase initially. To ensure that a small amount of alkane adhered to the tip of the Teflon tube, the capillary was then raised up into the alkane phase by a micro-manipulator positioned above the cuvette. Using a micro-syringe connected to the other end of the capillary, a minute amount of alkane was withdrawn into the capillary. Then, the capillary was lowered into the water phase again. Finally, an air bubble was formed at the tip of the capillary by pumping air through the capillary slowly, in the process creating an alkane film on the air bubble.

It should be possible for an alkane film to be broken by certain mechanical or thermal disturbances when it becomes sufficiently thin. Once the film ruptures, the surface under observation will be that of the air-water interface, and the shape of the air bubble will be
Fig. D-1  Experimental set-up for film tension measurements. To form a film, the capillary is raised up into the alkane phase by a micromanipulator positioned above the cuvette (step 1 to step 2). Then, using a micro-syringe connected to the other end of the capillary, a minute amount of alkane is withdrawn into the capillary (step 2). Finally, the capillary is lowered down into the water phase, and an air bubble coated with an alkane film is formed at the tip of the capillary by pumping air through the tube slowly (step 3).
determined by the interfacial tension of air-water in conjunction with gravity. Thus, after film rupture, ADSA-P measure the surface tension of water under these conditions. To test this in the experiment, the volume of the air bubble formed was increased continuously using the micro-syringe; consequently, the surface area of the air bubble was increased at a rate ranging from 0.5 to 3 mm$^2$/s. (The surface area of the air bubble was generally between 20 to 40 mm$^2$.) While the film was thinning, images of the air bubble were acquired at 0.3 s time intervals. The corresponding surface or film tension was then calculated by ADSA-P.

D.2.3 Interfacial Tension Measurement

As mentioned in Section II, the concept of film tension is closely analogous to that of surface (interfacial) tension. To study their relationship, interfacial tensions were also measured with ADSA-P. To measure the interfacial tension between alkane and water, an inverted pendant alkane drop was formed at the tip of the Teflon tube immersed in the water phase. To measure their respective surface tensions, air bubbles were formed in the two liquid phases [105,114,115].

D.2.4 Experimental Set-Up

The set-up was essentially the same as that of the usual ADSA-P [105,114,115]. Briefly, for both film and interfacial tension measurements, a drop or bubble was illuminated with a white light source (model V-WLP 1000, Newport Corp., Irvine, CA, USA) shining
through a heavily frosted diffuser (Fig. D-2). Images of the drop were obtained by a microscope (Leitz Apozoom, Leica, Willowdale, ON, Canada) linked to a monochrome charge-coupled device video camera (Cohu 4810, Infrascan, Inc., Richmond, BC, Canada). The video signal of the drop was transmitted to a digital video processor (Xvideo board, Parallax Graphics Inc., Santa Clara, CA, USA) which performed the frame grabbing and digitization of the image into 640×480 pixels with 256 grey levels. For each run, images were captured at 0.3 s intervals in order to observe the time-dependent film and interfacial tensions. A workstation (Sun SPARCstation 10, Sun Microsystems, Mountain View, CA, USA) was used to acquire the images from the digitization board. Image analysis schemes were used to determine the drop profile coordinates with sub-pixel resolution and correct for optical distortion [114,115]. The entire set-up, except for the workstation, was placed on a vibration-free table (Technical Manufacturing Corp., Peabody, MA, USA) to isolate the system from external disturbances (Fig. D-2). All the measurements reported here were conducted at room temperature of 25±0.2°C.

D.3 Results

For hexadecane and dodecane films, both static and dynamic measurements are presented: in the former, the measurements were conducted while the air bubble volume was kept constant and hence there was no noticeable thinning of the film during the experiment; in the latter, the measurements were conducted while the air bubble volume and surface area
Fig. D-2  Schematic of the experimental set-up for tension measurements using ADSA-P.
were continuously increased, resulting in thinning of the film. The experimental results reported were repeated on three different days; during each day multiple runs were conducted for each type of measurement, each run usually containing tens or hundreds of images. The 95% confidence limits presented below are based on a statistical analysis for all of the experiments conducted. For tetradecane films, only static measurements are reported.

