

Carnegie Mellon University

CARNEGIE INSTITUTE OF TECHNOLOGY

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF Doctor of Philosophy

TITLE Dilatational Rheology and Controlled Generation

of Microscale Complex Fluid Interfaces

PRESENTED BY Anthony Kotula

ACCEPTED BY THE DEPARTMENT OF

Chemical Engineering

SHELLEY ANNA

4/21/14

ADVISOR

DATE

LORENZ BIEGLER

4/21/14

DEPARTMENT HEAD

DATE

APPROVED BY THE COLLEGE COUNCIL

VIJAYAKUMAR BHAGAVATULA

4/21/14

DEAN

DATE

**Dilatational Rheology and Controlled Generation of Microscale Complex
Fluid Interfaces**

Submitted in partial fulfillment of the requirements for
the degree of
Doctor of Philosophy
in
the Department of Chemical Engineering

Anthony P. Kotula

B.S., Chemical Engineering, Drexel University

Carnegie Mellon University
Pittsburgh, PA

April, 2014

ACKNOWLEDGEMENTS

I gratefully acknowledge my thesis advisor, Professor Shelley Anna, for her guidance throughout my graduate career. It was her enthusiasm for research and constant support that made these years the most rewarding experience of my life to date. Shelley motivated me to reach my highest potential, and for that I will always be thankful.

I would like to thank my thesis committee – Professors Lynn Walker, Dennis Prieve, and Steve Garoff, for their teachings and guidance over the past five years. I would like to thank Lynn Walker especially for her suggestions to the work incorporated in this thesis during the Walker and Anna group meetings.

I owe a debt of gratitude to many colleagues past and present. Thanks to Nick Alvarez for being a patient source of advice while I was still learning how to function in a lab space. Thanks to Matt Reichert, who was always ready in the morning for coffee and a good discussion about research. Thanks to Chris N. for the tea breaks and work discussions. Thanks to Stephanie, Denise, Ben, Javier, and everyone else who made the 3rd floor CFE office an inviting atmosphere for research. Thank you to Max, Alison, Melissa, and Sharon for being fantastic friends. A special thank you to Jonathan Meade for his advice and support, which has enriched my life.

I would like to thank my parents, Patrick and Judy Kotula, for their unwavering support of my decision to pursue a Ph.D. I am where I am today because of their love, guidance, and sacrifice.

To all my friends, family, and teachers past and present, thank you!

This work was financially supported by the National Science Foundation Grant no. DMR-0933510, the John and Claire Bertucci Fellowship in Engineering, and the Department of Chemical Engineering.

ABSTRACT

Complex interfaces stabilized with materials including surfactants, polymers, and particles have dilatational properties that are important in processing emulsions and foams. Dilatational rheology is difficult to measure on interfaces due to the coupling of dilatation and shear inherent in common measurement apparatuses. Compounding the problem is the lack of control over complex interface formation in emulsification, which can obscure relationships between interfacial rheology and bulk emulsion properties.

This thesis provides tools to measure dilatational properties of interfaces and generate interfaces with controlled surface coverage. A small amplitude analysis of dilatational rheology on capillary pressure tensiometers is used to develop a method for separating intrinsic rheology from surface tension effects. This analysis is applied in dilatational measurements of insoluble interfaces at the microscale, and good agreement is observed between the microscale measurements and Langmuir trough measurements. The second half of the thesis focuses on the controlled generation of particle-stabilized interfaces. A two-lobed shape transition is observed for confined bubbles traveling in a surface active particle suspension, and a model is developed to predict the particle surface coverage on the bubble interface. This model is then applied to generate monodisperse bubbles with uniform nonspherical bubbles due to particle jamming at the interface. The tools developed in this thesis are crucial to future development of relationships between the dilatational rheology of interfaces and the bulk properties of emulsions and foams.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	ii
ABSTRACT.....	iv
TABLE OF CONTENTS.....	v
LIST OF TABLES.....	vii
LIST OF FIGURES	viii
CHAPTER 1: INTRODUCTION	1
CHAPTER 2: BACKGROUND	6
2.1 EQUILIBRIUM SURFACE TENSION.....	6
2.2 INTERFACIAL MECHANICAL PROPERTIES	7
2.3 SURFACE-ACTIVE MATERIALS	9
CHAPTER 3: REGULAR PERTURBATION ANALYSIS OF SMALL AMPLITUDE OSCILLATORY DILATATION OF AN INTERFACE IN A CAPILLARY PRESSURE TENSIO METER	20
3.1 INTRODUCTION.....	20
3.2 SMALL AMPLITUDE OSCILLATORY DILATATION OF A SPHERICAL CAP BUBBLE.....	25
3.3 SMALL AMPLITUDE DILATATIONAL MODULUS OF MODEL INTERFACES.....	33
3.4 IMPACT OF REGULAR PERTURBATION ANALYSIS ON EXPERIMENTS	52
3.5 SUMMARY	70
CHAPTER 4: MEASURING INTERFACIAL MECHANICS OF INSOLUBLE MONOLAYERS ON A SPHERICAL CAP INTERFACE.....	78
4.1 INTRODUCTION.....	78
4.2 MATERIALS	79
4.4 RESULTS.....	89
4.4 DISCUSSION	118
4.5 SUMMARY	124
CHAPTER 5: PROBING TIMESCALES FOR COLLOIDAL PARTICLE ADSORPTION USING SLUG BUBBLES IN A MICROCHANNEL	130

5.1 INTRODUCTION.....	130
5.2 MATERIALS AND METHODS.....	133
5.3 RESULTS.....	140
5.4 DISCUSSION	174
5.5 SUMMARY	177
CHAPTER 6: DYNAMIC PARTICLE LOADING DURING SLUG FLOW AND THE GENERATION OF MONODISPERSE BUBBLES OF NONEQUILIBRIUM SHAPES.....	184
6.1 INTRODUCTION.....	184
6.3 RESULTS.....	191
6.4 DISCUSSION	213
6.5 SUMMARY	217
CHAPTER 7: CONCLUSIONS	223

LIST OF TABLES

Table 3.1. Typical operating parameters for capillary pressure tensiometers, including the typical radii of curvature R and oscillation frequency f . Experiments either control the volume inside V_{in} or outside V_{out} the capillary, the radius of curvature R , or the hydrostatic pressure p_{in} inside the capillary as the device input. The measured output parameters include the pressure inside or outside p_{out} the capillary, or the radius of curvature. The uncertainties in the various input and response are also included where reported in the literature.....	63
Table 3.2. Relevant dimensionless parameters for various capillary pressure tensiometers.....	64
Table 6.1. Device geometries and fluid phase compositions for the experiments considered. Dimensions include the radius of the capillary R , square glass capillary or microfluidic channel depth H and width W , and the length between the droplet generation site and the channel outlet L_c . Relevant particle conditions include the particle radius r_p , the particle concentration, and the concentration C of L-lysine-HCl or CTAB in the outer phase.....	190
Table 6.2. Parameter values used to generate the stationary vesicle shapes shown in Figure 6.7.....	201

LIST OF FIGURES

Figure 3.1. Schematic diagram of a capillary pressure tensiometer. The bubble pinned at the capillary tip can be either smaller or larger than a hemisphere with the same radius of curvature R . The minimum radius of curvature for the bubble occurs when R is equal to the radius of the capillary tip R_c 26

Figure 3.2. Schematic illustration of the surface stresses acting on a section of an interface with radius of curvature R 28

Figure 3.3. The small amplitude dilatational modulus of an insoluble monolayer modeled by the Langmuir isotherm and the Boussinesq-Scriven constitutive equation. The model parameters are $T = 298$ K, $\Gamma_{max} = 10^{-5}$ mol/m², $n = 2.5 \times 10^{-14}$ mol, $\kappa^s = 85$ mN/m, and $R_c = 30$ μ m. (a) The frequency dependence of the modulus for $b_1 = 0.66$. (b) The dependence of the modulus on b_1 , for a fixed frequency of $\omega = 0.4$ s⁻¹. The vertical lines in (a) and (b) indicate $\omega = 0.4$ s⁻¹ and $b_1 = 0.66$, respectively. 38

Figure 3.4. The small amplitude dilatational modulus of an interface with a soluble monolayer modeled by the Langmuir isotherm and the Boussinesq-Scriven constitutive equation. The model parameters are $T = 298$ K, $\varepsilon_0 = 60$ mN/m, $D = 10^{-10}$ m²/s, $\omega_0 = 5$ s⁻¹, and $\kappa^s = 0.3$ mN-s/m. (a) The frequency dependence of the modulus for $b_1 = 0.66$. (b) The dependence of the modulus on b_1 , for a fixed frequency of $\omega = 0.1$ s⁻¹. The vertical lines in (a) and (b) indicate $\omega = 0.1$ s⁻¹ and $b_1 = 0.66$, respectively. 45

Figure 3.5. The crossover frequencies in the complex modulus as a function of the b_1 given by equation (3.43) (solid line) and equation (3.44) (dashed lines). The physical parameters used are given in the captions of Figures 3.3 and 3.4, respectively. The inset plots the crossover frequency versus the radius of curvature of the interface for the soluble monolayer with dilatational viscosity (dashed line). The dotted line in the inset is the crossover frequency of an interface with constant Gibbs elasticity and dilatational viscosity, and the solid line is the crossover frequency for pure diffusion of soluble surfactant to a spherical interface. 51

Figure 3.6. Grayscale contour plot of (a) H_A normalized by H_R and (b) H_P normalized by H_R for a viscous insoluble interface. Darker regions indicate higher values. The solid contour lines indicate where the value of H_A/H_R or H_P/H_R is unity. The parameters used to generate these plots are $\Delta R_1 = 0.443$, $\Delta R_2 = 0.233$, $b_1 = 0.984$, and $\varepsilon = 0.2$. The small box on both figures at (3.08, 4.98) rad indicates the values of the phase shifts for oscillation at $b_1 = 0.984$ and $\omega = 1$ rad/s. 56

Figure 3.7. Critical pressure amplitude above which (a) H_A or H_P and (b) H_R exceeds 10% as a function of the normalized equilibrium radius. The analysis was performed at angular frequencies of 0.5 rad/s (●), 1 rad/s (■), and 10 rad/s (▲). In (a), the filled symbols correspond to cases in which H_A exceeds 10% first, and the

open symbols correspond to cases in which H_p exceeds 10% first. The system parameters are given in the caption of Figure 3.3..... 60

Figure 3.8. Schematic diagram of common capillary pressure tensiometers. (a) volume control of internal fluid, (b) volume control of external fluid, (c) pressure control of internal fluid . The region marked by the dashed box indicates the capillary tip, which corresponds to Figure 3.1..... 62

Figure 3.9. Operating diagram showing the measurable range of dilatational viscosities for a viscous insoluble monolayer with constant interfacial tension for the configuration and physical parameters corresponding to the microtensiometer of Alvarez *et al.*⁴⁷ 69

Figure 4.1 Schematic diagram of the microtensiometer and additional components used in experiments. (A) 3.5 mL sample reservoir, (B) glass capillary, (C) pressure transducer, (D) oscillating motor and piston, (E) linear compression pump, (F) hydrostatic pressure head, (G) fluid exchange system. The expanded image at lower right shows a magnified view of the capillary tip with a pinned bubble. Three-way valves are indicated with the $\otimes$ symbol. The tubing connecting the capillary to the hydrostatic pressure head is colored black in sections that are filled with water 82

Figure 4.2. Effect of initial concentration of fatty acid or phospholipid dissolved in isopropanol on the surface pressure achieved after fluid exchange for (◆) DMPC, (●) PA, and (■) DPPC. The dashed line denotes zero surface pressure. Error bars correspond to the standard deviation based on three experiments..... 91

Figure 4.3. Effect of fluid exchange rate on the initial surface pressure. Symbols correspond to three different concentrations at (●) 0.01, (■) 0.05, and (▲) 0.2 mg/mL in isopropanol. Filled points correspond to the surface pressure after a single rinse, open symbols correspond to a second rinse with DI water. The horizontal dashed line indicates the equilibrium spreading pressure for palmitic acid at 20°C. Error bars represent uncertainty from propagation of error. 93

Figure 4.4. Surface pressure of DMPC as a function of (a) the surface area of the spherical cap interface, and (b) the scaled surface area. The initial surface pressures are (□) 2.5 mN/m, (▼) 6.5 mN/m, (▽) 15 mN/m, (○) 25 mN/m, and (●) 27.5 mN/m. The solid line in Figure 4.4b is the DMPC isotherm reported by Kubo *et al.*²² measured at 20°C on a water subphase in a Langmuir trough. Horizontal error bars represent uncertainty in the radius of curvature and capillary radius. Vertical error bars estimated from uncertainty in the radius and pressure are within the symbol size..... 95

Figure 4.5. Dilatational modulus of DMPC versus angular frequency ω at surface pressures indicated in the upper right of each plot. The modulus is plotted in terms of (●) $|E^*|$ plotted on the left axis and (○) δ plotted on the right axis. The dashed

line indicates the zero value for the phase angle in each plot. The scaling of the axes is the same for all plots. 97

Figure 4.6. A comparison of (●) the Gibbs elasticity E and (○) the in-phase component of the dilatational modulus E' over the measured range of surface pressures for DMPC..... 98

Figure 4.7. Surface pressure of palmitic acid versus (a) the surface area of the spherical cap interface, and (b) the surface area scaled by χ . The initial surface pressures and initial dilatation rates are (■) 0 mN/m and $-3 \times 10^{-3} \text{ s}^{-1}$, (▼) 5.5 mN/m and $-3 \times 10^{-3} \text{ s}^{-1}$, (◇) 8.5 mN/m and $-2 \times 10^{-4} \text{ s}^{-1}$, (○) 9.7 mN/m and $-1 \times 10^{-2} \text{ s}^{-1}$. The solid line in Figure 4.7b is the palmitic acid isotherm reported by Lipp *et al.*²⁸ measured on a water subphase at 16°C. 101

Figure 4.8 Dilatational modulus of palmitic acid versus angular frequency ω at surface pressures indicated in the upper right of each plot. The modulus is plotted in terms of (●) $|E^*|$ plotted on the left axis and (○) δ plotted on the right axis. The scaling of the ω and $|E^*|$ axes is the same for all plots. The scaling for δ is the same within each row of plots. The dashed line indicates the zero value for the phase angle in each plot. 103

Figure 4.9. A comparison of (●) the Gibbs elasticity E and (○) the in-phase component of the dilatational modulus E' over the measured range of surface pressures for palmitic acid. 104

Figure 4.10. Surface pressure of DPPC versus (a) the surface area of the spherical cap interface, and (b) the surface area scaled by χ . The initial surface pressures are (■) 0 mN/m, (▽) 1 mN/m, (□) 2 mN/m, (●) 4.5 mN/m, (△) 7 mN/m, (▼) 10 mN/m, (○) 20.5 mN/m. The solid line in Figure 5.7b is a DPPC isotherm from the work of Kim *et al.*²⁹ measured on a water subphase at $21 \pm 1^\circ\text{C}$ 107

Figure 4.11. Dilatational modulus of DPPC versus angular frequency ω at surface pressures indicated in the upper right of each plot. The modulus is plotted in terms of (●) $|E^*|$ plotted on the left axis and (○) δ plotted on the right axis. The scaling of the ω and $|E^*|$ axes is the same for all plots. The scaling for δ is the same within each row of plots. The dashed line indicates the zero value for the phase angle in each plot. 109

Figure 4.12. A comparison of (●) the Gibbs elasticity E and (○) the in-phase component of the dilatational modulus E' over the measured range of surface pressures for DPPC. 110

Figure 4.13. Surface tension dynamics for a 1.5 μM Tween 80 during surfactant adsorption and wash-out. The final surface pressure for each run is (●) 4 mN/m, (▲) 7.5 mN/m, and (■) 14.5 mN/m. The open symbol in each curve indicates the time when the wash-out procedure was started. Three measurements of the dynamics to $\Pi = 4 \text{ mN/m}$ are shown to indicate reproducibility..... 112

Figure 4.14. Compression measurements for the insoluble component of Tween 80 at an air-water interface. (a) Surface pressure versus the surface area of the spherical cap bubble. Different shape symbols indicate runs at different starting surface pressures. Unfilled points were performed with 0.5 M NaCl in the water subphase. (b) The same data as in (a) collapsed to a single line by scaling the surface area by χ . The data is plotted with isotherms of four major fatty acids present in Tween 80. 115

Figure 4.15. Dilatational modulus of Tween 80 versus angular frequency ω at surface pressures indicated in the upper right of each plot. Filled symbols denote the value of $|E^*|$ plotted on the left axis and open symbols denote δ plotted on the right axis. The left plot is measured on a DI water subphase, and the right plot is measured on a 0.5 M NaCl subphase. The scaling of the ω , $|E^*|$, and δ axes is the same for both plots. The dashed line indicates the zero value for the phase angle in each plot. 116

Figure 4.16. A comparison of (●, ▲) the Gibbs elasticity E and (○, △) the in-phase component of the dilatational modulus E' over the measured range of surface pressures for Tween 80. Circular symbols area measured on a DI water subphase, triangular symbols are measured on a 0.5 M NaCl subphase. 117

Figure 5.1. Schematic diagram of the microfluidic device. The inset image shows a nitrogen bubble extending into the main channel prior to pinch-off. The channel width W is 142 μm . The distance from the T-junction to the device outlet L_c is 57 mm, and the channel depth is 42 μm as shown in the bottom-right corner of the diagram. 134

Figure 5.2. Dynamic surface tension measurements for (○) 2 wt% silica suspension, (□) 0.21 mM CTAB solution, and (■) 0.2wt%, (▲) 1 wt%, (●) 2 wt%, and (✕) 10 wt% silica-CTAB suspensions. Three repeated experiments for the 2 wt% silica-CTAB suspension are shown to indicate the representative repeatability for each system. 139

Figure 5.3. Representative bright-field images of the bubbles traveling along the microchannel at several distances downstream of the T-junction, shown in the left column. In all images, the direction of flow is from left to right. The channel width in all images is 142 μm 141

Figure 5.4. Bubble length as a function of position in the microchannel for (a) different bubble velocities generated in the 2 wt% silica-CTAB suspension ((▲) 2 wt% silica-CTAB suspension, $Q = 0.85$ mL/hr; (●) 2 wt% silica-CTAB suspension, $Q = 1.00$ mL/hr; (◆) 2 wt% silica-CTAB suspension, $Q = 1.67$ mL/hr) and (b) bubbles generated in different concentrations of the particle-surfactant suspension ((✕) 1 wt% silica-CTAB suspension, $Q = 1.00$ mL/hr; (■) 10 wt% silica-CTAB suspension, $Q = 1.00$ mL/hr.) Lines are bubble length predictions based on equations (5.2) and (5.3). The experimental data for (▲) ends abruptly due to bubble break up, shown in Figure 5.6. 144

Figure 5.5. Distance of the midpoint of the neck from the rear of the bubble as a function of the normalized bubble position within the channel. (a) The location normalized by the width W of the microchannel and (b) the location normalized by the instantaneous length of the bubble L for: (▲) 2 wt% silica-CTAB suspension, $L_i/W = 7.49 \pm 0.46$, $Q = 0.85$ mL/hr; (●) 2 wt% silica-CTAB suspension, $L_i/W = 4.72 \pm 0.10$, $Q = 1.00$ mL/hr; (◆) 2 wt% silica-CTAB suspension, $L_i/W = 3.031 \pm 0.042$, $Q = 1.67$ mL/hr; (✕) 1 wt% silica-CTAB, $L_i/W = 6.44 \pm 0.47$, $Q = 1.00$ mL/hr; (■) 10 wt% silica-CTAB, $L_i/W = 4.72 \pm 0.10$, $Q = 1.00$ mL/hr..... 147

Figure 5.6. Successive images of a bubble generated in the 10 wt% silica-CTAB suspension at $Q = 0.85$ mL/hr ($L_i/W = 4.72 \pm 0.10$) breaking up during the necking process in a microchannel. The arrow indicates the location of the neck breakup. The time step between images is 1.8 ms. The channel width is 142 μm 148

Figure 5.7. Images of stable bubbles produced in the microfluidic channel. The bubbles produced in a 2 wt% silica-CTAB suspension (left image, scale bar 200 μm) show elongated shapes outside of confinement, compared with the stable spherical bubbles produced in a 90 mM CTAB solution (right image, scale bar 250 μm). 149