D.3.1 Hexadecane-Water

D.3.1.1 Static Measurements

When a small amount of alkane adheres to the tip of the Teflon tube, a film can be created at the air-water interface by slowly forming an air bubble at the tip. Figure D-3 shows a typical image of an air bubble coated with a hexadecane film, inside the water phase; the tension value determined by ADSA-P is 80.60 mJ/m². Such a bubble can be maintained for 10 min or more, and Fig.D-4 shows the film tension over a time span of 5 min after the film was formed. In this figure, there is a slightly increasing trend of tension with time. By performing a linear regression, it was found that the slope of the line is $3.44 \times 10^{-4}$ mJ/m²/s, which corresponds to a tension increase of 0.2 mJ/m² in 10 min. Using a null hypothesis, i.e., assuming a zero slope, it follows that the trend is statistically significant, with a certainty larger than 99.9%. Presumably, the slight increase in tension is caused by film drainage due to gravity (see also the Discussion section). It is reasonable to assume that the tension would approach a plateau value asymptotically if the film could be maintained; however, the current
Fig. D-3  A typical image and its profile (right) of an air bubble coated with a hexadecane film, inside the water phase. The film tension analysed by ADSA-P from this single image is 80.60 mJ/m². It is noted that the profile is smooth.
Fig. D-4  A typical static hexadecane film tension measurement over a time span of 5 min, which results in a film tension of \( \gamma_{\text{avg}} = 80.60 \pm 0.01 \text{ mJ/m}^2 \) at the 95% confidence level.
technique cannot avoid external disturbances which cause film rupture (see also below).

Considering the small increase in tension, it was decided to average the data over the entire range to represent the film tension value. The average value in Fig. D-4 is 80.60 ± 0.01 mJ/m² at the 95% confidence level based on this single run; the overall average film tension calculated from ADSA-P is 80.67 ± 0.06 mJ/m² at the 95% confidence level (Table D-1) after taking into account four different runs. This tension value is extremely high, compared with the surface tension of pure water which is about 72.14 mJ/m² at 25°C.

Table D-1. Interfacial Tensions and Film Tensions (mJ/m²) from Static Measurements

<table>
<thead>
<tr>
<th>Interface</th>
<th>Hexadecane</th>
<th>Tetradecane</th>
<th>Dodecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-Water</td>
<td>72.73 ± 0.01</td>
<td>72.53 ± 0.01</td>
<td>72.61 ± 0.01</td>
</tr>
<tr>
<td>Air-Alkane</td>
<td>27.23 ± 0.01</td>
<td>26.41 ± 0.04</td>
<td>23.68 ± 0.01</td>
</tr>
<tr>
<td>Alkane-Water</td>
<td>53.53 ± 0.01</td>
<td>52.70 ± 0.04</td>
<td>52.39 ± 0.01</td>
</tr>
<tr>
<td>(Air-Alkane) + (Alkane-Water)</td>
<td>80.76 ± 0.02</td>
<td>79.11 ± 0.08</td>
<td>76.07 ± 0.02</td>
</tr>
<tr>
<td>Alkane Film on Water</td>
<td>80.67 ± 0.06</td>
<td>79.03 ± 0.02</td>
<td>77.20 ± 0.02</td>
</tr>
</tbody>
</table>

Note: The sum of the interfacial tensions between air and alkane and between alkane and water is approximately equal to the alkane film tension. The error limits are at the 95% confidence level. The experimental temperature was 25 ± 0.2°C.

It was expected that complete film coverage on the air-water interface could be generated only if there was a sufficient amount of alkane at the tip of the Teflon tube. Otherwise, the resulting surface of the air bubble would be water. To test this idea, the following procedure was adopted: A series of air bubbles were formed and released from the
tip of the Teflon tube by continually pumping air with the micro-syringe. As long as a hexadecane film forms, a certain amount of the alkane will be removed with each air bubble, gradually depleting the hexadecane "reservoir" at the tip. Consequently, a point may be reached where there is insufficient alkane to form a film. Figure D-5 shows a typical image of an air bubble created under this condition. It is noted that two kinks, or discontinuity points, appear in the neck region of the bubble profile (Fig. D-5b). These kinks are believed to indicate a "ring" of the residual alkane accumulated at the base of the bubble; the resulting tension value is 72.70 mJ/m², which is close to that of water at 25°C. It is also noted that the kinks correspond to the intersection points of three interfaces: air-water, water-alkane, and alkane-air. In principle, the Quadrilateral Relation can be used to describe the equilibrium condition at this three-phase contact line. From the slopes of the air-water interface and water-alkane interface, two contact angles can be obtained. Therefore, line tension may be calculated through the Quadrilateral Relation from this three-phase contact line configuration, provided that interfacial tensions can also be obtained.

D.3.1.2 Dynamic Measurements

To confirm the two different tension values, shown above, resulting from the same system but different procedures (one identified as the alkane film tension and the other the interfacial tension between air and water), time-dependent tension measurements were performed: The volume of the air bubble was increased continuously by means of the syringe with a motor-driven plunger. The surface area was increased at three rates: 3.05, 0.61 and
Fig. D-5  A typical image of an air bubble after rupture of hexadecane film and its profile. The interfacial tension from this single image is 72.70 mJ/m². Note that two kinks appear in the neck region of the cross-sectional profile of the air bubble, as indicated by arrows, indicating the presence of a ring of hexadecane.
Consecutive images of an air bubble showing the hexadecane film rupture at $t = 0.64$ s. Before film rupture, the tension is approximately 80.0 mJ/m$^2$; after film rupture, the tension is approximately 72.6 mJ/m$^2$. The former represents film tension and the latter interfacial tension; the error limits associated with each tension value represent 95% confidence limits. The image at $t = 0.64$ s is blurred due to vibration accompanying film rupture, and hence it cannot be analysed by ADSA.
Fig. D-6b Profiles of the consecutive images (Fig. D-6a) of an air bubble showing the hexadecane film rupture at $t = 0.64$ s. The image at $t = 0.64$ s is blurred due to vibration accompanying film rupture, and hence it cannot be analysed by ADSA.
Fig. D-6c The neck regions of images at $t = 0.32$ and $3.15$ s (in Fig. D-6b) are magnified, where a smooth profile is seen for the bubble with film (A), but kinks appear after film rupture (B).
0.52 mm$^2$/s. The same initial surface area was used for all expansion rates to ensure valid comparison (see below). As the surface area is increased, film thinning occurs; one would then expect film rupture to occur at some point. Figure D-6 shows such a dynamic measurement, at a surface expansion rate of 3.05 mm$^2$/s, on a single bubble; images were acquired at 0.3 s time intervals. It is seen that a transition in the bubble profile occurs at time $t = 0.64$ s when the drop image vibrated severely and could not be processed by the image analysis program of ADSA-P (Fig. D-6a). Before the transition, optically "smooth" profiles are observed (Figs. D-6b and D-6c). After the transition, kinks emerge in the neck region of the drop profile (Figs. D-6b and D-6c), and remain throughout the experiment (lasting up to 10 min, not shown in Fig. D-6). When analysing the images with ADSA-P, the tension before the transition is approximately 80.0 mJ/m$^2$, and the tension after the transition is approximately 72.6 mJ/m$^2$. At the transition, an abrupt change in the tension occurs, corresponding to a tension decrease of approximately 7.4 mJ/m$^2$.

From Fig. D-6a, it is also noted that a black spot appears in the bright central area of the bubble image after the transition, at times $t = 1.55, 3.15$ and 3.46 s. (The bright central area is caused by the light which is transmitted through a relatively small area of the bubble which is essentially perpendicular to the incident light beam.) This black spot is believed to be a small hexadecane droplet adhering to the bubble surface, preventing the light from being transmitted. This black spot slides down along the air-water interface with the passage of time (see images at $t = 3.15$ s and $t = 3.46$ s). This indicates that, at the transition, the film ruptures into small droplets, which consequently slide down along the air-water interface due to gravity and coalesce into a "ring". This confirms the above supposition of film tension and
Fig. D-7  Dynamic tension measurement for the hexadecane-water system; the air bubble surface area is increased at a rate of 3.05 ± 0.02 mm²/s, corresponding to a volume increase at a rate of 2.12 ± 0.02 mm³/s. (The errors represent the standard deviations from the linear regression procedure). An approximately 7.4 mJ/m² sudden drop in tension accompanies film rupture. A linear curve fit to the tension values before film rupture is also shown.
film rupture.