Figure 5.8. Bubble velocities for various (a) bubble lengths and (b) silica-CTAB concentrations: (○) DI water, $L_i/W = 6.19 \pm 0.23$, $Q = 0.70$ mL/hr; (□) 2 wt% silica suspension, $L_i/W = 3.895 \pm 0.092$, $Q = 0.90$ mL/hr; (▲) 2 wt% silica-CTAB suspension, $L_i/W = 7.49 \pm 0.46$, $Q = 0.85$ mL/hr; (●) 2 wt% silica-CTAB suspension, $L_i/W = 4.72 \pm 0.10$, $Q = 1.00$ mL/hr; (◆) 2 wt% silica-CTAB suspension, $L_i/W = 3.031 \pm 0.042$, $Q = 1.67$ mL/hr; (✕) 1 wt% silica-CTAB, $L_i/W = 6.44 \pm 0.47$, $Q = 1.00$ mL/hr; (■) 10 wt% silica-CTAB, $L_i/W = 4.72 \pm 0.10$, $Q = 1.00$ mL/hr. The DI water and 2 wt% silica suspension velocities are included in both graphs to emphasize the velocity changes that occur in the presence of silica-CTAB suspensions..... 152

Figure 5.9. Schematic diagram of the bubble dynamics resulting from adsorption of surface-active particles. Particles adsorb and pack at the rear of the bubble, leading to a no-slip (NS) boundary condition at the rear bubble interface compared with a shear-free condition (S) at the leading edge. Added drag from the immobile interface reduces the bubble speed. 155

Figure 5.10. Schematic diagram of the shape of a long bubble confined within a rectangular capillary at low Re and Ca . The three distinct regions of the bubble interface include the end cap region, the thin film region, and the corner region. 158

Figure 5.11. Schematic diagram of the assumed particle arrangement at the air-water interface. The particles are assumed to form a hexagonally close packed structure with no spacing between the particles (left), or there can be uniform spacing between particles that results in an effective packing radius of $r_p + \epsilon$... 160

Figure 5.12. Comparison of the models for particle flux to the bubble interface in the thin film (—), the channel corner (····), and the end cap region with particle spacing $\varepsilon = 0$ (- - -). Also shown is the rate of growth of the neck region for the end cap model with particle spacing $\varepsilon = 2$ nm (— · —). These models are compared with experimental data for bubbles generated in a silica-CTAB suspension at (a) 1 wt%, (b) 2 wt%, and (c) 10 wt% silica. The volumetric flow rates are $Q = 1$ mL/hr for the 2 wt% and 1 wt% solutions, and $Q = 0.42$ mL/hr for the 10 wt% solution. The initial lengths of the bubbles are (a) $L_i/W = 4.72 \pm 0.10$, (b) $L_i/W = 6.44 \pm 0.47$, and (c) $L_i/W = 4.72 \pm 0.10$ 169

Figure 5.13. Characteristic bubble shape observed in a circular capillary when generated in a 2 wt% silica-CTAB suspension. 173

Figure 6.1. Schematic diagram of the microfluidic device. The inset image shows a nitrogen bubble extending into the main channel prior to pinch-off. The lower right shows the rectangular cross-section of the microchannel with the channel width W and height H . The distance from the T-junction to the device outlet is L_c 187

Figure 6.2. Schematic diagram of the co-flow capillary device. The major components of the device are (A) 580 μm ID circular or 500 μm square glass capillary, (B) 300 μm ID circular glass capillary, (C) barbed T-connector, (D) flexible silicone tubing, and (E) 0.030" ID LDPE tubing. 188

Figure 6.3. Particle packing at the interface of an octanol droplet flowing in a latex particle suspension in a (a) circular and (b) square glass capillary. Image (b) is taken through a flat face of the square capillary. Image (c) shows an image of the particles at the octanol droplet interface in the circular capillary. Droplet motion in images is from left to right. For images (a) and (c), $Q_i = 0.1$ mL/hr and $Q_o = 1$ mL/hr. For image (b), $Q_i = 0.3$ mL/hr and $Q_o = 3$ mL/hr. 192

Figure 6.4. Particle-stabilized area A_p at the rear of the droplet versus time in the circular capillary. Inset images show representative droplets for the indicated times. Error bars result from propagated error based on the standard deviation of the bubble velocity. Error bars in the surface area are propagated based on the standard deviation of the length of the particle-covered region. Values and standard deviations are based on measurement of 5 drops. 194

Figure 6.5. Particle-stabilized area A_p versus residence time for droplets generated in Case A. Vertical error bars represent the standard deviation of five measurements. Horizontal error bars are propagated based on the standard deviation of the bubble velocity based on five measurements. Inset images show the octanol lens at three different residence times. The scale bar in each image is 1 mm. 195

Figure 6.6. Sequential images of a bubble generated in a CTAB-silica mixture exhibiting a nonequilibrium shape outside of confinement. The time elapsed from

the first image is shown in the upper left of each image. The outer diameter of the capillary is 1 mm. The second bubble observed in the second and third images was generated at the inner capillary and is not due to break-up within the capillary or pinch-off at the capillary end. 197

Figure 6.7. Range of nonequilibrium shapes produced in microchannels and in circular capillaries organized by reduced volume. The numbers above each image indicate reduced volume for the bubbles in the image. Bubbles in the bottom row of images are generated in microfluidic devices, and bubbles in the middle row are generated in a circular capillary. The images in the top row correspond to axisymmetric shapes generated from a minimization of free energy in the vesicle shape. The bubbles produced to the right of vertical dashed line in each row are monodisperse. Bubbles to the left of the dashed line are produced as part of a mixture of bubble shapes. The scale bar for the images of bubbles generated in the circular capillary is 1 mm. The scale bar for the bubbles generated using microfluidics is 200 μm 199

Figure 6.8. Ratio of the particle-stabilized length L_p relative to the length of the bubble inside the channel L_b versus the residence time τ_{res} relative to the adsorption timescale τ_{ads} . The different symbols represent the different cases from Table 6.1: (∇) Case C – bubble trains, ($\square$) Case D – bubble trains, ($\circ$) Case D – continuous slug flow, ($\bullet$) Case E – single bubbles, ($\blacktriangle$) Case F – single bubbles, ($\blacksquare$) Case G – single bubbles. The inset images show the distance L_p measured on bubbles with different reduced volumes. The scale bar for the left inset image is 200 μm . The scale bar for the right inset image is 1 mm. Error bars represent a standard deviation in measured parameters for 5 bubbles. 209

Figure 6.9. Reduced volume of the bubble shape and length scale ratio versus placement in a bubble train of ($\circ, \bullet$) 6 and ($\square, \blacksquare$) 8 bubbles. The open symbols indicate the reduced volume, and the filled symbols indicate L_p/L_b . Two bubble trains of 6 bubbles are plotted to indicate reproducibility. Error bars in the reduced volume are a standard deviation based on calculating the volume and surface area of both halves of the 2D projection of the bubble shape. 210

Figure 6.10. (a) Image of bidisperse bubble shapes due to break-up of bubbles at the outlet and (b) histogram of the reduced volume for the bubbles shown in (a). (c) Images of the bubble break-up at the outlet of the microchannel, showing a nonuniform bubble shape prior to break-up. The outlet at the right of each image is dark due to light scattering from the edge of the microfluidic device. The channel width for the images in (c) is 96 μm 212

CHAPTER 1

INTRODUCTION

The interface between two immiscible fluids can be stabilized by a variety of materials including surfactants, proteins, polymers, and solid particles. Fluid interfaces stabilized by these materials deform differently under an imposed stress, which influences properties such as the rheology and long-term stability of emulsions and foams. In order to control bulk properties, the relevant mechanical properties of the interface must be characterized. Interfacial rheological measurements can be conducted relating stress and strain at the interface. Despite more than a century of study of the mechanical properties of fluid interfaces, it is difficult to separate the intrinsic mechanics of the interface from the fluid mechanics acting on the surface or transport of surface-active material between the interface and the bulk liquid.

In rheology, the ideal way to measure fluid properties is to isolate the type of deformation in order to probe specific stress contributions. For example, the ideal way to measure the shear modulus of a fluid would be to generate a purely shearing flow. The same principle should be applied when measuring the rheology of fluid interfaces. To measure dilatational properties, a purely dilatational deformation must be generated. Also, the way in which interfaces are generated for interfacial rheological measurements does not necessarily correspond to the interfaces generated through high shear emulsification methods. The goal of this thesis is to improve the measurement of the dilatational properties

of complex fluid interfaces by better control over the generation of and deformation of these interfaces.

It is important to understand the rheology of a simple interface before explaining phenomena at the bubble or foam length scale. We can measure dilatational rheological properties for various interfaces by using microscale bubbles pinned at a capillary tip, but this thesis first addresses how the input and measured parameters are related to the desired interfacial rheological properties. Chapter 3 develops the relevant theory for measuring dilatational rheology using the microtensiometer, an in-house device capable of generating a purely dilatational strain at the interface. This chapter also describes ways of separating intrinsic rheological properties of the interface from the measured dilatational modulus, which we show is not a material property.

The techniques developed for measuring dilatational properties using the microtensiometer are applied in Chapter 4 to measure the properties of insoluble surfactant layers at an air-water interface. A procedure is developed to generate insoluble layers at an interface by exchanging a surfactant-soluble fluid with water; the resulting amount of insoluble material at the interface is controlled by the fluid exchange rate and the initial concentration of dissolved surfactant. The interface is probed using steady dilatation to measure equilibrium surface tension and oscillatory dilatation to measure the dilatational rheology of the interface. In order to confirm our measurement method, the surface properties of palmitic acid, dimyristoylphosphatidylcholine (DMPC), and dipalmitoylphosphatidylcholine (DPPC) measured on the microtensiometer are compared with measurements

from the literature. The interfacial properties of the insoluble component of a nonionic surfactant, Tween 80, are also measured.

Although the surface properties of interfaces can be measured as a function of surface coverage, is it difficult to experimentally determine a direct relationship between interfacial rheology and the bulk foam and emulsion properties. This is because there is no guarantee that the interfaces generated during emulsification are equivalent to those interfaces measured on conventional apparatuses for dilatational rheology. Common methods of generating foams and emulsions with complex interfaces involve high-shear homogenization; however, in these methods there is no control over the amount of material adsorbed at the interface or the size distribution of dispersed droplets and bubbles. Chapters 5 and 6 address this issue for a surface-active mixture of a cationic surfactant, cetyltrimethylammonium bromide, and colloidal silica nanoparticles.

Chapter 5 shows that confined slug bubbles traveling in the particle-surfactant mixture exhibit unique shape transitions due to the adsorption of particles at the bubble interface. As the bubble travels down the microchannel it exhibits a two-lobed shape due to particle adsorption and packing at rear of the bubble. By modeling the mass transport problem of convection-dominated particle mass transfer to the interface, we show that the shape transitions within the microchannel agree well with the growth of the particle stabilized region predicted by the model. The flux of particles to the interface is dominated by particle flux to the end cap regions, and the additional particle adsorption in the thin film and corner regions of the microchannel are negligible due to depletion

effects. Our results show that particle adsorption can be used to control surface coverage of particles on bubble interfaces.

In Chapter 6, we directly apply the particle adsorption model to show that the particle adsorption timescale relative to the residence time of the bubble in the device is a critical dimensionless timescale for the generation of monodisperse bubbles of uniform nonequilibrium shapes. We first address the assumptions in the previous chapter of particle packing at the rear of the dispersed phase by directly observing large (radius = 1 μm) latex particles adsorbing to an octanol slug droplet traveling in a confining capillary of circular or square cross-section. Particles are observed to pack at the rear of the droplet for both channel geometries, and the increase in particle packing as a function of residence time indicates that adsorption occurs during translation in the channel.

We then use the nanoparticle-surfactant mixture to generate monodisperse bubbles in uniform nonequilibrium shapes. These particle-stabilized capsules exhibit shapes unlike those of equilibrium vesicles at a similar reduced volume due to the dynamic process used to generate the bubbles. Using the transport model developed in Chapter 5, we develop a direct relationship relating the particle-stabilized length of the bubble to the residence time of the bubble in the microchannel. This relationship is shown to collapse the experimental results onto two lines depending on the device cross-section geometry, which is attributed to the bubble shape transitions that occur in rectangular microchannels. We also discuss issues in bubble generation that can cause deviations from uniform bubble

shapes due to particle mass transfer hindrance in trains of bubbles and bubble break-up at the channel outlet.

The results of this thesis show that precise dilatational measurement and generation of complex fluid interfaces can be performed in a straightforward manner. The methods described to generate and measure insoluble layers can be extended to a variety of other insoluble materials at air-water or oil-water interfaces. The adsorption timescales described in Chapters 5 and 6 provide a simple criterion for generating particle-stabilized interfaces. Together, these methods provide the tools for generating emulsions and foams with controllable interfacial properties.

CHAPTER 2

BACKGROUND

2.1 EQUILIBRIUM SURFACE TENSION

The surface tension σ of an interface separating two immiscible fluid phases is a tensile force per unit length acting within the plane of the interface that arises due to cohesive forces between molecules. An interface separating two “clean” fluid phases like air and solute-free water will have a constant surface tension independent of the rate of deformation. When the interface is curved the surface tension generates a force per unit area acting normal to the interface that manifests as a pressure difference Δp between the fluid phases:

$$\Delta p = 2H\sigma \quad (2.1)$$

where H is the mean curvature of the interface. For example, a spherical air bubble of radius R in water will have a mean curvature of R^{-1} , which means that the air pressure inside the bubble will exceed the pressure in the water phase by $2\sigma/R$. The relationship described in equation (2.1), called the Laplace equation, is useful in explaining droplet and bubble shapes, as well as free surface deformation due to fluid flow.¹

The mechanical properties of the interface can change dramatically when a surface-active material is present. The presence of a surface-active material at an air-water interface tends to decrease the surface tension from the measured value of the “clean” interface. This difference between the surface tension of the clean interface σ_0 and the surface tension corresponding to a surface concentration Γ of surface-active material adsorbed at the interface is called the surface pressure Π :

$$\Pi = \sigma_0 - \sigma(\Gamma). \quad (2.2)$$

The surface pressure can be measured for both stable and metastable interfaces.² The surface pressure of a stable interface can be measured independent of the compression rate of the interface, but metastable interfaces have a compression rate dependent surface pressure due to the formation of a second phase on the interface above a critical surface concentration. The surface pressure corresponding to this critical surface concentration is the equilibrium spreading pressure.

2.2 INTERFACIAL MECHANICAL PROPERTIES

When surface-active materials are adsorbed at an interface, we can model the interface as having intrinsic rheological properties – that is, the interface is treated as a two dimensional material independent of the fluid phases surrounding it. These properties relate the stresses in the interface to the deformation and deformation rates on the interface, analogous to rheological properties relating stress and strain in a bulk fluid phase. Different types of deformation yield different stress responses for the same interface, so ideally one would want to measure each deformation mode and the corresponding stress separately.

There are three basic deformation modes on a planar surface: shear, extension, and dilatation. When the interface is curved, a fourth type of deformation, bending, can become significant. A simple shearing strain on a square patch of interface with side length a deforms the interface into a parallelogram with base and height dimensions equal to a . An extensional strain deforms the same initial square into a rectangle with side lengths b and a^2/b . The total surface area is unchanged as the shape changes in shear and extension. A

dilatational deformation occurs when all sides of the square interface are expanded or compressed isotropically to side length $a+\delta a$, meaning that the shape of the interface stays the same while the surface area changes. The strain at the interface due to dilatation is $\delta a/a$. A pure bending deformation is a change in the curvature H of the interface at constant surface area.³ All four deformation modes can be present on a droplet interface, although the magnitude of the stress response from each deformation will vary based on the rheological properties of the droplet. Although there is much interest in measuring properties due to shear,⁴⁻⁶ extension,⁷⁻⁹ and bending¹⁰⁻¹² at fluid interfaces, the majority of our work focuses on purely dilatational deformations.

Just as in the rheology of bulk fluids, there are different ways to probe the relationship between dilatation and the resulting stress at the interface. Generally interfaces are strain-controlled, meaning that changes in the surface area are regulated and the resulting surface stress P^s is measured. The total surface stress includes both the surface pressure as well as stresses that arise due to the deformation of the interface. When small amplitude oscillatory dilatation at a frequency ω and amplitude ΔA is generated at a complex interface, the resulting surface stress will oscillate at the same frequency with amplitude ΔP^s that is shifted by a phase angle Φ . The relationship between stress ΔP^s and strain $\Delta A / A_{eq}$ is then reported as a dilatational modulus, E^*

$$E^* = E' + iE'' = \frac{dP^s}{d \ln A} e^{i\Phi} \approx A_{eq} \frac{\Delta P^s}{\Delta A} e^{i\Phi}. \quad (2.3)$$

E^* is a complex quantity that consists of an in-phase E' and out-of-phase E'' component; for a zero phase angle, the surface stress oscillations are in-phase

with the surface dilatation and $E'' = 0$, while for a phase angle of $\pi/2$ the stress oscillations are completely out-of-phase with the dilatation and $E' = 0$. A more detailed analysis of the dilatational modulus is given in Chapter 3 for apparatuses that do not measure surface stress or strain directly.

The dilatational modulus of complex interfaces is an important property that is linked to the microstructural characteristics of many different systems. On the single droplet scale, the dilatational rheology of a droplet interface affects the droplet mobility in flow,¹³ droplet deformation and break-up,^{14, 15} as well as droplet and bubble coalescence.^{16, 17} Dilatational stresses are also predicted to affect the strength of vesicle and capsule adhesion.^{18, 19} The dilatational modulus is directly linked to both the bulk and shear modulus of emulsions and foams.^{20, 21} The long-term stability of emulsions^{22, 23} and foams²⁴⁻²⁶ also depends on the magnitude of the dilatational modulus. In biological systems, the dilatational rheology of lung surfactant is critical to respiration,²⁷ and ultrasound contrast bubbles used in medical imaging have dilatational properties that can dramatically affect the performance of the bubbles as contrast agents.²⁸

2.3 SURFACE-ACTIVE MATERIALS

Interfaces can be stabilized by a variety of different surface active materials including soluble surfactants,^{29, 30} insoluble layers,^{2, 31} and solid colloidal particles.³² In Chapter 4 we focus primarily on insoluble layers comprised of palmitic acid, dimyristoylphosphatidylcholine (DMPC), or dipalmitoylphosphatidylcholine (DPPC), and in Chapters 5 and 6 we address

particle-stabilized interfaces comprised of mixtures of silica nanoparticles and a cationic surfactant.

2.3.1 INSOLUBLE LAYERS

Insoluble layers are formed when a substance that does not dissolve in water is spread at an air-aqueous interface. Lipids are a common type of molecule that form insoluble layers at fluid interfaces. Monolayers of lipid materials including phospholipids and fatty acids can be used as model systems for understanding processes in lipid bilayers.³³ Lipids are also a major component of pulmonary surfactant³⁴ and tear films protecting the eye,³⁵ which means that their mechanical response at interfaces is important in daily biological function.

Because insoluble monolayers do not desorb from the interface, it is possible to measure the surface pressure as a function of the surface area. When insoluble monolayers are spread in a dilute monolayer over the interface such that the molecules do not interact, the interface is described as a two-dimensional gas with surface pressures generally below 0.1 mN/m.³⁶ As the interface is compressed and the surface concentration increases, the monolayer forms a liquid-expanded region for surface pressures of the order of 1 mN/m, then transitions to a condensed phase at higher surface pressures. Phase coexistence regions of liquid expanded and condensed phases on the interface are possible; in this region, the surface pressure plateaus to approximately constant values as the interface is compressed.³⁷ In the condensed phase, the molecules are packed closely, and the hydrocarbon chains align parallel to one another but tilted relative to the interface. Further compression of the interface aligns the molecules

perpendicular to the interface and the interface acts like a two-dimensional solid.³⁷ Not all of these phase transitions are present for a specific molecule.

Fatty acid molecules are comprised of a carboxylic acid group attached to a hydrocarbon chain. The simplest fatty acids that form insoluble layers have a saturated unbranched hydrocarbon chain consisting of 14 to 22 carbon atoms.³⁸ Palmitic acid is a saturated fatty acid with a 16-carbon chain. Fatty acids are known to form spread monolayers when deposited on an aqueous subphase in a Langmuir trough. When the subphase has a $\text{pH} > 10$, the carboxyl group becomes ionized, which leads to increased solubility with the subphase;³⁹ however these effects are negligible below a pH of 6.4 for long-chain fatty acids like palmitic acid.⁴⁰ Fatty acids have an equilibrium spreading pressure, which is the surface pressure reached for a monolayer in equilibrium with the crystal phase at the interface.⁴¹ For palmitic acid at 20°C , the equilibrium spreading pressure is approximately 10 mN/m.⁴¹ Monolayers compressed to surface pressures above this value will spontaneously form crystals at the interface to return the surface pressure to the equilibrium value. At 20°C , palmitic acid forms a condensed phase at low surface pressures that persists until the solid phase is reached at approximately 25 mN/m.⁴² This is greater than the equilibrium spreading pressure, meaning that the interface must be compressed rapidly enough to avoid significant crystal formation.⁴³ The fact that surface pressure-area diagrams are reproducible across different measurement apparatuses and research groups indicates that the monolayer is in a metastable state during compression.