Figure D-7 shows the tension results over a larger time span, when the surface area is increased at a rate of 3.05 mm²/s, corresponding to a bubble volume increasing at a rate of 2.12 mm²/s. It is seen that with film thinning, the film tension increases gradually up to about 80.0 mJ/m² when film rupture occurs; accompanying this, there is a sharp decrease in the tension value to 72.6 mJ/m². After this transition, the surface tension remains constant at about 72.6 mJ/m² even though the surface area continues to increase at the same rate. One of the interesting features observed is the gradual increase in film tension along with the thinning of the film. A linear curve-fit to these tension values results in a slope of 1.01 ± 0.10 mJ/m²/s with a correlation coefficient of 0.957 (Fig. D-7). To relate the film tension to thinning, the ratio of this slope to the surface expansion rate has to be calculated, which turns out to be 0.331 mJ/m²/mm². This means that the film tension increases by 0.331 mJ/m² for every mm² surface area increase. To relate this surface area increase to film thinning, the absolute value of the surface area has to be used. Therefore, in our experiments the same initial surface area of the bubble was always used for different bubble expansion measurements to ensure valid comparison (see below). The purpose of drawing a straight line through the tension data in Fig. D-7 and subsequent figures was to allow for a comparison between different rates of surface expansion. Upon further thinning, a final tension value might well be approached asymptotically, if rupture can be prevented.

Figures D-8 and D-9 are dynamic film tensions recorded when the surface areas are increased at rates of 0.61 and 0.52 mm²/s, respectively. Similarly, the tension value increases up to approximately 80.0 mJ/m² as the surface area is increased, followed by a sharp decrease
Fig. D-8  Dynamic tension measurement for the hexadecane-water system, similar to that in Fig. D-7, except that the air bubble surface area is increased at a rate of 0.61 ± 0.01 mm²/s, corresponding to a volume increase at a rate of 0.44 ± 0.01 mm³/s. The decrease in tension accompanying film rupture is again 7.4 mJ/m².
Fig. D-9  Dynamic tension measurement for the hexadecane-water system, similar to that in Fig. D-7, except that the air bubble surface area is increased at a rate of 0.52 ± 0.02 mm²/s, corresponding to a volume increase at a rate of 0.36 ± 0.01 mm³/s. The tension decrease upon film rupture is also 7.4 mJ/m².
in tension, corresponding to film rupture. After film rupture, the film tension drops to approximately 72.6 mJ/m². A linear curve-fit to the film tension values, before film rupture, results in the slopes of 0.24 ± 0.03 mJ/m²/s (with a correlation coefficient of 0.869) and 0.12 ± 0.01 mJ/m²/s (with a correlation coefficient of 0.834) for the two surface expansion rates of 0.61 and 0.52 mm²/s, respectively (Figs. D-8 and D-9).

Again, to relate these film tension increases to the film thinning, the ratios of these slopes to the surface expansion rates need to be calculated: 0.393 and 0.231 mJ/m²/mm² for Figs. D-8 and D-9, respectively. These ratios are reasonably close to that calculated from Fig. D-7, i.e., at 0.331 mJ/m²/mm². Comparing these three ratios calculated from Figs. D-7 to D-9, it is seen that the film tension seems to be related only to the film thinning, not to the rate of the surface area increase; the surface expansion rate in Fig. D-7 differs from those in Figs. D-8 and D-9 by almost an order of magnitude while the ratio of film tension to surface area remains roughly the same.

D.3.1.3 Interfacial Tensions

To measure interfacial tension between air and water, the capillary was placed into the water phase before the alkane was carefully added on the top of the water. This eliminated the possibility for alkane to come in contact with the tip of the Teflon tube and hence prevented the possibility of film formation. The air-water interfacial tension was measured on an air bubble formed at the tip of the Teflon tube, resulting in a value of 72.73 ± 0.01 mJ/m² at the 95% confidence level (Table D-1). This value is close to that observed after film
rupture in Figs. D-5 to D-9. The interfacial tensions between air and alkane and between water and alkane are also listed in Table D-1. It is observed that the sum of the interfacial tensions between air and hexadecane and between hexadecane and water is equal to the film tension, within the error limits at the 95% confidence level.

D.3.2 Tetradecane-Water

The film tension of tetradecane at the air-water interface was shown in Table D-1, along with relevant interfacial tensions of the tetradecane-water system. Similar to that observed in the hexadecane-water system, the sum of the two interfacial tensions of air-tetradecane and of tetradecane-water is equal to tetradecane film tension, within the error limits at the 95% confidence level. Note that for this system only static measurements are presented, as this system shows behaviour very similar to that of the hexadecane system in both static and dynamic measurements [125].