DMPC and DPPC are two phospholipids, each with two fatty acid tails connected to a choline headgroup by a glycerophosphoric acid group. The fatty acid chains in DMPC are myristic acid, a 14-carbon saturated fatty acid, and the chains in DPPC are palmitic acid. The effect of pH on the measured surface pressures of these monolayers is not significant until pH 9 for DPPC⁴⁴ and above pH 10 for DMPC.⁴⁵ Below the melting temperatures for DMPC and DPPC (23.0°C and 41.2°C, respectively), the equilibrium spreading pressure measured for these phospholipids is less than 1 mN/m,⁴⁶ meaning that most surface pressure measurements are made while the interface is in a metastable state. Despite this, compression rate effects are not commonly observed on phospholipid monolayers spread on a Langmuir trough.⁴⁷ DMPC exhibits a liquid expanded phase over the entire surface pressure range at room temperature,⁴⁸ while DPPC shows three regions: a liquid expanded phase, a coexistence region of liquid expanded and condensed phases, and a condensed phase at higher surface pressures.

2.3.2. PARTICLES

Particle stabilized emulsions and foams have a variety of uses in pharmaceuticals,⁴⁹ composite materials,⁵⁰ cosmetics,⁵¹ and food products.⁵² Catalytically-active particles can be used to both stabilize an emulsion and promote chemical reactions at the fluid interface.^{53, 54} Solid particles adsorbed at fluid interfaces have been recognized as efficient emulsion stabilizers since the early 1900s.^{55, 56} Colloidal particles with sizes ranging from approximately 10 nm – 1 μm at fluid interfaces have properties that are significantly different from molecular surfactants. Adsorbed particles require a large amount of energy to

desorb from fluid interfaces; for example, a particle of 10 nm radius requires over 1000 times more energy than a surfactant molecule to detach from the interface.⁵⁷ This allows for the generation of bubbles and droplets in nonequilibrium shapes due to the formation of a jammed particle network at the interface.^{58, 59} The finite size of the particles prevents coalescence of stabilized interfaces due to steric effects.⁶⁰

Surfactants are often added to particle suspensions to alter the wettability of particles and enhance the adsorption of particles to the interface.⁶¹⁻⁶³ A mixture of colloidal silica and a cationic surfactant, CTAB, is an example of such a system.⁶⁴ Colloidal silica with a negative surface charge cannot stabilize fluid interfaces alone due to the favorable aqueous phase wettability of the particles. The addition of CTAB to the suspension causes adsorption of the positively-charged surfactant molecules to the particle surface,⁶⁵ which decreases the particle wettability. During a bulk emulsification process, CTAB-modified silica particles tend to form multilayers at fluid interfaces,⁶⁶ and nonspherical bubble and droplet shapes are occasionally observed for different oil-water and air-water systems.^{61, 67} Mixtures of particles and surfactants are useful in floatation processes⁶⁴ and foam stabilization.⁶⁸

1. Clift, R.; Grace, J. R.; Weber, M. E., *Bubbles, Drops, and Particles*. Dover Publications, Inc.: Mineola, 2005.
2. Gaines, G. L., *Insoluble monolayers at liquid-gas interfaces*. 1966.
3. Kralchevsky, P. A., Micromechanical description of curved interfaces, thin films, and membranes: I. Quasistatics. *Journal of colloid and interface science* **1990**, 137, (1), 217-233.
4. Erni, P.; Fischer, P.; Windhab, E. J.; Kusnezov, V.; Stettin, H.; Luger, J., Stress-and strain-controlled measurements of interfacial shear viscosity and viscoelasticity at liquid/liquid and gas/liquid interfaces. *Review of scientific instruments* **2003**, 74, (11), 4916-4924.
5. Krgel, J.; Derkatch, S. R., Interfacial shear rheology. *Current Opinion in Colloid & Interface Science* **2010**, 15, (4), 246-255.
6. Krgel, J.; Derkatch, S.; Miller, R., Interfacial shear rheology of protein-surfactant layers. *Advances in colloid and interface science* **2008**, 144, (1), 38-53.
7. Verwijlen, T.; Leiske, D.; Moldenaers, P.; Vermant, J.; Fuller, G., Extensional rheometry at interfaces: Analysis of the Cambridge Interfacial Tensiometer. *Journal of Rheology (1978-present)* **2012**, 56, (5), 1225.
8. Jones, D. B.; Middelberg, A. P., Direct determination of the mechanical properties of an interfacially adsorbed protein film. *Chemical engineering science* **2002**, 57, (10), 1711-1722.
9. Dimitrijević-Dwyer, M.; Middelberg, A. P., The extensional viscoelasticity of protein-coated interfaces. *Soft Matter* **2011**, 7, (17), 7772-7781.
10. Evans, E. A., Bending elastic modulus of red blood cell membrane derived from buckling instability in micropipet aspiration tests. *Biophysical journal* **1983**, 43, (1), 27-30.
11. Evans, E.; Rawicz, W., Entropy-driven tension and bending elasticity in condensed-fluid membranes. *Physical Review Letters* **1990**, 64, (17), 2094.
12. Dobereiner, H.-G., Properties of giant vesicles. *Current Opinion in Colloid & Interface Science* **2000**, 5, (3), 256-263.
13. Schwalbe, J. T.; Phelan Jr, F. R.; Vlahovska, P. M.; Hudson, S. D., Interfacial effects on droplet dynamics in Poiseuille flow. *Soft Matter* **2011**, 7, (17), 7797-7804.

14. Williams, A.; Janssen, J.; Prins, A., Behaviour of droplets in simple shear flow in the presence of a protein emulsifier. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1997**, 125, (2), 189-200.
15. Pozrikidis, C., Effects of surface viscosity on the finite deformation of a liquid drop and the rheology of dilute emulsions in simple shearing flow. *Journal of non-newtonian fluid mechanics* **1994**, 51, (2), 161-178.
16. Reichert, M. D. Using Microscale Interfaces to Connect Transport Dynamics, Interfacial Mechanics, and Coalescence Behavior for a Model Oil-Dispersant-Aqueous System. CARNEGIE MELLON UNIVERSITY, 2013.
17. Malcolm, A. S.; Dexter, A. F.; Katakdhond, J. A.; Karakashev, S. I.; Nguyen, A. V.; Middelberg, A. P., Tuneable control of interfacial rheology and emulsion coalescence. *ChemPhysChem* **2009**, 10, (5), 778-781.
18. Ramachandran, A.; Leal, G., A scaling theory for the hydrodynamic interaction between a pair of vesicles or capsules. *Physics of Fluids (1994-present)* **2010**, 22, (9), 091702.
19. Ramachandran, A.; Anderson, T. H.; Leal, L. G.; Israelachvili, J. N., Adhesive interactions between vesicles in the strong adhesion limit. *Langmuir* **2010**, 27, (1), 59-73.
20. Edwards, D. A.; Brenner, H.; Wasan, D. T., *Interfacial transport processes and rheology*. Butterworth-Heinemann Boston: 1991.
21. Flumerfelt, R. W., Effects of dynamic interfacial properties on drop deformation and orientation in shear and extensional flow fields. *Journal of colloid and interface science* **1980**, 76, (2), 330-349.
22. Dicharry, C.; Arla, D.; Siquin, A.; Graciaa, A.; Bouriat, P., Stability of water/crude oil emulsions based on interfacial dilatational rheology. *Journal of colloid and interface science* **2006**, 297, (2), 785-791.
23. Dickinson, E., Milk protein interfacial layers and the relationship to emulsion stability and rheology. *Colloids and Surfaces B: Biointerfaces* **2001**, 20, (3), 197-210.
24. Monteux, C.; Fuller, G. G.; Bergeron, V., Shear and dilational surface rheology of oppositely charged polyelectrolyte/surfactant microgels adsorbed at the air-water interface. Influence on foam stability. *The Journal of Physical Chemistry B* **2004**, 108, (42), 16473-16482.

25. Wasan, D.; Nikolov, A.; Lobo, L.; Koczko, K.; Edwards, D., Foams, thin films and surface rheological properties. *Progress in Surface Science* **1992**, 39, (2), 119-154.
26. Stocco, A.; Drenckhan, W.; Rio, E.; Langevin, D.; Binks, B. P., Particle-stabilised foams: an interfacial study. *Soft Matter* **2009**, 5, (11), 2215-2222.
27. Bangham, A.; Morley, C.; Phillips, M., The physical properties of an effective lung surfactant. *Biochimica et Biophysica Acta (BBA)-Lipids and Lipid Metabolism* **1979**, 573, (3), 552-556.
28. Sarkar, K.; Shi, W. T.; Chatterjee, D.; Forsberg, F., Characterization of ultrasound contrast microbubbles using in vitro experiments and viscous and viscoelastic interface models for encapsulation. *The Journal of the Acoustical Society of America* **2005**, 118, (1), 539-550.
29. Möbius, D.; Miller, R.; Fainerman, V. B., *Surfactants: Chemistry, Interfacial Properties, Applications: Chemistry, Interfacial Properties, Applications*. Elsevier: 2001; Vol. 13.
30. Joos, P., *Dynamic surface phenomena*. VSP: 1999.
31. MacRitchie, F., *Chemistry at interfaces*. Elsevier: 1990.
32. Binks, B. P.; Horozov, T. S., *Colloidal Particles at Liquid Interfaces*. Cambridge University Press: Cambridge, 2006.
33. Stefaniu, C.; Brezesinski, G.; Möhwald, H., Langmuir monolayers as models to study processes at membrane surfaces. *Advances in colloid and interface science* **2014**.
34. Veldhuizen, R.; Nag, K.; Orgeig, S.; Possmayer, F., The role of lipids in pulmonary surfactant. *Biochimica et Biophysica Acta (BBA)-Molecular Basis of Disease* **1998**, 1408, (2), 90-108.
35. Craig, J. P.; Tomlinson, A., Importance of the lipid layer in human tear film stability and evaporation. *Optometry & Vision Science* **1997**, 74, (1), 8-13.
36. Hiemenz, P. C.; Rajagopalan, R., *Principles of Colloid and Surface Chemistry, revised and expanded*. CRC Press: 1997; Vol. 14.
37. Kaganer, V. M.; Möhwald, H.; Dutta, P., Structure and phase transitions in Langmuir monolayers. *Reviews of Modern Physics* **1999**, 71, (3), 779.

38. Overbeck, G. A.; Moebius, D., A new phase in the generalized phase diagram of monolayer films of long-chain fatty acids. *The Journal of Physical Chemistry* **1993**, 97, (30), 7999-8004.
39. Lyons, C.; Rideal, E. K., On the Stability of Unimolecular Films. Part III. Dissolution in Alkaline Solutions. *Proceedings of the Royal Society of London. Series A* **1929**, 124, (794), 344-355.
40. Spink, J. A., Ionization of monolayers of fatty acids from C₁₄ to C₁₈. *Journal of Colloid Science* **1963**, 18, (6), 512-525.
41. Boyd, G.; Schubert, J., Energy relations in unimolecular film formation: the spreading of cetyl alcohol and palmitic acid on aqueous surfaces. *The Journal of Physical Chemistry* **1957**, 61, (10), 1271-1275.
42. Bibo, A. M.; Peterson, I. R., Phase diagrams of monolayers of the long chain fatty acids. *Advanced Materials* **1990**, 2, (6-7), 309-311.
43. Rabinovitch, W.; Robertson, R.; Mason, S., Relaxation of surface pressure and collapse of unimolecular films of stearic acid. *Canadian Journal of Chemistry* **1960**, 38, (10), 1881-1890.
44. Lucero, A.; Rodríguez Niño, M.; Gunning, A.; Morris, V.; Wilde, P.; Rodríguez Patino, J., Effect of hydrocarbon chain and pH on structural and topographical characteristics of phospholipid monolayers. *The Journal of Physical Chemistry B* **2008**, 112, (25), 7651-7661.
45. Mercado, F. V.; Maggio, B.; Wilke, N., Phase diagram of mixed monolayers of stearic acid and dimyristoylphosphatidylcholine. Effect of the acid ionization. *Chemistry and physics of lipids* **2011**, 164, (5), 386-392.
46. Mansour, H. M.; Zograf, G., Relationships between equilibrium spreading pressure and phase equilibria of phospholipid bilayers and monolayers at the air-water interface. *Langmuir* **2007**, 23, (7), 3809-3819.
47. Jyoti, A.; Prokop, R.; Li, J.; Vollhardt, D.; Kwok, D.; Miller, R.; Möhwal, H.; Neumann, A., An investigation of the compression rate dependence on the surface pressure-surface area isotherm for a dipalmitoyl phosphatidylcholine monolayer at the air/water interface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1996**, 116, (1), 173-180.
48. Park, C.; Schmitt, F.; Evert, L.; Schwartz, D.; Israelachvili, J.; Knobler, C., Film balance and fluorescence microscopic investigation of the effects of Ca²⁺ on mixed DMPC/DMPG monolayers. *Langmuir* **1999**, 15, (1), 202-206.

49. Dinsmore, A.; Hsu, M. F.; Nikolaides, M.; Marquez, M.; Bausch, A.; Weitz, D., Colloidosomes: selectively permeable capsules composed of colloidal particles. *Science* **2002**, 298, (5595), 1006-1009.
50. Menner, A.; Verdejo, R.; Shaffer, M.; Bismarck, A., Particle-stabilized surfactant-free medium internal phase emulsions as templates for porous nanocomposite materials: poly-pickering-foams. *Langmuir* **2007**, 23, (5), 2398-2403.
51. Rayner, M.; Marku, D.; Eriksson, M.; Sjöö, M.; Dejmek, P.; Wahlgren, M., Biomass-based particles for the formulation of Pickering type emulsions in food and topical applications. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2014**.
52. Dickinson, E., Food emulsions and foams: Stabilization by particles. *Current Opinion in Colloid & Interface Science* **2010**, 15, (1), 40-49.
53. Faria, J.; Ruiz, M. P.; Resasco, D. E., Phase-Selective Catalysis in Emulsions Stabilized by Janus Silica-Nanoparticles. *Advanced Synthesis & Catalysis* **2010**, 352, (14-15), 2359-2364.
54. Zhou, W.-J.; Fang, L.; Fan, Z.; Albela, B.; Bonneviot, L.; De Campo, F.; Pera-Titus, M.; Clacens, J.-M., Tunable catalysts for solvent-free biphasic systems—Pickering Interfacial Catalysts over amphiphilic silica nanoparticles. *Journal of the American Chemical Society* **2014**.
55. Ramsden, W., Separation of Solids in the Surface-Layers of Solutions and 'Suspensions' (Observations on Surface-Membranes, Bubbles, Emulsions, and Mechanical Coagulation).--Preliminary Account. *Proceedings of the Royal Society of London* **1903**, 156-164.
56. Pickering, S. U., Cxcvi.—emulsions. *Journal of the Chemical Society, Transactions* **1907**, 91, 2001-2021.
57. Binks, B. P., Particles as surfactants—similarities and differences. *Current Opinion in Colloid & Interface Science* **2002**, 7, (1), 21-41.
58. Pawar, A. B.; Caggioni, M.; Ergun, R.; Hartel, R. W.; Spicer, P. T., Arrested coalescence in Pickering emulsions. *Soft Matter* **2011**, 7, (17), 7710-7716.
59. Subramaniam, A. B.; Abkarian, M.; Mahadevan, L.; Stone, H. A., Colloid science: Non-spherical bubbles. *Nature* **2005**, 438, (7070), 930-930.
60. Hunter, T. N.; Pugh, R. J.; Franks, G. V.; Jameson, G. J., The role of particles in stabilising foams and emulsions. *Advances in colloid and interface science* **2008**, 137, (2), 57-81.

61. Binks, B. P.; Kirkland, M.; Rodrigues, J. A., Origin of stabilisation of aqueous foams in nanoparticle–surfactant mixtures. *Soft Matter* **2008**, 4, (12), 2373-2382.
62. Akartuna, I.; Studart, A. R.; Tervoort, E.; Gonzenbach, U. T.; Gauckler, L. J., Stabilization of oil-in-water emulsions by colloidal particles modified with short amphiphiles. *Langmuir* **2008**, 24, (14), 7161-7168.
63. Garbin, V.; Crocker, J. C.; Stebe, K. J., Nanoparticles at fluid interfaces: Exploiting capping ligands to control adsorption, stability and dynamics. *Journal of colloid and interface science* **2012**, 387, (1), 1-11.
64. Hassander, H.; Johansson, B.; Törnell, B., The mechanism of emulsion stabilization by small silica (Ludox) particles. *Colloids and surfaces* **1989**, 40, 93-105.
65. Wang, W.; Gu, B.; Liang, L.; Hamilton, W. A., Adsorption and structural arrangement of cetyltrimethylammonium cations at the silica nanoparticle-water interface. *The Journal of Physical Chemistry B* **2004**, 108, (45), 17477-17483.
66. Binks, B. P.; Rodrigues, J. A.; Frith, W. J., Synergistic interaction in emulsions stabilized by a mixture of silica nanoparticles and cationic surfactant. *Langmuir* **2007**, 23, (7), 3626-3636.
67. Ravera, F.; Ferrari, M.; Liggieri, L.; Loglio, G.; Santini, E.; Zanobini, A., Liquid–liquid interfacial properties of mixed nanoparticle–surfactant systems. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2008**, 323, (1), 99-108.
68. Carn, F.; Colin, A.; Pitois, O.; Vignes-Adler, M.; Backov, R., Foam Drainage in the Presence of Nanoparticle– Surfactant Mixtures. *Langmuir* **2009**, 25, (14), 7847-7856.

CHAPTER 3

REGULAR PERTURBATION ANALYSIS OF SMALL AMPLITUDE OSCILLATORY DILATATION OF AN INTERFACE IN A CAPILLARY PRESSURE TENSIO METER

3.1 INTRODUCTION

Interfacial rheology is the study of the response of complex fluid interfaces to deformation, and is an important aspect of the bulk rheological properties of fluid-fluid dispersions.¹ Through rheological measurements of complex fluid interfaces, the stress generated within an interface due to a specific type of surface deformation can be linked to the interfacial microstructure.

Surface deformation can be categorized according to fundamental modes including shear, extensional, dilatational, and bending. Interfacial shear stresses arise from deformations in the shape of the interface and extensional stresses arise from an expansion of the interface. Bending stresses are related to changes in the interfacial curvature. Although shear, extension, and bending stresses can all occur at a constant surface area, the stress due to dilatational deformation arises from expansions in the interfacial area while preserving the interface shape. The dilatational motion of an interface is analogous to the volume expansion of a compressible fluid. One significant difference is that although very few single-phase fluids are compressible, the interface between two fluid phases is often highly compressible. This property allows for the formation of new interfaces during droplet break-up or the nucleation and dissolution of gas bubbles in liquid. Dilatational stresses have been linked to emulsion and foam stability, as well as the bulk viscosity of these systems.^{2,3}

Dilatational rheology focuses on the response of a fluid-fluid interface to axisymmetric expansion or compression. There are a variety of ways that interfaces can resist dilation due to the wide array of materials that can be adsorbed at fluid interfaces. Examples of dilatational rheological responses due to the intrinsic microstructure of the interface include the dilatational viscosity and the viscoelasticity of adsorbed proteins, polymers, and particles.⁴ For example, proteins exhibit conformational changes at the air-water interface which promote aggregation, leading to an increase in the dilatational modulus.⁵ The dilatational modulus of polymers at air-liquid interfaces depends on polymer chain interactions, and the modulus will vary depending on the solvent quality of the liquid.⁶ Solid particles at the interface can interact through colloidal⁷ and capillary⁸ forces that can cause an increase in the modulus through particle clustering.⁹ In purely dilatational flows on the interface, there are only isotropic contributions to the measured interfacial stress. The interfacial tension σ is an isotropic stress that depends on the instantaneous surface concentration Γ of adsorbed species through a thermodynamic equation of state. The surface tension is a two-dimensional counterpart to the hydrostatic pressure of a three-dimensional fluid.¹ Other stresses may arise due to deformation of the interface – these extra stresses τ depend on the rate of deformation of the interface and may also depend on the surface composition.

An ideal measurement of the dilatational stresses on the interface would involve the shape-preserving expansion of an interface for fixed surface tension. This is rarely achievable in practice since compositional changes that alter surface

tension often accompany expansion of the interface. A common approach to measuring dilatational properties is by small amplitude oscillatory dilation, and the relationship reported between the surface area dilation and the change in the surface stresses is the modulus $d\sigma / d \ln A$, sometimes called the “dilatational viscoelasticity.”^{2, 4, 10, 11} The inverse of this value is termed the compressibility, which is normally measured during a lateral compression of the interface on a Langmuir trough.¹² When a surface-active material is irreversibly adsorbed to the interface, the surface tension varies with changes in the instantaneous concentration of surface-active material at the interface, meaning that the measured modulus is the sum of static and dynamic surface stresses. If the material at the interface has a soluble component, then the surface concentration (and therefore the surface tension) will be a time-dependent function related to the bulk mass transfer to/from the dilating interface. Mass transport results in an apparent interfacial viscoelasticity that requires accurate knowledge of the relevant transport parameters in order to separate from the dynamic surface stresses.¹³ It is desirable from a rheology standpoint to separate the surface tension stresses from the dynamic stresses to enable development of constitutive models relating the dynamic stresses to the interfacial microstructure.

An ideal apparatus for dilatational rheological measurements is one in which the interfacial deformation is well-characterized and independent of the interfacial stress response; however, it is often difficult to avoid mixed flows of shear and dilation at the interface. Dilatational apparatuses either perform measurements on a flat interface (“trough” methods) or on an interface with some

curvature (“drop/bubble” methods). The most common trough system is the Langmuir trough, where a barrier at one end of the trough is used to expand or compress a monolayer at an air-water interface, and the surface pressure is measured by a Wilhelmy plate.¹⁴ This system has been shown to excite both shear and dilatational modes on the interface, and two Wilhelmy plates must be used to separate the stresses due to shear and dilation.¹⁵ Although other devices have been proposed to generate uniform dilation on a planar fluid interface,^{16, 17} these devices must extend into the bulk fluid, and the resulting flow problem is difficult to decouple to measure only interfacial stresses.¹⁰ Recently, Verwijlen *et al.* have developed an attachment for commercial rotational rheometers that can measure the dilatational properties of flat interfaces.¹⁸ This system generates a mixed flow field of shear and dilatation that can be used to measure the complex dilatational viscosity.

Common drop/bubble approaches to dilatational measurements include the pendant bubble apparatus and the capillary pressure tensiometer. In the pendant bubble apparatus, a bubble generated at a capillary tip is distorted by gravity into a shape which is related to the surface tension of the interface at equilibrium through the Young-Laplace equation. The pendant bubble apparatus is a useful tool to measure surface tension dynamics through an automated image acquisition and analysis system,¹⁹ but the analysis assumes that the only stress at the interface is the thermodynamic surface tension. During oscillatory measurements this system is known to excite both shear and dilation on the interface due to the presence of two distinct radii of curvature.²⁰ Because capillary pressure

tensiometers generally have a single radius of curvature, these apparatuses have the potential to measure purely dilatational properties of fluid interfaces.

In this work, we present an analysis of interfacial dilatational measurements using a capillary pressure tensiometer approach. By determining the effects of the geometry on the measured dilatational modulus, we will show that the surface tension stresses can be separated from the extra stresses. We will first use a regular perturbation expansion for pressure-controlled small amplitude oscillation in order to calculate the dilatational modulus based on experimentally-measured parameters, namely the pressure jump and the radius. We will then apply this perturbation expansion approach on two common interfacial models that exhibit both surface tension stresses and interfacial rheology through dilatational extra stresses. Our analysis shows that the dilatational modulus of these complex interfaces will vary with the radius of curvature of the interface based on whether the interface is soluble or insoluble with the bulk phase. In order to separate surface tension from intrinsic rheological parameters, we describe a useful methodology that can be applied to capillary pressure tensiometers that uses a measurement of the crossover frequency at various spherical cap sizes. The crossover frequency is shown to vary with the geometry in a way that indicates surface tension effects for either soluble or insoluble layers at the interface.

After showing the methodology for measurements on capillary pressure tensiometer systems, we revisit the small-amplitude assumption made in these apparatuses to develop an analytical approximation for higher harmonics in the

rate of dilatation and the surface stress based on oscillations in the pressure and the radius that can be applied in-line on a measurement apparatus. We discuss the practical measurement of the dilatational modulus on various capillary pressure tensiometers, including the microtensiometer. Due to the small length scales, a measurement of the dilatational modulus on the microtensiometer contains negligible contributions due to gravity, viscous stresses, and inertia. Lastly, we construct an operating diagram for the microtensiometer measuring the modulus of purely viscous interface.

3.2 SMALL AMPLITUDE OSCILLATORY DILATATION OF A SPHERICAL CAP BUBBLE

Consider a small bubble pinned at the tip of a capillary tube. If gravity is negligible, then the bubble surface will form a spherical cap with uniform radius of curvature R . For a static bubble, the Laplace equation describes the relationship between surface tension σ and the discontinuous pressure jump Δp across the curved interface,

$$\sigma = \frac{\Delta p R}{2}. \quad (3.1)$$

Oscillation of the pressure inside the bubble results in a change in bubble volume and commensurate dilation and compression of the bubble surface area. The associated shape change of the bubble depends on the pinning condition at the rim of the capillary. If the contact angle is allowed to vary, the bubble maintains a spherical cap shape and the radius of curvature oscillates in response to the pressure change. If the contact angle remains fixed, then the shape must deviate from a spherical cap, but at small amplitude, a spherical cap shape may

still be assumed. An oscillating interface that maintains a spherical cap shape undergoes a purely dilatational deformation.^{11, 20} The kinematics of the deformation may be quantified in terms of the dilatational strain rate, $\dot{\delta} = d \ln A / dt$, where the instantaneous surface area is given in terms of the bubble radius R and the radius of the capillary tube R_c ,

$$A = 2\pi R \left(R \pm \sqrt{R^2 - R_c^2} \right). \quad (3.2)$$

The plus or minus sign is chosen depending on whether the interface is larger or smaller than the hemisphere, as shown in Figure 3.1.

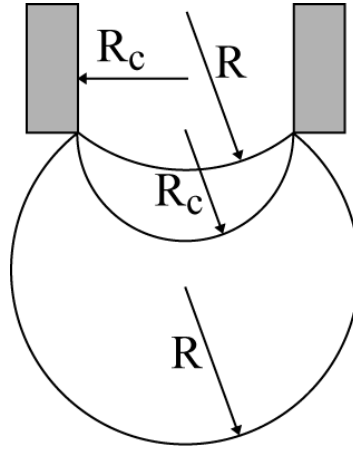


Figure 3.1. Schematic diagram of a capillary pressure tensiometer. The bubble pinned at the capillary tip can be either smaller or larger than a hemisphere with the same radius of curvature R . The minimum radius of curvature for the bubble occurs when R is equal to the radius of the capillary tip R_c .

The response of the interface to oscillation results from the dilatational stresses within the interface, which arise from both surface tension and extra stresses imparted by the microstructure of the interface. The normal force balance at the interface relates the surface excess normal stress P^s to the discontinuous pressure jump across the interface in the absence of body forces and bulk fluid stresses, given by^{1, 21, 22}

$$P^s = \frac{\Delta p R}{2}. \quad (3.3)$$

The surface excess normal stress can be expressed in terms of components of the surface excess pressure tensor $\mathbf{P}^s$,¹ which can be written in spherical coordinates as

$$\mathbf{P}^s = \begin{bmatrix} \sigma + \tau_{\theta\theta} & \tau_{\theta\phi} & \tau_{\theta r} \\ \tau_{\phi\theta} & \sigma + \tau_{\phi\phi} & \tau_{\phi r} \\ \tau_{r\theta} & \tau_{r\phi} & \sigma + \tau_{rr} \end{bmatrix}, \quad (3.4)$$

where θ is the azimuthal angle, ϕ is the polar angle measured from the apex of the bubble, and r is the coordinate directed outward normal to the interface. As shown schematically in Figure 3.2, the stresses $\tau_{\theta\theta}$ and $\tau_{\phi\phi}$ are dilatational interfacial stresses, $\tau_{\phi\theta}$ and $\tau_{\theta\phi}$ are shear interfacial stresses, and $\tau_{\phi r}$ and $\tau_{r\phi}$ are bending stresses. The bending stresses are directed outward normal to the plane of the interface, and typically occur due to transverse shear stresses generated when the interfacial structure has a nonzero thickness.²¹

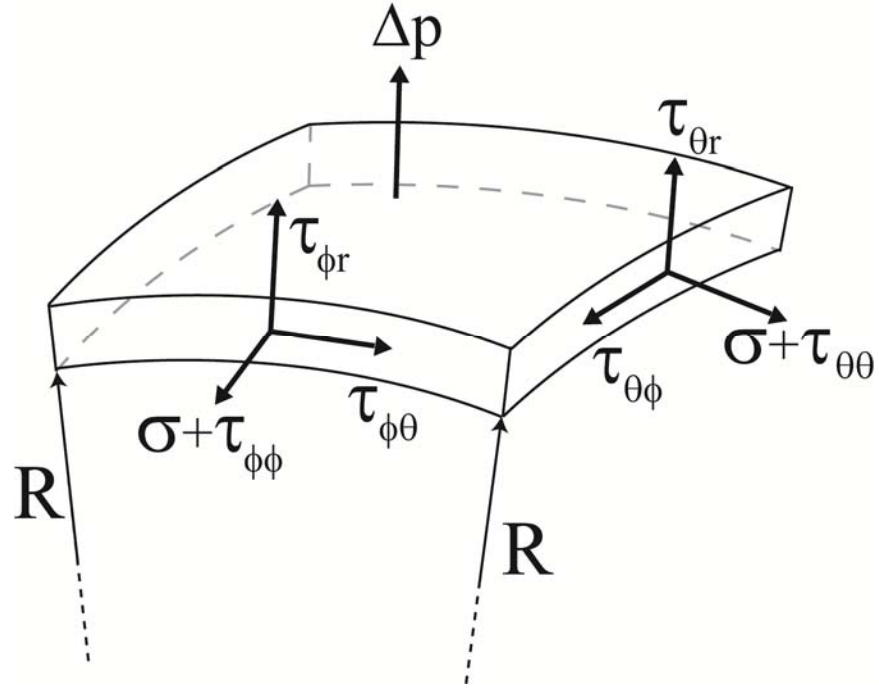


Figure 3.2. Schematic illustration of the surface stresses acting on a section of an interface with radius of curvature R .

Applying equation (3.4) to the normal stress balance for a spherical cap bubble undergoing axisymmetric small amplitude oscillation yields a surface excess normal stress given by

$$P^s = \sigma + \frac{1}{2}(\tau_{\theta\theta} + \tau_{\phi\phi}) - \tau_{\phi r} \cot \phi - \frac{d\tau_{\phi r}}{d\phi}. \quad (3.5)$$

The surface excess normal stress P^s includes contributions from interfacial dilation and bending, but not shear. Complex interfaces such as particle monolayers²³ exhibit nonzero bending moduli that can be important when measuring properties of curved interfaces.²² The Helfrich model²⁴ can be used to estimate the magnitude of the bending stress, which depends on both the bending modulus and radius of curvature of the interface, $\tau_{\phi r} \approx E_B / R^2$.²⁵ For an

interfacial radius of 30 μm , the bending modulus E_B must be greater than $2 \times 10^8 kT$ to change the measured surface stress by 1 mN/m. Small bending moduli on the order of $0.1 - 10 kT$ are common for surfactant monolayers²⁶ and lipid bilayers,²⁷ whereas highly packed particle-coated interfaces can exhibit bending moduli of the order of $10^{10} - 10^{12} kT$.^{23, 28} Although the bending modulus cannot be neglected for some interfaces, in this paper we will restrict the analysis to interfaces with a negligible bending modulus compared with the surface tension and dilatational stresses.

Combining equations (3.3) and (3.5) while neglecting bending stresses produces a relationship between quantities that are experimentally measured or controlled and the interfacial stresses, given by

$$\frac{\Delta p R}{2} = \sigma + \frac{1}{2}(\tau_{\theta\theta} + \tau_{\phi\phi}). \quad (3.6)$$

When surface tension alone contributes to the interfacial stress, equation (3.1) is recovered.

The surface excess normal stress is commonly related to the dilatational strain via a dilatational modulus, defined by

$$E \equiv \frac{dP^s}{d \ln A} = \frac{d\sigma}{d \ln A} + \frac{1}{2} \frac{d(\tau_{\theta\theta} + \tau_{\phi\phi})}{d \ln A}. \quad (3.7)$$

The contribution to the modulus from surface tension alone is denoted the Gibbs modulus, and the compressibility measured on a Langmuir trough is the inverse of the Gibbs modulus.

Equation (3.7) shows that even when a purely dilatational deformation is imposed, and interfacial shear stresses, bending stresses, and bulk fluid

contributions can be neglected, a measurement of the dilatational modulus still contains possible contributions from both surface tension and dilatational extra stresses. In a typical experimental apparatus, either pressure or radius/volume is controlled, and the other is measured. Thus, the interfacial stress contains both a measured and a controlled quantity, and experiments are neither purely stress nor strain rate controlled. The interfacial response therefore must be interpreted in the context of a constitutive model for the interfacial stresses.

To obtain an expression for the dilatational modulus in terms of an arbitrary interfacial constitutive model, let us assume that sinusoidal oscillations are imposed in the pressure jump across the interface, such that

$$\Delta p = p_a (1 + \varepsilon \sin \omega t) \quad (3.8)$$

where p_a is an equilibrium pressure offset and ε is the relative amplitude of the pressure oscillation. The response of the radius to pressure fluctuations is given by equation (3.6), meaning that it depends on the surface equation of state *and* the rheological constitutive model describing the extra surface stresses. The oscillatory response of the radius for an arbitrary interface can be written in terms of a regular perturbation expansion in the parameter ε ²⁹

$$R = R_{eq} \left(1 + \varepsilon g_1(t) + \varepsilon^2 g_2(t) + O(\varepsilon^3) \right), \quad (3.9)$$

where the equilibrium radius R_{eq} , and the specific functions g_1 and g_2 can be found once an interfacial rheological model is specified. Small amplitude oscillations are imposed such that order ε^2 and higher terms can be neglected.

Combining equations (3.3), (3.8) and (3.9) gives the expansion for the surface excess normal stress,

$$P^s = \frac{\Delta p R}{2} = \frac{p_a R_{eq}}{2} \left(1 + \varepsilon (\sin \omega t + g_1) + \varepsilon^2 (g_1 \sin \omega t + g_2) + O(\varepsilon^3) \right). \quad (3.10)$$

An expansion for the interfacial area can be found by combining equations (3.2) and (3.9)

$$A = 2\pi R_{eq}^2 (1 \pm b_1) \left[1 + \left(\pm \frac{(1 \pm b_1)}{b_1} g_1 \right) \varepsilon + \left(\left(\frac{(1 \pm b_1)(2b_1 \mp 1)}{2b_1^3} \right) g_1^2 + \left(\pm \frac{(1 \pm b_1)}{b_1} g_2 \right) \right) \varepsilon^2 + O(\varepsilon^3) \right], \quad (3.11a)$$

where

$$b_1 = \sqrt{1 - \left(\frac{R_c}{R_{eq}} \right)^2} \quad (3.11b)$$

is a dimensionless geometric parameter that describes the equilibrium shape of the bubble. As $b_1 \rightarrow 0$ the spherical cap approaches a hemisphere, and as $b_1 \rightarrow 1$ the spherical cap approaches either a sphere much larger than the capillary or a flat interface at the capillary tip, depending on whether the bubble is larger or smaller than the hemispherical cap. The term outside the square brackets in equation (3.11a) is the equilibrium surface area, A_{eq} .

The amplitudes of the first and second order terms in the above expansions can be used to determine the dilatational modulus in the small amplitude limit. Following from equation (3.7), the dilatational modulus in oscillatory dilatation can be expressed as a complex function given by

$$E^* = E' + iE'' = \frac{dP^s}{d \ln A} e^{i\Phi} \approx A_{eq} \frac{\Delta P_1^s}{\Delta A_1} e^{i\Phi} \quad (3.12)$$

where ΔP_1^s and $\Delta A_1 / A_{eq}$ are the amplitudes of the surface stress and the area strain in the small amplitude limit. The phase angle Φ is a measure of the time lag between the surface stress and area strain oscillations. The magnitude of the complex modulus is given by $|E^*| = \sqrt{(E')^2 + (E'')^2}$. The complex modulus is determined by substituting the first order coefficients of equations (3.10) and (3.11) into equation (3.12), such that

$$\pm 2\pi R_{eq}^2 \frac{(1 \pm b_1)^2}{b_1} g_1 \varepsilon = \Delta A_1 \sin(\omega t + \phi_A) \text{ and} \quad (3.13)$$

$$\frac{p_a R_{eq}}{2} (\sin \omega t + g_1) \varepsilon = \Delta P_1^s \sin(\omega t + \phi_p) \quad (3.14)$$

where ϕ_A and ϕ_p are the phase angles of the area and surface stress oscillations, respectively. The total phase angle of the complex modulus is the difference of the surface stress and area phase angles, $\Phi = \phi_p - \phi_A$.

To first order, the oscillations of the radius can be written as

$$R = R_{eq} (1 + \Delta R_1 \varepsilon \sin(\omega t + \phi_{R1})) \quad (3.15)$$

where the phase angle ϕ_{R1} is chosen such that the scaled radial oscillation amplitude ΔR_1 is always positive. From equation (3.15) we can calculate the equilibrium surface area, A_{eq} , the amplitudes and phase angles for the surface area, equation (3.13), and the surface stress, equation (3.14). The resulting dilatational modulus expressed in terms of the scaled radial amplitude is given by

$$|E^*| = \frac{b_1}{1-b_1} \frac{\sqrt{\Delta R_1^2 + 2\Delta R_1 \cos \phi_{R1} + 1}}{\Delta R_1} \left(\frac{p_a R_{eq}}{2} \right). \quad (3.16)$$

The measured amplitude of the radial oscillations R_a is related to the scaled radial amplitude by

$$\Delta R_1 = \frac{R_a}{\varepsilon R_{eq}}. \quad (3.17)$$

The total phase angle Φ is given by

$$\Phi = \tan^{-1} \left(\frac{\Delta R_1 \sin \phi_{R1}}{1 + \Delta R_1 \cos \phi_{R1}} \right) - \tan^{-1} \left(\frac{\sin \phi_{R1}}{\cos \phi_{R1}} \right). \quad (3.18)$$

The inverse tangent function must be calculated as the principal value of the complex argument in order to obtain physically realistic values for the real and imaginary components of the complex modulus. Equations (3.16) through (3.18) allow for direct calculation of the dilatational modulus based solely on measured parameters.

3.3 SMALL AMPLITUDE DILATATIONAL MODULUS OF MODEL INTERFACES

In this section, we will apply the asymptotic analysis described above to two model interfaces that contain both surface tension and extra interfacial stresses. The extra interfacial stresses will be modeled using the Boussinesq-Scriven constitutive equation,³⁰ which is the equivalent of a Newtonian interface, assuming a linear relationship between the stress and the rate of area dilation. For an oscillating spherical cap the Boussinesq-Scriven model specializes to

$$\frac{1}{2} (\tau_{\theta\theta} + \tau_{\phi\phi}) = \kappa^s \dot{\delta} = \kappa^s \frac{1}{A} \frac{dA}{dt}. \quad (3.19)$$

where κ^s is the interfacial dilatational viscosity.

For an insoluble monolayer with no transport of species from the bulk fluid, the surface tension σ depends on the instantaneous surface concentration Γ of adsorbed species through an equation of state. For the Langmuir equation of state, the relationship between surface pressure Π and surface concentration is given by

$$\Pi = \sigma_0 - \sigma(\Gamma) = -R_g T \Gamma_{\max} \ln \left(1 - \frac{\Gamma}{\Gamma_{\max}} \right) \quad (3.20)$$

where σ_0 is the interfacial tension of the pure fluid-fluid interface, R_g is the ideal gas constant, T is the temperature, and $\Gamma_{\max}$ is the maximum surface concentration. The instantaneous surface concentration can be expressed in terms of the number of moles adsorbed on the interface n divided by the interfacial area A , such that $\Gamma = n / A$. The interfacial area can be expressed in terms of the asymptotic expansion given in equation (3.11).