D.3.3 Dodecane-Water

In this system, both static and dynamic measurements were performed, in a manner similar to that for the hexadecane-water system. In the static measurement, when there was a film at the air-water interface, a smooth air bubble profile was observed. The resulting film tension was $77.20 \pm 0.02$ mJ/m$^2$ at the 95% confidence level (Table D-1). When there was insufficient alkane to form a film at the air-water interface, two kinks appeared in the neck
region of the cross-sectional profile of the air bubble as before, due to the formation of a “ring” of alkane at the base. The resulting surface tension was \(72.61 \pm 0.01\) mJ/m\(^2\) at the 95% confidence level (Table D-1).

Figure D-10 shows the tension behaviour as a function of time when the surface area is increased at three different rates: 1.04, 0.90 and 0.84 mm\(^2\)/s. In general, the same pattern as before is observed for all three expansion rates: an initial gradual increase in tension up to about 76.0 mJ/m\(^2\), and then film rupture, resulting in a sharp decrease in the tension value to about 72.0 mJ/m\(^2\) which is close to the surface tension of water. Accompanying film rupture, the air bubble profile changes from smooth to kinked, due to formation of an alkane ring, as illustrated in Fig. 6 for the hexadecane system. It is noted that with the slowest surface expansion rate a change in slope occurs at a tension value of 76 mJ/m\(^2\) (Fig. D-10c). After this break, the tension value increases more slowly up to about 77 mJ/m\(^2\), close to the static film tension value, before film rupture. The ratios of the average rate of increase of film tension to the rate of surface expansion are again similar for all three area increase rates.

The surface (or interfacial) tensions between air and dodecane and the interfacial tension between dodecane and water were also measured just as for the hexadecane-water system; the results are presented in Table D-1. It is noted that the sum of the surface tension between air and dodecane and the interfacial tension between dodecane and water is approximately equal to the dodecane film tension (Table D-1).
Fig. D-10 Dynamic tension measurement for the dodecane-water system, similar to that in Fig. D-7; the air bubble surface area is increased at a rate of (a) $1.04 \pm 0.01 \text{ mm}^2/\text{s}$, (b) $0.90 \pm 0.03 \text{ mm}^2/\text{s}$ and (c) $0.84 \pm 0.02 \text{ mm}^2/\text{s}$. Film rupture is accompanied by a decrease in tension of approximately $4.0 \text{ mJ/m}^2$. A linear curve fit to the tension values before film rupture is also shown in (a) and (b). In (c) a change in slope occurs at about $76 \text{ mJ/m}^2$, and two linear curve fits to the two branches are shown.
D.4 Discussion

The main point in the measurements is, of course, the fact that the observed film tension is approximately equal to the sum of water-alkane interfacial tension and alkane surface tension. This finding is not surprising within the framework of well established film theory. When a liquid is sufficiently thick, the interaction forces between the two surfaces of the film become negligible; therefore, the surface properties of the film are identical to those of macroscopic liquid from which the film is formed. Consequently, the surface mechanical properties of the film become equivalent to the sums of those of the two surfaces. This is precisely the case for both the hexadecane and tetradecane systems, where, from Table D-1, the sum of the two surface (interfacial) tensions is equal to the film tension, within the error limits at the 95% confidence level.

Matters are quite different for the water-dodecane system, where the film tension is 77.20 ± 0.02 mJ/m², whereas the sum of the two interfacial tensions is 76.07 ± 0.02 mJ/m². The difference of about 1.1 mJ/m² will, presumably, have to be attributed to the interaction forces between the two bounding surfaces of the film. The parameter used for quantifying such interactions is disjoining pressure [139-143].

Considering that disjoining pressure $\pi$ becomes negligible for large film thickness and that the product $\pi h$ (with $h$ being film thickness) has the unit of surface or film tension, the film tension $\gamma_f$ can be, in principle, related to the sum of the two surface tensions as follows

$$\gamma_f = \gamma_1^s + \gamma_2^s + O(\pi h) \tag{D-1}$$
where $\gamma_1$ and $\gamma_2$ are the two interfacial tensions, and $O$ stands for the order of magnitude. Equation (D-1) can be derived from relevant equations by Derjaguin and Gutop [144,145], and Ivanov and Kraichevsky [146]. From Eq. (D-1), if the disjoining pressure is negligible, the film tension should be just the sum of the two interfacial tensions, which are exactly the cases of hexadecane and tetradecane films. The difference of about 1.1 mJ/m$^2$ in the case of the dodecane system is then attributed to disjoining pressure effects. If this is indeed the case, the disjoining pressure would be positive, i.e., repulsion would occur between the two surfaces of the film. It is well known, from statistical thermodynamics [147], that the disjoining pressure is negative if only van der Waals forces are operative. However, in the present case, because of the presence of water, more complex responses, including repulsion, cannot be excluded a priori.