Applying equations (3.19) and (3.20) to the components of the interfacial stress in equation (3.6), and then comparing terms of the same order in equation (3.10) yields an equilibrium surface stress in the zeroth order term that depends only on the equation of state,

$$\sigma_{eq} \equiv \frac{p_a R_{eq}}{2} = \sigma_0 + R_g T \Gamma_{\max} \ln \left(1 - \frac{n}{\Gamma_{\max} A_{eq}} \right). \quad (3.21)$$

The first order terms yield a differential equation for the function g_1 that contains equation of state parameters, the surface concentration Γ_{eq} corresponding to the equilibrium area, and the dilatational viscosity,

$$\frac{dg_1}{dt} = -(\alpha + \beta) g_1 - \alpha \sin \omega t, \quad (3.22)$$

where the coefficients α and β are given by

$$\alpha = \left(\frac{b_1}{\mp 1 - b_1} \right) \frac{\sigma_{eq}}{\kappa^s}, \text{ and} \quad (3.23a)$$

$$\beta = \frac{R_g T \Gamma_{\max} n}{(\Gamma_{\max} A_{eq} - n) \kappa^s} = \frac{\varepsilon_0}{\kappa^s}. \quad (3.23b)$$

The minus or plus sign in equation (3.23a) depends on whether the spherical cap is larger or smaller than the hemisphere, respectively. The constant ε_0 , denoted the Gibbs elasticity, characterizes the slope of the surface tension with respect to the surface concentration near the equilibrium surface coverage, $\varepsilon_0 = -(\partial \sigma / \partial \ln \Gamma)_{eq} = \Gamma_{eq} d\Pi / d\Gamma$. This value can be obtained through a measurement of the Π - A isotherm on a Langmuir trough.³¹ The parameters α and β defined in equation (3.23) represent inverse characteristic relaxation times that arise from the viscoelastic nature of the interface. The equilibrium interfacial tension provides one source of elasticity within the interface, while the Gibbs elasticity, characterizing the sensitivity of the surface tension to small changes in surface area, provides another. Both relaxation times also depend on the geometry of the spherical cap.

Solving equation (3.22) gives the response of the bubble to small amplitude pressure oscillation,

$$g_1 = -\frac{\alpha}{(\alpha + \beta)^2 + \omega^2} \left[\omega e^{-(\alpha + \beta)t} + (\alpha + \beta) \sin \omega t - \omega \cos \omega t \right]. \quad (3.24)$$

The response is characterized by a transient offset that decays exponentially at a rate characterized by the sum of α and β , and a steady state oscillation with a

frequency-dependent magnitude that depends on the two characteristic relaxation times.

The complex dilatational modulus of the insoluble Boussinesq-Scriven interface is found by substituting the steady-state oscillatory part of equation (3.24) into equations (3.13), (3.14), and then (3.12), obtaining the simple form

$$E^* = \varepsilon_0 + i\kappa^s \omega \quad (3.25)$$

where the real part of the modulus E' corresponds to the Gibbs modulus and the imaginary part of the modulus E'' is proportional to the dilatational viscosity. While the complex modulus of this model interface does not depend on the curvature of the interface, the real part of the modulus depends on the total surface area if the number of moles of adsorbed species remains fixed during the oscillatory experiment. This form of the complex modulus is also obtained from the phenomenological Voight constitutive model, which assumes constant elasticity and constant viscosity of the interface.³²

Figure 3.3a is a log-log plot of the small amplitude dilatation modulus as a function of frequency for a single bubble shape corresponding to a fixed spherical cap radius with $b_1 = 0.66$. The real and imaginary components are plotted along with the absolute magnitude. At this bubble size, the real and imaginary components of the modulus are equal at a critical frequency ω_c . For frequencies below the critical value, the modulus is predominantly elastic, with a nearly constant magnitude corresponding to the Gibbs modulus. For frequencies greater than the critical value, the modulus is predominantly viscous, growing linearly with frequency with a slope equal to the dilatational viscosity.

Keeping the number of moles of adsorbed species constant and decreasing the surface area of the spherical cap results in an increase in both surface concentration and Gibbs modulus. Figure 3.3b is a semilog plot of the modulus as a function of b_1 , defined in equation (11b), for a fixed number of moles adsorbed, $n = 2.5 \times 10^{-14}$ mol and a fixed frequency of $\omega = 0.4 \text{ s}^{-1}$ for the model parameters given. The real part of the modulus increases from a smaller plateau value near the hemispherical interface to a larger plateau value as the bubble approaches a flat interface at the capillary tip. The imaginary component of the modulus is independent of geometry. This behavior does not account for the possibility in a real system that the dilatational viscosity may depend on the surface composition.³³⁻³⁵ In effect, the experiment modeled in Figure 3.3b probes the isotherm of the adsorbed insoluble monolayer by placing a fixed mass at the interface and systematically varying the surface area.

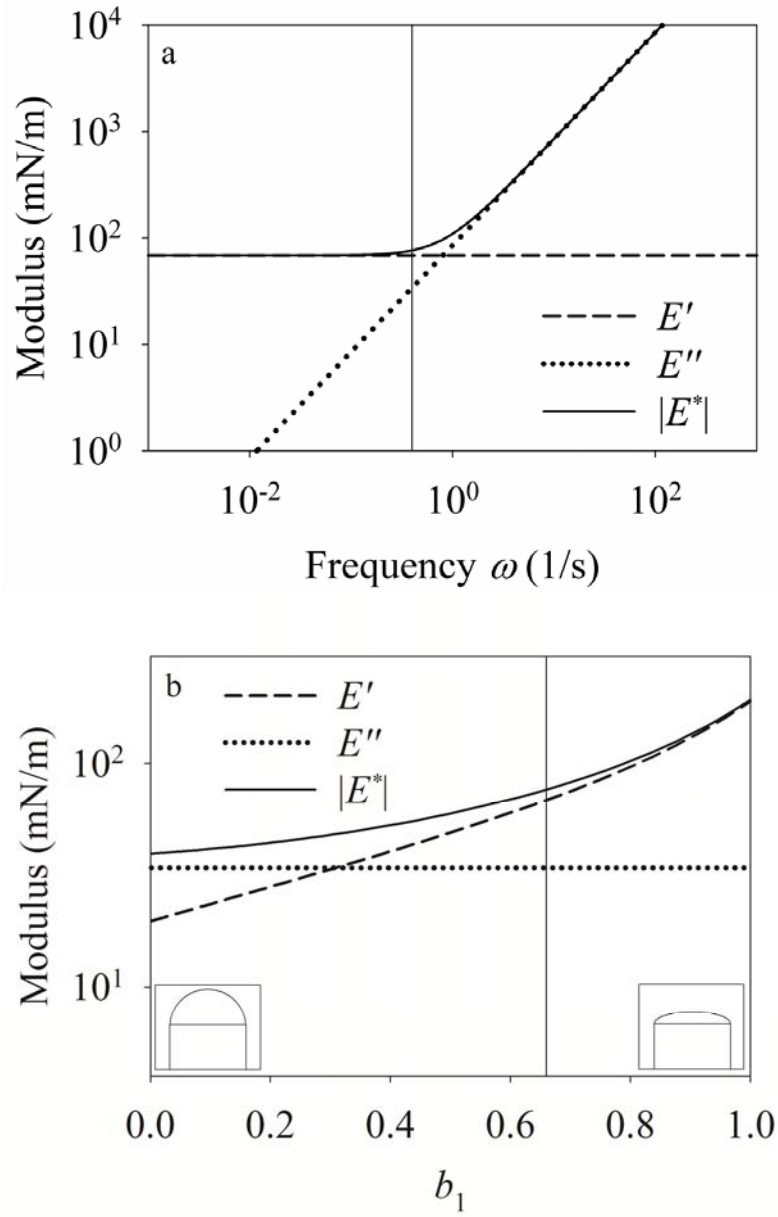


Figure 3.3. The small amplitude dilatational modulus of an insoluble monolayer modeled by the Langmuir isotherm and the Boussinesq-Scriven constitutive equation. The model parameters are $T = 298$ K, $\Gamma_{max} = 10^{-5}$ mol/m 2 , $n = 2.5 \times 10^{-14}$ mol, $\kappa^s = 85$ mN-s/m, and $R_c = 30$ μ m. (a) The frequency dependence of the modulus for $b_1 = 0.66$. (b) The dependence of the modulus on b_1 , for a fixed frequency of $\omega = 0.4$ s $^{-1}$. The vertical lines in (a) and (b) indicate $\omega = 0.4$ s $^{-1}$ and $b_1 = 0.66$, respectively.

The phase shift of the radius response to pressure oscillations can be found by applying equation (3.15) for the viscous insoluble monolayer, and is given by

$$\phi_{R1} = \tan^{-1} \left(\frac{\omega}{-(\alpha + \beta)} \right). \quad (3.26)$$

The purely elastic interface limit ($\kappa^s = 0$) corresponds to a real-valued complex modulus for which $\alpha \rightarrow \infty$ and $\beta \rightarrow \infty$ according to equation (3.28), and the phase shift vanishes, $\phi_{R1} \rightarrow 0$. The purely viscous interface limit ($\varepsilon_0 = 0$) corresponds to an imaginary-valued complex modulus for which $\beta = 0$ and the phase shift depends on the spherical cap geometry, the surface tension, and the dilatational viscosity. In this limit, the maximum phase shift occurs when the dilatational viscosity is much greater than the surface tension such that $\alpha \rightarrow 0$ and the radius response is completely out of phase with the pressure oscillations such that $\phi_{R1} \rightarrow \pi/2$. The two extremes place physical bounds on the phase shift of the radius oscillations of $\pi/2 < \phi_{R1} < \pi$. It is important to note that this phase angle range is not equal to the phase angle range of Φ between surface area and surface stress oscillations, which is $0 < \Phi < \pi/2$.

When the surface-active species adsorbing at the interface are soluble in the bulk liquid, the surface concentration arises from equilibrium partitioning between the interface and the bulk solution. As the interface deforms, mass transfer between interface and bulk drives the system toward equilibrium. Mass transfer occurs in finite time, leading to a time-dependent surface tension that enters the dilatational modulus via equation (3.6) separate from other interfacial rheology contributions. Assuming diffusion-limited transport to the dilating spherical cap interface, the species mass balance at the interface is

$$\frac{\partial \Gamma}{\partial t} + \Gamma_{eq} \frac{1}{A} \frac{dA}{dt} = D \left(\frac{\partial c}{\partial r} \right)_{r=R} \quad (3.27)$$

which depends on the instantaneous local bulk concentration c and the bulk diffusivity D of the species in solution. The bulk concentration is governed by the diffusion equation in spherical coordinates

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right). \quad (3.28)$$

For this analysis, we assume the bulk liquid is located in a sample cell exterior to the bubble, and that the volume of the sample cell is large enough to avoid significant depletion of surface active material from the bulk solution, which can reduce the bulk concentration and influence the transport dynamics.³⁶ Consistent with the earlier analysis for an insoluble interface, we assume that the surface pressure is governed by the Langmuir equation of state, equation (3.20), and that the interfacial rheology follows the Boussinesq-Scriven constitutive model, equation (3.19). Solubility is accounted for by solving the total surface stress equation, equation (3.6), simultaneous with the mass transport problem given by equations (3.27) and (3.28).

To solve the problem, the surface concentration is first written as a regular perturbation expansion in the parameter ε

$$\Gamma = \Gamma_{eq} \left(1 + \varepsilon f_1 + O(\varepsilon^2) \right). \quad (3.29)$$

Expanding equation (3.6) in terms of the small parameter gives

$$p_a (1 + \varepsilon \sin \omega t) = \frac{2\sigma_{eq}}{R_{eq}} - \varepsilon \frac{2}{R_{eq}} \left[g_1 \sigma_{eq} + \frac{R_g T \Gamma_{eq} \Gamma_{\max}}{(\Gamma_{\max} - \Gamma_{eq})} f_1 + \frac{\mp 1 - b_1}{b_1} \kappa^s \frac{dg_1}{dt} \right] + O(\varepsilon^2) \quad (3.30)$$

where the equilibrium surface tension is given by equation (3.21).

The bulk diffusion equation (3.28) is solved by taking the Laplace transform with respect to t , with the initial condition that at time $t = 0$ the bulk concentration is constant, $c = c_\infty$, and the interface is at equilibrium. Boundary conditions are provided by equation (3.27) at the bubble interface and the far field condition that as $r \rightarrow \infty$ the bulk solution approaches $c \rightarrow c_\infty$. In the Laplace domain (denoted by overbar), equation (3.28) can be written as a second order ordinary differential equation

$$\frac{\partial^2 \bar{c}}{\partial r^2} + \frac{2}{r} \frac{\partial \bar{c}}{\partial r} - \frac{s}{D} \bar{c} = -\frac{c_\infty}{D}. \quad (3.31)$$

Solving this equation and applying the far field boundary condition yields

$$\bar{c} = \frac{c_\infty}{s} + \frac{C_1}{r} e^{-\sqrt{\frac{s}{D}} r}. \quad (3.32)$$

where C_1 is an unknown parameter that is a function of s . To impose the interfacial mass balance at the interface, equation (3.27), we first perform a perturbation expansion on the boundary condition. To highest order, the boundary condition becomes

$$\Gamma_{eq} \varepsilon \frac{\partial f_1}{\partial t} + \Gamma_{eq} \left(\pm \frac{(1 \pm b_1)}{b_1} \right) \varepsilon \frac{dg_1}{dt} = D \left(\frac{\partial c}{\partial r} \right)_{r=R_{eq}}; \quad (3.33)$$

applying the Fourier transform and equation (3.32) yields

$$\Gamma_{eq} \varepsilon s \bar{f}_1 + \Gamma_{eq} \left(\pm \frac{(1 \pm b_1)}{b_1} \right) \varepsilon s \bar{g}_1 = -\frac{D}{R_{eq}^2} \left(1 + R_{eq} \sqrt{\frac{s}{D}} \right) C_1 e^{-\sqrt{\frac{s}{D}} R_{eq}}. \quad (3.34)$$

In order to reach equation (3.34), we have assumed that at time zero we are starting from an equilibrium state. We will assume that there is a local equilibrium between the surface concentration and the bulk concentration at R_{eq} imposed at all times. When the fluctuations are small, the deviation in the bulk concentration at the interface relative to the deviation in the surface concentration ($\varepsilon \bar{f}_1$) away from equilibrium values is equal to the local slope of the isotherm, or

$$\frac{\bar{c}_{r=R_{eq}} - \frac{c_\infty}{s}}{\varepsilon \bar{f}_1 \Gamma_{eq}} = \frac{C_1}{\varepsilon \bar{f}_1 \Gamma_{eq} R_{eq}} e^{-\sqrt{\frac{s}{D}} R_{eq}} = \left(\frac{dc}{d\Gamma} \right)_{eq}. \quad (3.35)$$

This relationship can be used to eliminate C_1 from equation (3.34), which can be rearranged to show the relationship between the unknown radius and surface concentration oscillations in the Laplace domain as

$$\bar{f}_1 = \frac{\mp 1 - b_1}{b_1} \frac{s}{s + (s\omega_0)^{1/2} + (\omega_0\omega_R)^{1/2}} \bar{g}_1. \quad (3.36)$$

Equation (3.36) reveals two characteristic frequencies that arise from the transport problem. $\omega_0 = D (dc / d\Gamma)_{eq}^2$ is a characteristic frequency of diffusion assuming an intrinsic length scale arising from the slope of the adsorption isotherm, and $\omega_R = D / R_{eq}^2$ is a characteristic frequency of diffusion assuming the relevant length scale is the radius of curvature of the bubble interface. Taking the Laplace transform of equation (3.30) and applying equation (3.36) allows us to solve for the unknown function describing the radial oscillations in the Laplace domain as

$$\bar{g}_1 = \frac{-\alpha\omega}{(\omega^2 + s^2) \left(s + \alpha + \beta \left(\frac{s}{s + (s\omega_0)^{1/2} + (\omega_0\omega_R)^{1/2}} \right) \right)}. \quad (3.37)$$

The definitions for α and β are given by equation (3.23). For spherical cap geometries smaller than a hemisphere, the only poles of equation (3.37) are at $\pm i\omega$.

We only need to calculate the steady-state oscillations of the interface in order to calculate the relevant parameters for the dilatational modulus, although the complete oscillation history including start-up effects can be obtained from equation (3.37). Taking into account the branch point at the origin, equation (3.37) is solved using the method of residues to obtain

$$g_1 \approx \frac{\alpha \left[\left(\omega(a_1^2 + a_2^2) + \beta a_1 \right) \cos \omega t - \left(\alpha(a_1^2 + a_2^2) + \beta a_2 \right) \sin \omega t \right]}{(a_1^2 + a_2^2)(\alpha^2 + \omega^2) + \beta(2a_1\omega + 2a_2\alpha + \beta)} \quad (3.38)$$

where the dimensionless coefficients are given by

$$a_1 = \left(\frac{\omega_0}{2\omega} \right)^{1/2} + \left(\frac{\omega_0}{\omega} \right)^{1/2} \left(\frac{\omega_R}{\omega} \right)^{1/2} \quad (3.39a)$$

$$a_2 = 1 + \left(\frac{\omega_0}{2\omega} \right)^{1/2}. \quad (3.39b)$$

Using equations (3.13) and (3.14) to determine the amplitude and phase shift of the pressure and area oscillations results in a complex modulus that is written in the compact form

$$E^* = \frac{\varepsilon_0}{1 + \left(\frac{\omega_R}{i\omega} \right)^{1/2} \left(\frac{\omega_0}{i\omega} \right)^{1/2} + \left(\frac{\omega_0}{i\omega} \right)^{1/2}} + i\kappa^s \omega. \quad (3.40)$$

The real and imaginary parts of the complex modulus in equation (3.40) are plotted as a function of frequency in Figure 3.4a for a constant capillary radius of 30 μm and transport parameters typical of a surfactant system. At low frequencies, diffusion and adsorption to the dilating interface are fast enough that the instantaneous surface concentration remains approximately constant and the modulus is small. In the low frequency limit, E' scales as $\omega^{3/2}$ and is smaller than E'' , which increases linearly with ω . At high frequencies, the modulus approaches the limit of an insoluble monolayer with a dilatational viscosity, equation (3.25). In contrast to the insoluble monolayer model; however, the equilibrium composition of the interface is independent of the available surface area and depends only on the bulk concentration.

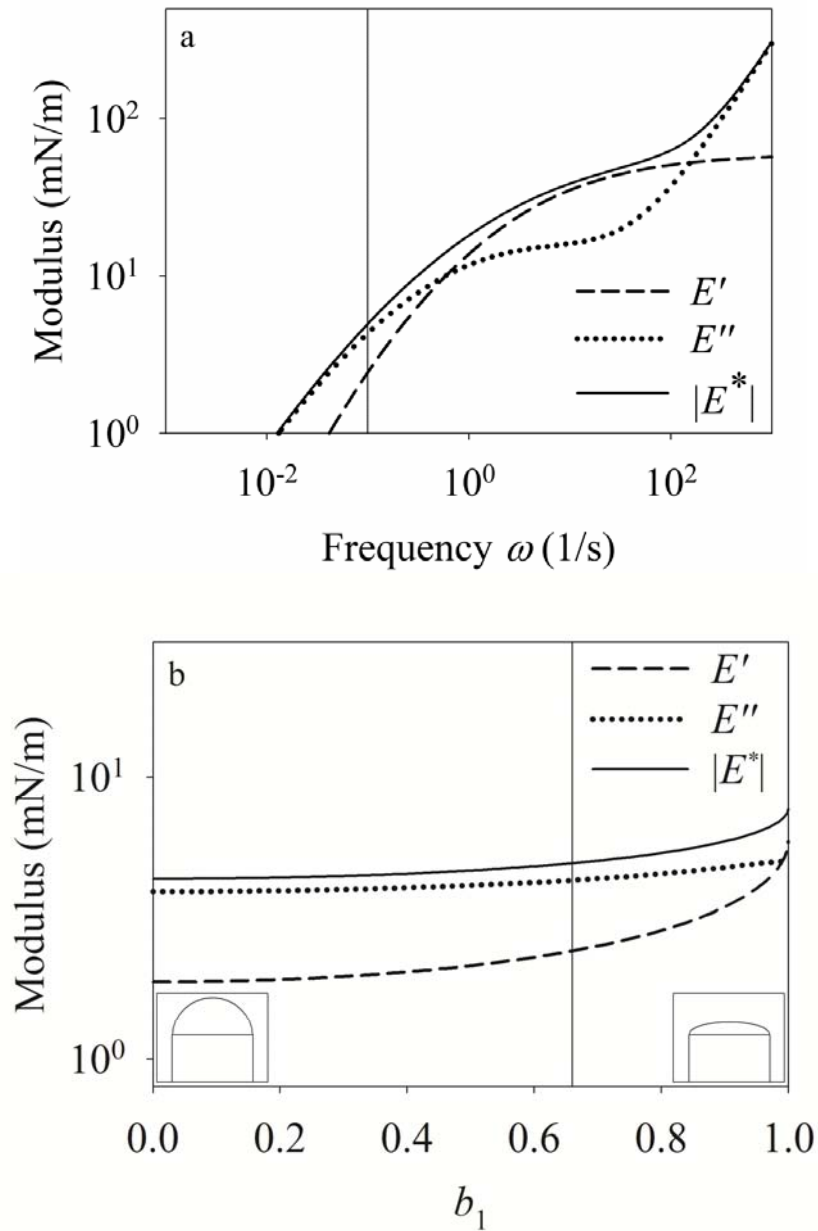


Figure 3.4. The small amplitude dilatational modulus of an interface with a soluble monolayer modeled by the Langmuir isotherm and the Boussinesq-Scriven constitutive equation. The model parameters are $T = 298$ K, $\varepsilon_0 = 60$ mN/m, $D = 10^{-10}$ m 2 /s, $\omega_0 = 5$ s $^{-1}$, and $\kappa^s = 0.3$ mN-s/m. (a) The frequency dependence of the modulus for $b_1 = 0.66$. (b) The dependence of the modulus on b_1 , for a fixed frequency of $\omega = 0.1$ s $^{-1}$. The vertical lines in (a) and (b) indicate $\omega = 0.1$ s $^{-1}$ and $b_1 = 0.66$, respectively.

The geometric dependence of the modulus is shown in Figure 3.4b, with the components of the modulus plotted as a function of the geometric parameter b_1 at a fixed frequency. Small values of b_1 correspond to a nearly hemispherical drop, which is the smallest possible radius of curvature for a pinned spherical cap. As b_1 increases, the droplet interface approaches a flat interface, and the real part of the modulus increases, becoming greater than the imaginary part at $b_1 = 0.992$. The complex modulus of equation (3.40) is the sum of a modulus developed for diffusion-limited transport to a spherical interface³⁷ and a modulus due to the intrinsic surface rheology. As b_1 approaches unity, the characteristic frequency ω_R goes to zero and the component of the modulus arising from diffusion-limited transport limits to that of a planar interface.³⁸

Both insoluble and soluble monolayers with dilatational viscosity exhibit a transient offset pressure with exponential dependence on time, and a steady state oscillatory response. In the case of an insoluble monolayer with dilatational viscosity, equation (3.24) indicates that the transient offset will grow rather than decay if the sum $\alpha + \beta$ is negative. In this situation, the interface is unstable to start-up pressure oscillations. Rearranging the inequality, the criterion for stable oscillation in terms of physical parameters and the system geometry becomes

$$\frac{\varepsilon_0}{\sigma_{eq}} > - \left(\frac{b_1}{\mp 1 - b_1} \right) \quad (3.41)$$

where the minus or plus sign is used when the spherical cap interface is larger or smaller than the hemisphere, respectively. When the spherical cap shape is smaller than a hemisphere, the right side of the inequality is always negative,

meaning that this system is stable to start-up oscillations. When the interface is larger than a hemisphere, stability depends on whether the ratio of the Gibbs modulus ε_0 to the equilibrium surface tension is greater than the function on the right hand side that depends on the equilibrium radius of the interface and the radius of the capillary at which the interface is pinned. Stability does not depend on the magnitude of the pressure oscillation, the frequency, or the dilatational viscosity, although it is necessary for the interface to exhibit a dilatational viscosity in order for the transient offset pressure to appear.

Checking the stability of the soluble monolayer with dilatational viscosity to start-up pressure oscillations requires inspection of the poles of equation (3.37) describing the first harmonic oscillations in the Laplace domain. As long as the real parts of the solutions to the equation

$$s + \alpha + \beta \left(\frac{s}{s + (s\omega_0)^{1/2} + (\omega_0\omega_R)^{1/2}} \right) = 0 \quad (3.42)$$

are negative, then the initial transient in the radial oscillations will decay to a stable steady state oscillatory response. For physical systems, the variables β , ω_0 , and ω_R in this equation are positive regardless of the spherical cap geometry. When the spherical cap interface is less than a hemisphere, then α is also positive and equation (3.42) has no real roots, meaning that the system is stable to start-up oscillations. Conversely, a negative value for the parameter α leads to a positive real root, meaning that the system is unstable. For example, given the physical conditions listed in the caption of Figure 3.4 with an interface of the same radius but larger than the hemisphere ($\alpha=-0.197$), there is a positive root at

$s = 6.03 \times 10^{-4}$. When there is no diffusion of species to the interface, then $\omega_0 = \omega_r = 0$ and the stability criterion for the start-up oscillations is given by equation (3.41).

In situations where the system is unstable to the initial pressure oscillation, the radius will increase continuously until the interface detaches from the end of the capillary and a bubble or droplet of the inner phase fluid is ejected. We note that it is only possible to calculate a modulus when the system is stable to start-up oscillations, since the modulus is determined based on steady-state oscillation about an equilibrium pressure and radius.

The measured dilatational modulus is not a material property in general because the underlying mechanisms lead both to geometry dependence as well as to real and imaginary components that are not strictly elastic or viscous. However, if properly interpreted, the information obtained from the measured dilatational modulus can be useful. For example, the response of a bubble to small amplitude oscillations has been used previously to measure the transport properties of surfactants³⁹ when interfacial rheology is negligible. However, equations (3.25) and (3.40) highlight the general need to separate both surface tension effects and transport behavior from intrinsic interfacial rheology. The regular perturbation analysis described here provides a framework for analysis of arbitrary interfaces, and the geometry dependence provides a potential method of separating transport and rheology contributions and distinguishing between different interfacial rheological responses. Here we consider ways to use

geometry to distinguish experimentally between the two model systems that we have analyzed.

Both insoluble and soluble monolayers with dilatational viscosity exhibit one or more crossover frequencies ω_c at which the real and imaginary parts of the complex modulus are equal to one another, as shown in Figures 3.3a and 3.4a. The crossover frequency depends on the shape of the spherical cap. For example, the crossover frequency $\omega_{c,i}$ of an insoluble monolayer with dilatational viscosity is given by the ratio of Gibbs elasticity to the dilatational viscosity. For the Langmuir equation of state, the crossover frequency is given by

$$\omega_{c,i} = \frac{\Re T \Gamma_{\max}}{\kappa^s} \frac{(n / \Gamma_{\max})}{A_{eq} - (n / \Gamma_{\max})}. \quad (3.43)$$

For a fixed number of moles of adsorbed species n , the crossover frequency increases as the equilibrium surface area increases. When the spherical cap is smaller than the hemisphere, increasing surface area corresponds to increasing the interface radius of curvature for a fixed capillary radius.

A soluble monolayer with dilatational viscosity exhibits up to two crossover frequencies. The crossover frequencies $\omega_{c,s}$ are obtained by equating the real and imaginary components of equation (3.40), which leads to the equation

$$R_{eq} = \frac{2D \left(\frac{dc}{d\Gamma} \right)_{eq}}{\left(\left(\frac{\varepsilon_0}{\kappa^s} + (2\omega_0 \omega_{c,s})^{1/2} \right)^2 - 4\omega_{c,s} \left(\omega_{c,s} + (2\omega_0 \omega_{c,s})^{1/2} - \frac{\varepsilon_0}{\kappa^s} + \omega_0 \right) \right)^{1/2} - \frac{\varepsilon_0}{\kappa^s} - (2\omega_0 \omega_{c,s})^{1/2}}. \quad (3.44)$$

Figure 3.5 compares the crossover frequencies for the two model interfaces as a function of b_1 . In the figure, the spherical cap is smaller than a hemisphere and the capillary radius is $R_c = 30 \mu\text{m}$. Other model parameters are

the same as those used to generate Figures 3.3 and 3.4. Figure 3.5 can be obtained experimentally by generating an equilibrium interface containing adsorbed species and performing frequency sweeps for a series of spherical cap radii for the same initial interface.

Figure 3.5 shows that an insoluble interface has a nearly constant crossover frequency for small values of b_1 , where the interface is nearly hemispherical. As b_1 increases, approaching a flat interface, the crossover frequency increases by about tenfold to reach the flat interface value. This behavior reflects the increase in the Gibbs elasticity for increasing surface area for a fixed number of moles of adsorbed species n . For a soluble interface, there are two crossover frequencies at this set of conditions, shown by the dashed lines in Figure 3.5.

The larger crossover frequency is equal to the characteristic frequency ε_0 / κ^s , which is independent of the total surface area (and radius of curvature) for the soluble monolayer. The smaller crossover frequency corresponds to the characteristic frequency for purely diffusion-limited transport to a spherical interface, given by $\omega_c = D / R_{eq} (dc / d\Gamma)_{eq}$. In this case, the crossover frequency approaches a nearly constant value near the hemisphere, and decreases by several orders of magnitude as the radius of curvature increases, consistent with expectations for diffusive transport to a spherical interface.⁴⁰ The importance of the radius of curvature on the dilatational modulus has been experimentally confirmed by Reichert *et al.*⁴¹

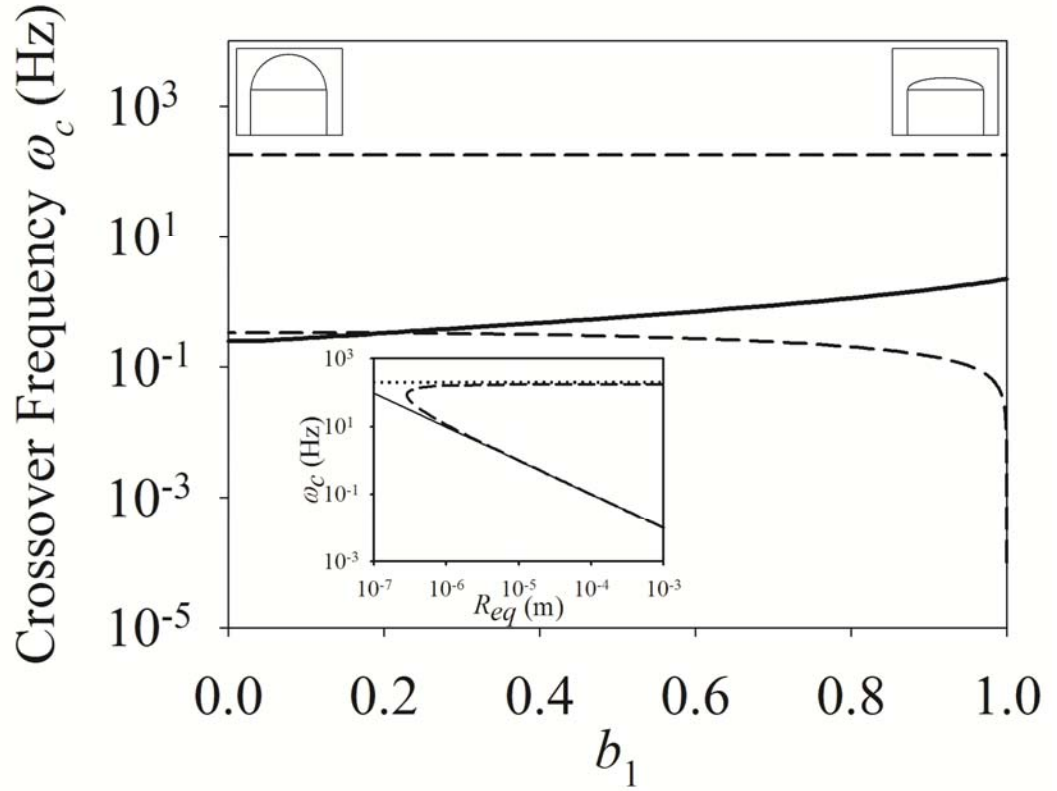


Figure 3.5. The crossover frequencies in the complex modulus as a function of b_1 given by equation (3.43) (solid line) and equation (3.44) (dashed lines). The physical parameters used are given in the captions of Figures 3.3 and 3.4, respectively. The inset plots the crossover frequency versus the radius of curvature of the interface for the soluble monolayer with dilatational viscosity (dashed line). The dotted line in the inset is the crossover frequency of an interface with constant Gibbs elasticity and dilatational viscosity, and the solid line is the crossover frequency for pure diffusion of soluble surfactant to a spherical interface.

The inset of Figure 3.5 shows the dependence of the crossover frequency for a soluble interface with dilatational viscosity as a function of the (dimensional) equilibrium radius of curvature, R_{eq} , which is obtained from the zeroth-order solution to the perturbation expansion of the stress balance for the given interfacial stress balance. For very small values of the equilibrium radius,

there is no crossover frequency because the imaginary part of the complex modulus is greater than the real part for all frequencies. For the physical parameters chosen here, the curvature of the interface at which no crossover frequency exists is approximately $R_{eq} \approx 100$ nm, which is a value that cannot be observed on any existing experimental apparatus. For experimentally realizable interfaces in which the equilibrium radius can vary from tens to hundreds of micrometers, the crossover frequencies given by the lower branch of equation (3.44) can span two to four orders of magnitude.

For the two model interfaces considered here, the crossover frequency dependence on radius reveals fundamental differences in the two interfaces, whereas a frequency sweep at a single spherical cap size may not reveal these differences. For example, a soluble interface sampled at higher frequencies than the characteristic frequencies ω_0 and ω_R would appear the same as an insoluble interface. Varying the radius of curvature of the interface shifts the characteristic frequencies relative to the experimental frequencies, allowing for the transport mechanisms to be probed at different scales.

3.4 IMPACT OF REGULAR PERTURBATION ANALYSIS ON EXPERIMENTS

The regular perturbation analysis presented above provides a framework for determining the expected response of interfaces to small amplitude dilatational oscillation, once the interfacial isotherm and constitutive models are known. However, the analysis also provides useful criteria to assess experiments for arbitrary interfaces, even when models are not available. In what follows, we use

the perturbation analysis to develop criteria for experimentally assessing the validity of the small amplitude assumption. Finally, we examine the operating space of several existing experimental apparatuses with respect to the small amplitude analysis and other physical limitations.

The small amplitude assumption requires that the response of the interface to pressure oscillations remains sinusoidal at the input frequency with no higher harmonics. The area dilatation rate and the surface stress are the fundamental quantities for which a small amplitude response should be maintained, but neither is directly measured in experiments. Although the magnitude of the higher harmonics can be determined in post-processing of experiments through a Fourier analysis of the oscillatory data,⁴² in this case it would be beneficial to obtain a real-time estimate of the amplitudes of the higher harmonics in the surface stress and dilatation rate based on harmonic analysis of the measured radius response. The harmonic ratio H , defined as the ratio of the magnitude of the response at the second harmonic 2ω to that at the first harmonic ω , will be used to develop criteria for linearity of the response of each of the quantities of interest.

Let us assume that the steady-state oscillation of the radius exhibits a second order response to the sinusoidal pressure oscillation, equation (3.15), such that

$$R = R_{eq} \left(1 + \Delta R_1 \varepsilon \sin(\omega t + \phi_{R1}) + \Delta R_2 \varepsilon^2 \sin(2\omega t + \phi_{R2}) \right). \quad (3.45)$$

The amplitudes of the first and second harmonics, $\Delta R_1 \varepsilon$ and $\Delta R_2 \varepsilon^2$, respectively, are both positive. The harmonic ratio for the radius is given by

$$H_R = \frac{\Delta R_2 \varepsilon}{\Delta R_1} \quad (3.46)$$

The magnitudes of the second order terms in the area dilatation rate and surface stress are found and the harmonic ratios calculated by applying equation (3.45) in place of equation (3.15) in the perturbation analysis above. The resulting harmonic ratio for the surface area oscillation is given by

$$H_A = \varepsilon \sqrt{\left(\frac{2b_1+1}{4b_1^2}\right)^2 \Delta R_1^2 + 2\left(\frac{2b_1+1}{4b_1^2}\right) \Delta R_2 \sin(\phi_{R2} - 2\phi_{R1}) + \left(\frac{\Delta R_2}{\Delta R_1}\right)^2} \quad (3.47)$$

and the harmonic ratio for the surface stress is given by

$$H_P = \frac{\varepsilon \sqrt{\frac{\Delta R_1^2}{4} - \Delta R_1 \Delta R_2 \sin(\phi_{R2} - \phi_{R1}) + \Delta R_2^2}}{\sqrt{\Delta R_1^2 + 2\Delta R_1 \cos \phi_{R1} + 1}}. \quad (3.48)$$

The harmonic ratio of the surface area depends on the spherical cap geometry and the radius oscillations, but the harmonic ratio of the interfacial stress depends only on the radius oscillations. Both harmonic ratios H_A and H_P are nonlinear functions of H_R , and either can be larger or smaller than H_R for a given set of conditions. Thus, a first order response in the radius does not guarantee a first order response in the two fundamental quantities of interest to interfacial rheology.

As an example, Figures 3.6a and 3.6b contain simplified contour maps of H_A and H_P normalized by H_R for the viscous insoluble monolayer over the allowable range of phase shifts. Limits on the first order phase shift ϕ_{R1} are given in the discussion of equation (3.26), while the second order phase shift ϕ_{R2} can vary from 0 to 2π . In Figure 3.6, the harmonic ratio of the radius is kept fixed at

$H_R = 0.105$, which corresponds to the model parameters given in the caption of Figure 3.3 for the viscous insoluble interface. The contour maps are colored such that black regions correspond to harmonic ratios that are larger than H_R , and white regions correspond to harmonic ratios that are less than H_R . Over the entire range of phase shifts, the normalized values of the harmonic ratios vary from $0.355 < H_A/H_R < 1.645$ and $0.020 < H_P/H_R < 1.549$.

In experiments, a common criterion is that the harmonic ratio should be lower than 0.1 for a small amplitude response, such that second order harmonics are less than 10% of the first order harmonics. Following this criterion for the case considered in Figure 3.6, the radius response is at the upper limit of the small amplitude response, and the resulting area and surface stress responses can be significantly more or less linear. The complicated shape of the contour maps shown in Figure 3.6 requires that both the area and the surface stress harmonic ratios be estimated to determine whether the overall response is at small amplitude. However, equations (3.46) – (3.48) can be used to rapidly estimate these responses, requiring only that the magnitudes of the first and second order harmonics of the radius oscillations be determined experimentally. Therefore, it is possible to experimentally confirm the validity of the small amplitude assumption for an arbitrary complex interface, without knowledge of a specific constitutive model.

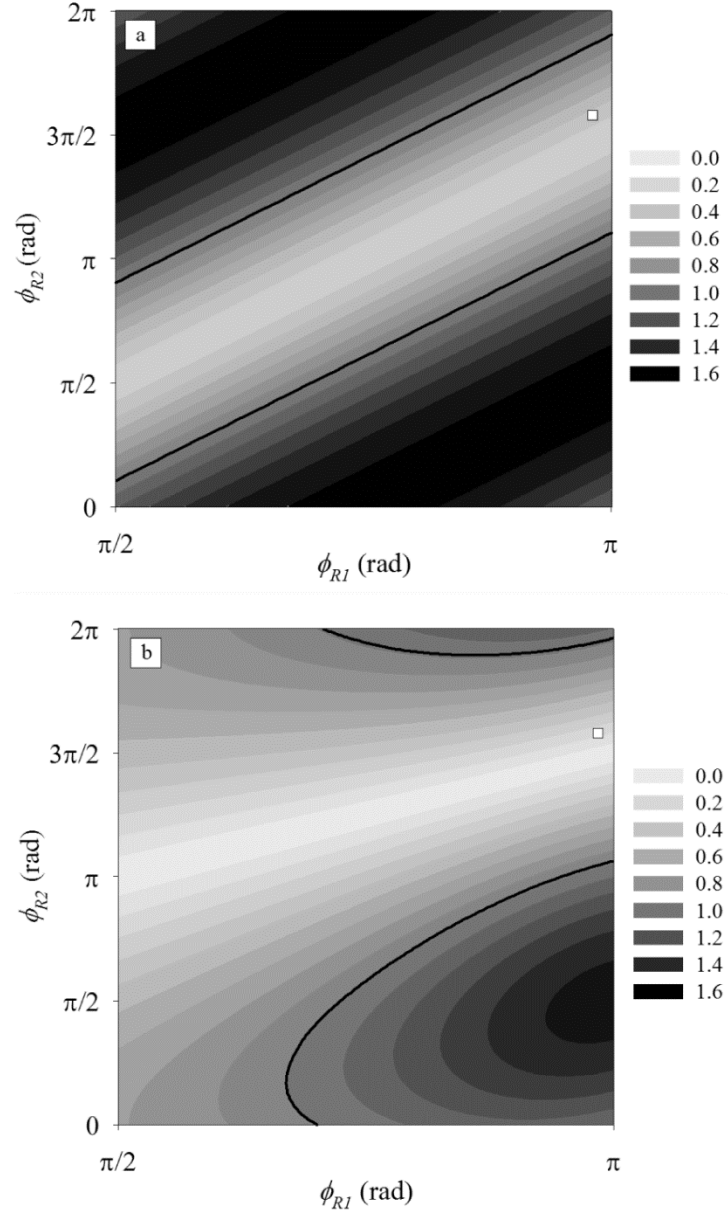


Figure 3.6. Grayscale contour plot of (a) H_A normalized by H_R and (b) H_P normalized by H_R for a viscous insoluble interface. Darker regions indicate higher values. The solid contour lines indicate where the value of H_A/H_R or H_P/H_R is unity. The parameters used to generate these plots are $\Delta R_1 = 0.443$, $\Delta R_2 = 0.233$, $b_1 = 0.984$, and $\varepsilon = 0.2$. The small box on both figures at $(3.08, 4.98)$ rad indicates the values of the phase shifts for oscillation at $b_1 = 0.984$ and $\omega = 1$ rad/s.