The differences between the results of the static and dynamic measurements also require comment. In the static measurements the bubble was formed relatively quickly and allowed to equilibrate for approximately five minutes before measurements were made. During this time film drainage will presumably have occurred. In the dynamic measurements data acquisition was started as soon as the bubble, growing with a constant volume flow rate, was big enough, i.e., non-spherical shape, to allow interpretation by ADSA-P. An increase in tension is observed as the film is thinning (Figs. D-7 to D-10). This effect could be due to the fact that the films are initially quite thick, and of uneven thickness, as sketched in Fig. D-11. The resulting tension exerted along the thick alkane layer is the vectorial sum of the two bounding surface tensions. If the two surface tension vectors (along the surfaces) are not parallel, the sum of the vectors will be less than the simple addition of their absolute values.
Fig. D-11  Schematic of a thick alkane layer on an air bubble with a relatively small surface area at the beginning of an expansion experiment. The two surface tension vectors, of the inner and outer surfaces of the alkane layer, are not parallel, resulting in a smaller total tension value than the sum of water-alkane interfacial tension and alkane surface tension.
As a result, a relatively low "film" tension value is obtained initially. As the alkane layer becomes thinner with the increase in surface area, the film thickness will become more uniform. Eventually, the alkane layer becomes thin enough that the two bounding surfaces become parallel, i.e., the alkane film has a constant film thickness everywhere on the surface. The film tension is the sum of the two parallel surface tension vectors, i.e., \( \gamma_f = \gamma_1 + \gamma_2 \), provided that the film is still thick enough so that there are no disjoining pressure effects. Unfortunately, the film ruptures in the majority of cases before this point is reached. In the static measurement, on the other hand, rupture occurs much later. The reason for this is presumably that natural drainage of the film is a much gentler process than the forced drainage due to film expansion. It is interesting that in a single case, for dodecane (Fig. D-10c) the dynamic value of the tension exceeds the sum of \( \gamma_1 \) and \( \gamma_2 \). A break in the \( \gamma \) values, just above 76 mJ/m\(^2\) (\( \gamma_1 + \gamma_2 = 76.07 \) mJ/m\(^2\)) occurs, and the slope of the subsequent data may contain information about disjoining pressure and film thickness.

Finally, there is one more feature of the data which requires comment: Error limits are significantly larger in the presence of films than in their absence. There is no obvious explanation for this fact. Speculation that fluid dynamic processes in the film could cause temporal distortions in the drop shape is probably not correct: Our basic measuring stick is the pixel, which, in these experiments, is approximately 10 \( \mu \)m. It seems unlikely that such dynamic effects could have amplitudes well in excess of this length.
D.5 Conclusions

1. The method presented provides a new approach to film tension measurement, which requires only axisymmetric bubble shapes, rather than spherical ones. The measurements can be carried out under both static and dynamic conditions.

2. The alkane film tension found is equal to the sum of the surface (interfacial) tensions of air-alkane and of alkane-water for both hexadecane and tetradecane films at the air-water interface. In the case of dodecane films, the static film tension as well as a single dynamic value are larger than the sum of the two interfacial tensions, possibly indicating disjoining pressure effects.

3. Film rupture has been shown in the abrupt change in the shape of the air bubble as well as in the sudden decrease in the tension value. Before film rupture, the film tension measured increases with the increase in surface area, and the ratio of the tension increase rate to the surface expansion rate is independent of the surface expansion rate. This indicates that the dynamic film tension is related only to film thinning.

4. An important three-phase contact line configuration is observed after “film rupture”. This may allow for a new line tension determination while one of the three interfacial tensions is monitored simultaneously.
References


30. Mitchell, D.F., Ph.D. Thesis, Clarkson College of Technology, Postdam, N.Y., USA,
1976.


97. Lane, J. E., J. Colloid Interface Sci. 52, 155 (1975).