For the viscous insoluble monolayer, the results of the regular perturbation analysis can be used to determine pressure amplitudes that may be applied to achieve a linear response. After incorporating equations (3.19) and (3.20), equation (3.6) is solved numerically for the time-dependent radial oscillations in response to an applied sinusoidal pressure of amplitude ε and angular frequency ω using an explicit fourth/fifth-order Runge-Kutta method (ode45 in MATLAB). The physical parameters used are given in the caption of Figure 3.3, and the capillary radius is held fixed at 30 μm . From the radial oscillations, we use equation (3.2) to calculate the surface area for a spherical cap smaller than the hemisphere, and the instantaneous stress due to the pressure jump and radius are equated with the surface stresses in equation (3.10). The steady-state radius, surface area, and surface stress are converted to the frequency domain by Discrete Fourier Transform, and the harmonic ratio H is recorded for each.

Figure 3.7a shows the critical value of the dimensionless pressure amplitude above which the harmonic ratio in either the surface area H_A or the total surface stress H_P exceeds 10% for spherical cap shapes smaller than the hemisphere. The critical dimensionless pressure amplitude is shown as a function of normalized radius $R_r = (R_{eq}/R_c - 1)$ for several frequencies. The normalized radius is related to b_1 by $R_r = [(1 - b_1^2)^{-1/2} - 1]$. Low values of the normalized radius correspond to the spherical cap approaching a hemisphere, and high values of the normalized radius correspond to the spherical cap approaching a flat interface. At very low values of the normalized radius corresponding to the shaded region on the left side of the plot, any pressure amplitude is large enough

to drive the interface past the hemisphere, violating the small-amplitude approximation. At these conditions, the pressure exceeds the maximum pressure for a hemispherical interface, and we expect the interface to grow continuously until a bubble is ejected from the capillary. At all frequencies for normalized radius $R_r < 1$, H_A surpasses 10% at lower values of the pressure amplitude compared with H_P . As the angular frequency of oscillation is increased, the critical pressure amplitude at which the surface area harmonic ratio surpasses 10% increases. For larger normalized radius values $R_r > 1$, $H_P > H_A$ at certain frequencies and spherical cap geometries indicated by the open symbols in Figure 3.7a. Increasing the angular frequency in this regime decreases the critical pressure amplitude above which the response in the surface stress or surface area contains significant second harmonic contributions.

The critical pressure amplitude above which the harmonic ratio for the radius H_R exceeds 10% is shown in Figure 3.7b as a function of normalized radius for frequencies $0.5 < \omega < 10$ rad/s. For all values of the normalized radius and frequency shown, H_R is greater than both H_A and H_P , resulting in critical pressure amplitudes smaller than those shown in Figure 3.7a. In contrast to Figure 3.7a, H_R exceeds 10% before the pressure amplitude can drive the interface past the hemisphere for smaller values of the normalized radius. For small values of the normalized radius approaching a hemisphere, increasing the frequency of oscillation increases the critical pressure amplitude. For large values of the normalized radius approaching a flat interface, the critical pressure amplitudes at which H_R exceeds 10% approach a constant value of $\varepsilon \approx 0.2$.

Applying the conditions simulated in Figure 3.5 for the viscous insoluble monolayer, and the results shown in Figure 3.7, we expect that H_A and H_P will be less than H_R for the conditions of Figure 3.6. The phase shifts $\phi_{R1} = 3.08$ rad and $\phi_{R2} = 4.98$ rad computed numerically at these conditions are located in the white region of Figures 3.6a and 3.6b; the values of the normalized harmonic ratios at these points are $H_A/H_R = 0.075$ and $H_P/H_R = 0.715$, consistent with expectations.

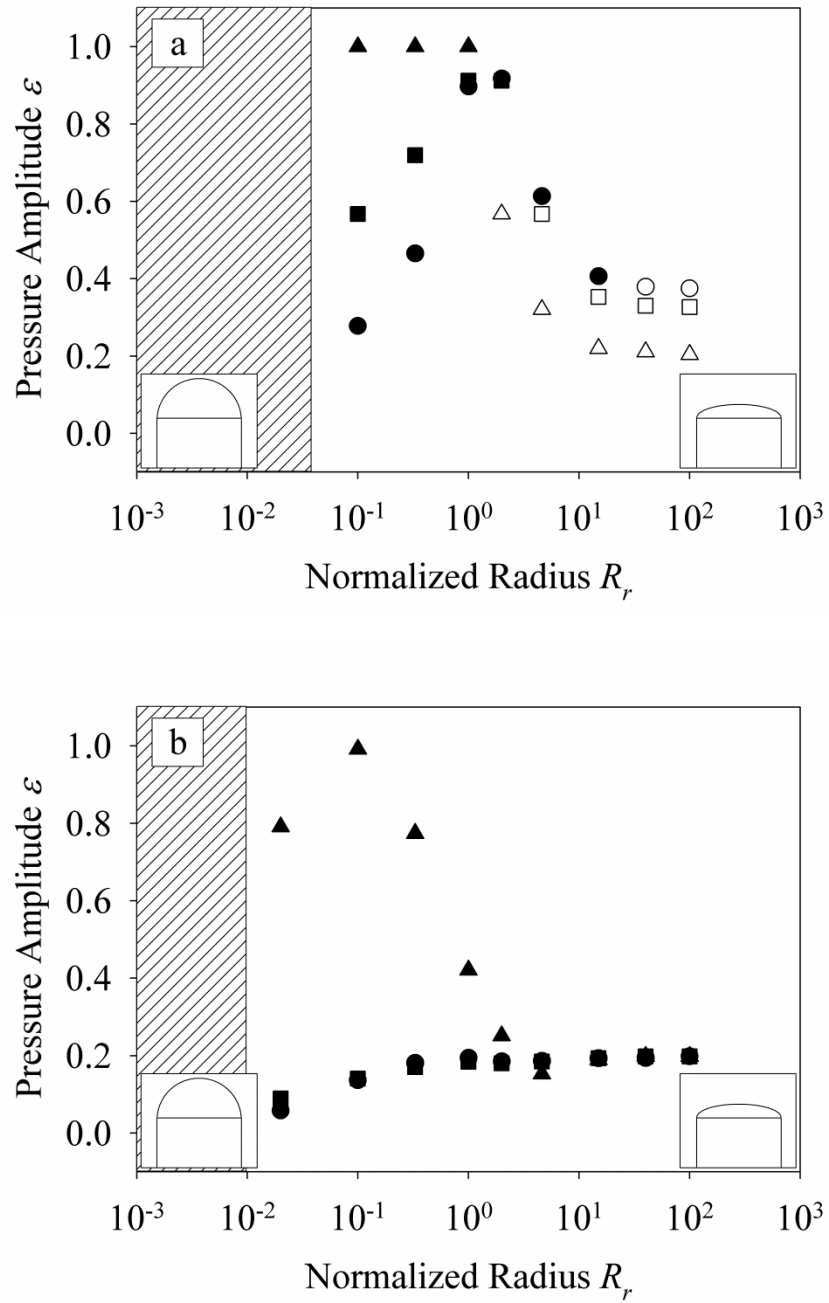


Figure 3.7. Critical pressure amplitude above which (a) H_A or H_P and (b) H_R exceeds 10% as a function of the normalized equilibrium radius. The analysis was performed at angular frequencies of 0.5 rad/s ($\bullet$), 1 rad/s ($\blacksquare$), and 10 rad/s ($\blacktriangle$). In (a), the filled symbols correspond to cases in which H_A exceeds 10% first, and the open symbols correspond to cases in which H_P exceeds 10% first. The system parameters are given in the caption of Figure 3.3.

The dilatation of a spherical cap interface can be achieved experimentally by forming a bubble or drop at the end of a circular capillary tube with small enough diameter that gravity is negligible. At these conditions, the interface is nearly spherical and the radius of the sphere can be observed optically and fitted using image processing tools. As the capillary radius gets smaller, the pressure jump across the interface becomes measurable; for this reason these configurations are often called “capillary pressure tensiometers.” Several configurations of capillary pressure tensiometers have been reported in the literature. While the operational details of each apparatus are reported elsewhere, the basic differences lie in the method of controlling the interface deformation. Equation 3.3 and the subsequent analysis show that the pressure jump and the radius of the interface are the key parameters in determining the dilatational modulus of the interface. Figure 3.8 shows three basic experimental configurations that have been reported in literature. Reported configurations include those in which the volume of the fluid inside the drop or bubble is controlled⁴³ (Figure 3.8a), those in which the volume of the fluid in the reservoir outside the drop or bubble is controlled^{44,45} (Figure 3.8b), and those in which the pressure in the fluid inside the drop or bubble is controlled^{46,47} (Figure 3.8c). In cases (a) and (b), the volume is oscillated and the resulting pressure jump is measured using commercial pressure transducers placed as shown in the diagram. The shape of the drop is either directly observed or it is inferred from the known volume oscillation of a piston. In case (c), the pressure jump across the interface is controlled by oscillating the hydrostatic head⁴⁷ on the inside of the interface

while keeping the outside of the interface at a fixed (atmospheric) pressure. In pressure-controlled devices, the radius of the interface is measured optically.

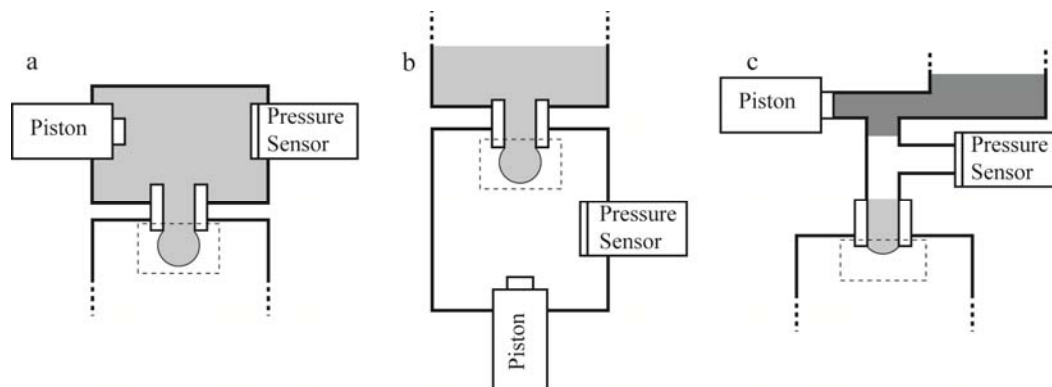


Figure 3.8. Schematic diagram of common capillary pressure tensiometers. (a) volume control of internal fluid, (b) volume control of external fluid, (c) pressure control of internal fluid. The region marked by the dashed box indicates the capillary tip, which corresponds to Figure 3.1.

There is uncertainty in experimentally determined dilatational modulus values arising from the measurement of pressure and radius. In cases where the interface is visualized optically, the shape of the interface is fit to a digitized image, and the accuracy of the radius depends on the calibrated pixel resolution of the imaging camera and the uncertainty in the shape fitting algorithm. The accuracy and resolution of the pressure transducer can vary. For volume-controlled capillary pressure tensiometers in which the radius is not directly observed, there is uncertainty arising from the accuracy of the volume displacement and the assumption of a spherical cap interface. Table 3.1 summarizes the type of control, the typical capillary radii and oscillation frequencies, and the uncertainties associated with pressure and radius/volume control for several reported apparatuses. It is worth noting that cases (a) and (b) in

Figure 3.8 typically correspond to spherical cap interfaces that are larger than a hemisphere, while case (c) requires spherical caps flatter than a hemisphere in order to hold the bubble at the capillary tip. Thus, in case (c), the shape of the interface will be stable to the start-up of pressure oscillations based on the stability criteria of equations (3.41) and (3.42). Cases (a) and (b) also remain stable since the volume is controlled; however, volume-controlled devices can exhibit a different instability arising from the presence of trapped gas bubbles in the capillary.⁴⁸

Device	Fig.	Input “In”	Response “Out”	R (m)	f (Hz)	Uncertainty	
						In	Out
Liggieri <i>et al.</i> ⁴³	3.8a	V_{out}	p_{out}	$(2.5-5) \times 10^{-4}$	0.2 – 100	-	-
Russev <i>et al.</i> ⁴⁴	3.8b	V_{in} or R	p_{in}	1×10^{-3}	0.05 – 1	-	12 Pa (1%)
Javadi <i>et al.</i> ⁴⁵	3.8b	V_{in} or R	p_{in}	2.5×10^{-4}	0.2 – 150	0.001 mm ³ (1%)	1 %
Alvarez <i>et al.</i> ⁴⁷	3.8c	p_{in}	R	$(3-10) \times 10^{-5}$	0.05 – 1	10 Pa (1%)	0.2 μ m (0.7%)

Table 3.1. Typical operating parameters for capillary pressure tensiometers, including the typical radii of curvature R and oscillation frequency f . Experiments either control the volume inside V_{in} or outside V_{out} the capillary, the radius of curvature R , or the hydrostatic pressure p_{in} inside the capillary as the device input. The measured output parameters include the pressure inside or outside p_{out} the capillary, or the radius of curvature. The uncertainties in the various input and response are also included where reported in the literature.

Equation (3.6) and the subsequent analysis assume that interfacial stresses arising from gravitational forces, viscous forces, and inertia from the bulk fluid phases are negligible. These contributions can be estimated using the typical operating parameters given in Table 3.1 for each capillary pressure tensiometer. For example, the Bond number describes the relative importance of gravity acting

to distort the shape of the bubble interface compared with surface tension acting to maintain the spherical shape, given by

$$Bo = \frac{\Delta\rho g R^2}{\sigma}, \quad (3.44)$$

where $\Delta\rho$ is the density difference between inner and outer fluids. MacLeod and Radke⁴⁹ have shown that for $Bo > 0.01$, the local curvature of the bubble begins to deviate significantly from a single radius of curvature. Table 3.2 summarizes typical values of the relevant dimensionless parameters for each apparatus listed in Table 3.1, considering an air bubble generated in DI water ($\sigma = 72 \text{ mN/m}$, $\Delta\rho = 1000 \text{ kg/m}^3$, $\mu = 1 \text{ mPa-s}$). Of the four apparatuses considered here, nonuniform curvature may be significant for the three volume-controlled devices.^{43,44,45} since they each operate at or above the Bond number limit specified. The Bond number may still be kept low in these cases if the inner and outer phases are limited to fluids of similar density. The microtensiometer device used by Alvarez *et al.*⁴⁷ operates at a Bond number well below the specified limit, so the spherical cap approximation is reasonable for this apparatus.

System	Figure	Bo	Ca	Re
Liggieri <i>et al.</i> ⁴³	7a	10^{-2}	$10^{-7} - 10^{-4}$	$10^{-2} - 10^1$
Russev <i>et al.</i> ⁴⁴	7b	10^{-1}	$10^{-8} - 10^{-7}$	$10^{-3} - 10^{-2}$
Javadi <i>et al.</i> ⁴⁵	7b	10^{-2}	$10^{-8} - 10^{-5}$	$10^{-4} - 10^{-1}$
Alvarez <i>et al.</i> ⁴⁷	7c	10^{-4}	$10^{-10} - 10^{-9}$	$10^{-6} - 10^{-5}$

Table 3.2. Relevant dimensionless parameters for various capillary pressure tensiometers.

A capillary number Ca can be used to estimate the relative importance of viscous shear stresses from the fluid surrounding the interface to the interfacial stresses during dilation. Small amplitude pressure oscillations imposed at angular frequency ω lead to oscillations in the height of the spherical cap interface of amplitude Δh . The cap height amplitude can be estimated from the radius oscillations through the expression $h = R - \sqrt{R^2 - R_c^2}$. For a bubble oscillating in a fluid of shear viscosity μ , the capillary number is given by

$$Ca = \frac{\mu \omega \Delta h}{P^s} \approx \frac{\mu \omega \Delta h}{\sigma} \quad (3.45)$$

where the total surface stress is approximated by the equilibrium surface tension. Applying previously reported measurements of the dilatational properties of interfaces in viscous oils⁵⁰ to equation (3.45) shows that the uncertainty in the measurement of the surface stresses will be of the order of 0.01 mN/m when $Ca \approx 10^{-6}$. The uncertainty increases with increasing capillary number, which increases with both frequency and amplitude. Table 3.2 suggests that the capillary pressure tensiometers described by Liggieri *et al.*⁴³ and Javadi *et al.*⁴⁵ may exhibit significant viscous effects when operated at higher frequencies, while the other two apparatuses may assume negligible viscous effects over the entire range of accessible frequencies. When viscous stresses are significant, there is an additional contribution to the pressure jump that depends on the viscous flow inside the capillary and the flow field generated by the expanding complex interface. Models for bubbles expanding in viscous fluids have been developed to account for the additional pressure jump.^{1,50,51}

The Reynolds number estimates the relative importance of inertia and viscous stresses in the fluid surrounding the interface. Estimating the characteristic velocity as $\omega\Delta h$ and the characteristic length scale as R , the Reynolds number is given by

$$Re = \frac{\rho\omega R\Delta h}{\mu}. \quad (3.46)$$

Significant fluid inertia will lead to additional contributions to the pressure jump across the interface, which will increase the uncertainty in the calculation of the surface stress. Jin *et al.*⁵² observed that there is agreement between finite Reynolds number simulations and Stokes flow simulations of droplet growth from a capillary tip⁵³ when $Re < 0.1$. Table 2 suggests that all four devices compared here operate with low to negligible inertia, except for the apparatus used by Liggieri *et al.*,⁴³ if operated at higher frequencies.

There is a trade-off when performing small-amplitude oscillatory measurements: the pressure amplitude must be kept low enough to remain within the small-amplitude limit, but must also be large enough that the pressure and surface area oscillations can be resolved. The ability to resolve these two quantities directly affects the ability to resolve the phase angle, which is critical in determining rheological parameters contained within the imaginary part of the modulus, like the dilatational viscosity. Since the interfacial response to dilatation is a result of the specifics of the complex interface, estimating the measurable range of interfacial properties must be done in the context of an interfacial constitutive model. For this discussion, the interface is assumed to be an air-water interface exhibiting properties of an insoluble viscous monolayer given by

equation (3.25), with zero Gibbs elasticity corresponding to a constant interfacial tension of 72 mN/m. Thus, the magnitude of the complex dilatational modulus for the model interface is given by $|E^*| = \kappa^s \omega$. The measurable range of dilatational viscosities will be estimated for the microtensiometer apparatus of Alvarez *et al.*,⁴⁷ since this device operates at small values of Bo , Ca , and Re , meaning that equation (3.6) adequately describes the stress balance at the interface.

The small amplitude limit and the resolution of the phase angle both depend on the equilibrium radius of curvature of the spherical cap interface. The smallest realizable radius of curvature corresponds to a hemispherical cap with radius equivalent to the smallest capillary tip available. For the microtensiometer, the minimum capillary radius is 20 μm . As the spherical cap interface becomes flatter, the radius of curvature increases, leading to larger Bond number values. The maximum radius of curvature occurs when gravitational distortion of the interface becomes significant ($Bo = 0.01$), which corresponds to $R_{eq} = 270 \mu\text{m}$ for a clean air-water interface. For a given equilibrium radius of curvature, limits on the measurable interfacial rheological parameters arise from the physically accessible values of the amplitudes of the radius and pressure jump oscillations. For example, in the microtensiometer device of Alvarez *et al.*, Table 3.1 indicates that the pressure amplitude must remain between the resolution of the pressure transducer (10 Pa) and half of the maximum transducer pressure (5 psi). The minimum resolvable radius amplitude is $R_{a,min} = 0.4 \mu\text{m}$, while the maximum radius amplitude is determined by the small amplitude limit. The small amplitude

analysis presented above is used to determine the conditions at which higher harmonics in the response become significant.

The resolution of the phase shift is based on the rate at which data is collected. For the microtensiometer, the data collection rate is limited to 7 Hz to allow for imaging of the interface radius. The phase angle between the radius and pressure oscillations is estimated by the oscillation frequency divided by the data acquisition frequency, which yields a minimum resolvable phase angle of 0.007 rad for the slowest oscillation frequency and 0.071 rad for the highest oscillation frequency in the microtensiometer.

The result of these experimental considerations is shown in Figure 3.9, which plots the measurable dilatational viscosity as a function of equilibrium radius of curvature for this example. Figure 3.9 shows that for small values of the equilibrium radius, the ability to resolve the phase angle determines both the upper and lower limits of the dilatational viscosity. For larger values of the radius, second harmonics become significant in the measured response for small dilatational viscosities. For this purely viscous model interface, the surface stress produces the largest harmonic ratio for small dilatational viscosities.

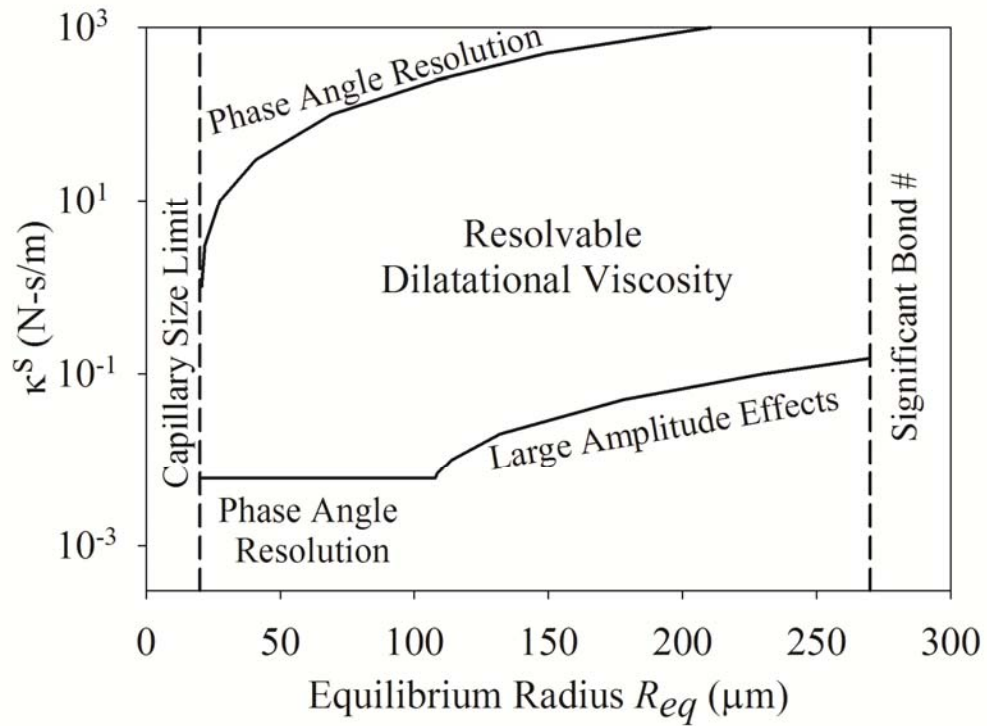


Figure 3.9. Operating diagram showing the measurable range of dilatational viscosities for a viscous insoluble monolayer with constant interfacial tension for the configuration and physical parameters corresponding to the microtensiometer of Alvarez *et al.*⁴⁷

Figure 3.9 shows that the dilatational viscosity can be measured between $6 \times 10^{-3} < \kappa^s < 1000$ N s/m for the realizable values of the radius of curvature. Literature values reported can range from 10^{-8} N s/m for soluble surfactant systems⁵⁴ to 10 N s/m for polymer monolayers,⁵⁵ suggesting that the microtensiometer apparatus is currently best suited for measuring relatively viscous interfaces. The phase shift resolution can be improved by increasing the data collection frequency (image acquisition rate) for a given oscillation frequency. In addition, increasing the oscillation frequency ω will allow smaller values of the dilatational viscosity to be resolved, but care should be taken to avoid significant contributions from viscous stress and inertia.

3.5 SUMMARY

Purely dilatational deformation of a complex fluid-fluid interface can be accomplished by oscillating the radius of a spherical cap shaped interface. However, despite the simple deformation mode, the experiment is neither stress- nor dilatation rate-controlled, and the response of the spherical interface to dilatation is determined by a number of mechanisms beyond the interfacial rheology that is desired. Thermodynamic contributions, i.e. surface tension changes as a result of surface concentration changes, transport of soluble components, bending stresses, gravity, and inertia and viscous stresses from the fluid surrounding the interface can all play a significant role. A regular perturbation expansion provides a useful framework for determining the response of an arbitrary complex interface to small amplitude oscillatory dilatation in the absence of bending stresses, gravity, and bulk inertia and viscous stresses. Dimensional analysis provides estimates of the relative importance of the remaining effects.

The perturbation analysis allows for the examination of the geometry and frequency dependence of the dilatational modulus for known interfacial constitutive equations. For example, the analysis shows that a viscous interface exhibits qualitative differences in behavior depending on whether insoluble or soluble components are adsorbed. The measured dilatational modulus cannot be considered a true material function because it depends on surfactant isotherm parameters, transport parameters, and the geometry of the interface, in addition to the dilatational viscosity. The qualitative differences in behavior of the soluble

and insoluble interfaces can be characterized through characteristic “crossover” frequencies at which the real and imaginary components of the dilatational modulus are equal. The crossover frequencies depend differently on radius of curvature of the interface as well as material parameters of interest, and the scaling behavior of these crossover frequencies can potentially be used in experiments to distinguish between constitutive models for an interface with unknown properties.

The perturbation analysis also allows for an *a priori* assessment of the small amplitude limit for an arbitrary interface. Since the controlled and measured quantities (pressure and radius) are involved in both the interfacial stress and strain rate, determining whether the small amplitude limit is maintained requires more than merely determining the magnitudes of the higher harmonics of the response function. For example, for the insoluble viscous layer, the conditions at which both kinematics and dynamics experience small amplitude oscillation occupy a rather complex and non-obvious region of the operating space. Fortunately, a generic criterion for estimating the relative importance of higher harmonics can be written analytically, without the need to know the interfacial constitutive equation. This criterion can therefore be assessed “on-the-fly” in experiments so that conditions can be adjusted rapidly if needed.

Finally, the perturbation analysis and generic criteria developed here are considered in the context of several previously reported capillary pressure tensiometers, which have been developed independently with several different experimental configurations. The influence of gravity, inertia, and viscous stresses

arising from the fluid surrounding the interface are assessed and reasonable operating limits defined in terms of the dimensionless Bond, capillary, and Reynolds numbers. Operating limits on the measurable material parameters are also assessed. In one specific example, the microtensiometer apparatus developed by Alvarez *et al.*,⁴⁶ the effects of gravity, inertia, and viscous stresses are shown to be negligible, but the current operating conditions limit the device to relatively large values of the dilatational viscosity for an insoluble viscous layer. Nevertheless, the high curvature of the interface makes the apparatus ideal for separating surface tension effects due to transport from intrinsic dilatational extra stresses.

1. Edwards, D. A.; Brenner, H.; Wasan, D. T., *Interfacial transport processes and rheology*. Butterworth-Heinemann Boston: 1991.
2. Ravera, F.; Loglio, G.; Kovalchuk, V. I., Interfacial dilational rheology by oscillating bubble/drop methods. *Curr. Opin. Colloid Interface Sci.* **2010**, 15, (4), 217-228.
3. Murray, B. S., Rheological properties of protein films. *Current Opinion in Colloid & Interface Science* **2011**, 16, (1), 27-35.
4. Sagis, L. M. C., Dynamic properties of interfaces in soft matter: Experiments and theory. *Reviews of Modern Physics* **2011**, 83, (4), 1367.
5. Freer, E. M.; Yim, K. S.; Fuller, G. G.; Radke, C. J., Interfacial rheology of globular and flexible proteins at the hexadecane/water interface: comparison of shear and dilatation deformation. *The Journal of Physical Chemistry B* **2004**, 108, (12), 3835-3844.
6. Langevin, D.; Monroy, F., Interfacial rheology of polyelectrolytes and polymer monolayers at the air–water interface. *Current Opinion in Colloid & Interface Science* **2010**, 15, (4), 283-293.
7. Tambe, D. E.; Sharma, M. M., The effect of colloidal particles on fluid-fluid interfacial properties and emulsion stability. *Advances in Colloid and Interface Science* **1994**, 52, 1-63.
8. Botto, L.; Lewandowski, E. P.; Cavallaro, M.; Stebe, K. J., Capillary interactions between anisotropic particles. *Soft Matter* **2012**, 8, (39), 9957-9971.
9. Dixit, H. N.; Homsy, G., Capillary effects on floating cylindrical particles. *Physics of Fluids* **2012**, 24, 122102.
10. Fuller, G. G.; Vermant, J., Complex Fluid-Fluid Interfaces: Rheology and Structure. *Annu. Rev. Chem. Biomol. Eng.* **2012**, 3, (1), 519-543.
11. Miller, R.; Liggieri, L.; Krotov, V., *Interfacial rheology*. Brill Leiden, The Netherlands: 2009.
12. Petty, M. C., *Langmuir-Blodgett films: an introduction*. Cambridge University Press: 1996.

13. Maru, H.; Mohan, T.; Wasan, D., Dilational viscoelastic properties of fluid interfaces—I. *Chemical Engineering Science* **1979**, 34, (11), 1283-1293.
14. Noskov, B.; Akentiev, A.; Bilibin, A. Y.; Zorin, I.; Miller, R., Dilational surface viscoelasticity of polymer solutions. *Adv. Colloid Interface Sci.* **2003**, 104, (1), 245-271.
15. Petkov, J. T.; Gurkov, T. D.; Campbell, B. E.; Borwankar, R. P., Dilatational and shear elasticity of gel-like protein layers on air/water interface. *Langmuir* **2000**, 16, (8), 3703-3711.
16. Benjamins, J.; de Feijter, J. A.; Evans, M. T. A.; Graham, D. E.; Phillips, M. C., Dynamic and static properties of proteins adsorbed at the air/water interface. *Faraday Discuss. Chem. Soc.* **1975**, 59, 218-229.
17. Loglio, G.; Tesei, U.; Cini, R., Measurement of interfacial dilational properties: A software-driven apparatus. *Rev. Sci. Instrum.* **1988**, 59, (9), 2045-2050.
18. Verwijlen, T.; Moldenaers, P.; Vermant, J., A fixture for interfacial dilatational rheometry using a rotational rheometer. *The European Physical Journal Special Topics* **2013**, 222, (1), 83-97.
19. Lin, S. Y.; McKeigue, K.; Maldarelli, C., Diffusion-controlled surfactant adsorption studied by pendant drop digitization. *AIChE journal* **1990**, 36, (12), 1785-1795.
20. Yeung, A.; Dabros, T.; Masliyah, J., Dissipative interfaces and departures from the Young-Laplace equation. *Langmuir* **1997**, 13, (24), 6597-6606.
21. Flügge, S., Stresses in shells. *Berlin: Springer, 1973, 2nd ed.* **1973**, 1.
22. Kralchevsky, P.; Eriksson, J.; Ljunggren, S., Theory of curved interfaces and membranes: mechanical and thermodynamical approaches. *Advances in Colloid and Interface Science* **1994**, 48, 19-59.
23. Yunker, P. J.; Gratale, M.; Lohr, M. A.; Still, T.; Lubensky, T. C.; Yodh, A. G., Influence of Particle Shape on Bending Rigidity of Colloidal Monolayer Membranes and Particle Deposition during Droplet Evaporation in Confined Geometries. *Phys. Rev. Lett.* **2012**, 108, (22), 228303.

24. Helfrich, W., Elastic properties of lipid bilayers: theory and possible experiments. *Zeitschrift für Naturforschung. Teil C: Biochemie, Biophysik, Biologie, Virologie* **1973**, 28, (11), 693.
25. Kaoui, B.; Ristow, G.; Cantat, I.; Misbah, C.; Zimmermann, W., Lateral migration of a two-dimensional vesicle in unbounded Poiseuille flow. *Physical Review E* **2008**, 77, (2), 021903.
26. Langevin, D., Influence of interfacial rheology on foam and emulsion properties. *Adv. Colloid Interface Sci.* **2000**, 88, (1), 209-222.
27. Beblik, G.; Servuss, R. M.; Helfrich, W., Bilayer bending rigidity of some synthetic lecithins. *J. Phys. France* **1985**, 46, (10), 1773-1778.
28. Planchette, C.; Lorenceau, E.; Biance, A.-L., Surface wave on a particle raft. *Soft Matter* **2012**, 8, (8), 2444-2451.
29. Leal, L. G., *Laminar flow and convective transport processes: scaling principles and asymptotic analysis*. Butterworth-Heinemann Boston:: 1992.
30. Scriven, L., Dynamics of a fluid interface equation of motion for Newtonian surface fluids. *Chem. Eng. Sci.* **1960**, 12, (2), 98-108.
31. Knobler, C. M., Recent developments in the study of monolayers at the air-water-interface. *Adv. Chem. Phys* **1990**, 77, 397-449.
32. Ivanov, I. B.; Danov, K. D.; Ananthapadmanabhan, K. P.; Lips, A., Interfacial rheology of adsorbed layers with surface reaction: on the origin of the dilatational surface viscosity. *Adv. Colloid Interface Sci.* **2005**, 114, 61-92.
33. Edwards, D.; Wasan, D., A micromechanical model of linear surface rheological behavior. *Chem. Eng. Sci.* **1991**, 46, (5), 1247-1257.
34. Tambe, D. E.; Sharma, M. M., Factors controlling the stability of colloid-stabilized emulsions. *J. Colloid Interface Sci.* **1994**, 162, 1-10.
35. Lishchuk, S.; Halliday, I., Effective surface viscosities of a particle-laden fluid interface. *Phys. Rev. E* **2009**, 80, (1), 016306.

36. Alvarez, N. J.; Walker, L. M.; Anna, S. L., A criterion to assess the impact of confined volumes on surfactant transport to liquid–fluid interfaces. *Soft Matter* **2012**.
37. Joos, P., *Dynamic surface phenomena*. VSP: 1999.
38. Lucassen, J.; Van Den Tempel, M., Dynamic measurements of dilational properties of a liquid interface. *Chem. Eng. Sci.* **1972**, 27, (6), 1283-1291.
39. Johnson, D. O.; Stebe, K. J., Oscillating bubble tensiometry: a method for measuring the surfactant adsorptive-desorptive kinetics and the surface dilatational viscosity. *J. Colloid Interface Sci.* **1994**, 168, (1), 21-31.
40. Alvarez, N. J.; Walker, L. M.; Anna, S. L., Diffusion-limited adsorption to a spherical geometry: The impact of curvature and competitive time scales. *Phys. Rev. E* **2010**, 82, (1), 011604.
41. Reichert, M. D.; Alvarez, N. J.; Brooks, C. F.; Grillet, A. M.; Mondy, L. A.; Anna, S. L.; Walker, L. M., Interfacial rheology and the importance of curvature on diffusion-limited surfactant systems. *Journal of Colloid and Interface Science* **2014**, Submitted.
42. Loglio, G.; Pandolfini, P.; Miller, R.; Makievski, A. V.; Krägel, J.; Ravera, F.; Noskov, B. A., Perturbation–response relationship in liquid interfacial systems: non-linearity assessment by frequency–domain analysis. *Colloids Surf., A* **2005**, 261, (1), 57-63.
43. Liggieri, L.; Attolini, V.; Ferrari, M.; Ravera, F., Measurement of the surface dilational viscoelasticity of adsorbed layers with a capillary pressure tensiometer. *J. Colloid Interface Sci.* **2002**, 255, (2), 225-235.
44. Russev, S. C.; Alexandrov, N.; Marinova, K. G.; Danov, K. D.; Denkov, N. D.; Lyutov, L.; Vulchev, V.; Bilke-Krause, C., Instrument and methods for surface dilatational rheology measurements. *Rev. Sci. Instrum.* **2008**, 79, (10), 104102-104102-10.
45. Javadi, A.; Krägel, J.; Makievski, A.; Kovalchuk, V.; Kovalchuk, N.; Mucic, N.; Loglio, G.; Pandolfini, P.; Karbaschi, M.; Miller, R., Fast dynamic interfacial tension measurements and dilational rheology of interfacial layers by using the capillary pressure technique. *Colloids Surf., A* **2012**, 407, 159-168.

46. Alvarez, N. J.; Walker, L. M.; Anna, S. L., A microtensiometer to probe the effect of radius of curvature on surfactant transport to a spherical interface. *Langmuir* **2010**, 26, (16), 13310-13319.
47. Alvarez, N. J.; Anna, S. L.; Saigal, T.; Tilton, R. D.; Walker, L. M., Interfacial Dynamics and Rheology of Polymer-Grafted Nanoparticles at Air–Water and Xylene–Water Interfaces. *Langmuir* **2012**, 28, (21), 8052-8063.
48. Liggieri, L.; Ravera, F.; Passerone, A., Drop formation instabilities induced by entrapped gas bubbles. *J. Colloid Interface Sci.* **1990**, 140, (2), 436-443.
49. MacLeod, C.; Radke, C., A growing drop technique for measuring dynamic interfacial tension. *J. Colloid Interface Sci.* **1993**, 160, (2), 435-448.
50. Alexandrov, N.; Marinova, K. G.; Danov, K. D.; Ivanov, I. B., Surface dilatational rheology measurements for oil/water systems with viscous oils. *J. Colloid Interface Sci.* **2009**, 339, (2), 545-550.
51. Kovalchuk, V.; Krägel, J.; Miller, R.; Fainerman, V.; Kovalchuk, N.; Zholkovskij, E.; Wüstneck, R.; Dukhin, S., Effect of the nonstationary viscous flow in the capillary on oscillating bubble and oscillating drop measurements. *Journal of Colloid and Interface Science* **2000**, 232, (1), 25-32.
52. Jin, F.; Gupta, N. R.; Stebe, K. J., The detachment of a viscous drop in a viscous solution in the presence of a soluble surfactant. *Physics of Fluids (1994-present)* **2006**, 18, (2), 022103.
53. Wong, H.; Rumschitzki, D.; Maldarelli, C., Theory and experiment on the low-Reynolds-number expansion and contraction of a bubble pinned at a submerged tube tip. *Journal of Fluid mechanics* **1998**, 356, 93-124.
54. Kao, R.; Edwards, D.; Wasan, D.; Chen, E., Measurement of interfacial dilatational viscosity at high rates of interface expansion using the maximum bubble pressure method. I. Gas—liquid surface. *J. Colloid Interface Sci.* **1992**, 148, (1), 247-256.
55. Monroy, F.; Ortega, F.; Rubio, R. G., Dilatational rheology of insoluble polymer monolayers: Poly (vinylacetate). *Phys. Rev. E* **1998**, 58, (6), 7629.

CHAPTER 4

MEASURING INTERFACIAL MECHANICS OF INSOLUBLE MONOLAYERS ON A SPHERICAL CAP INTERFACE

4.1 INTRODUCTION

Complex insoluble interfaces are of interest in numerous physiological and industrial processes. Biological interfaces such as biomembranes, vesicles, and the air-liquid interface of lung alveoli include predominantly water-insoluble components like phospholipids, fatty acids, and proteins.¹ Phospholipid monolayers are often studied as models for biological interfaces.² The equilibrium and dynamic properties of insoluble interfaces impact biological processes such as respiration³ and other physicochemical processes like emulsion stability⁴ and atmospheric aerosol formation.⁵

A common method of studying insoluble interfaces is to deposit a known mass of material onto a Langmuir film balance of well-defined surface area, then measure the surface pressure using a Wilhelmy plate during uniaxial compression of the interface. Interfacial rheology can be measured by oscillating the barriers that compress the interface. Oscillation frequencies are typically between 1 - 100 mHz. The resulting uniaxial deformation of the barriers leads to an interface response that is locally a mixture of dilatation and shear⁶ with the possibility of local anisotropic deformation.⁷ While a framework has been developed to separate surface tension effects from the intrinsic rheological response of the interface on a Langmuir trough,⁸ the interfacial shear and dilatational stresses appear as a sum in the analysis and thus cannot be separated. Insoluble monolayers can also be deposited at a pendant drop interface using a

syringe containing the insoluble material dissolved in a volatile solvent.⁹ The rheology of the interface is probed in a similar frequency range by oscillating the volume of the pendant drop. In this case, the deformation of the pendant drop interface is also a mixture of dilatation and shear due to the nonuniform curvature of the interface.¹⁰ As we have discussed in Chapter 3, capillary pressure tensiometers impose pure dilatational deformation, but the extremely small interfacial area leads to difficulty in reliably depositing insoluble layers.

In this chapter, we present a method of depositing insoluble layers onto interfaces in the microtensiometer using a miscible subphase exchange. The mechanical properties of the resulting interfaces are measured in equilibrium and in small amplitude oscillatory dilatation. We control the initial surface using the bulk concentration of water-insoluble surfactant dissolved in a water-miscible solvent, and the flow rate at which the solvent is exchanged for DI water. We use three common species: dimyristoylphosphatidylcholine (DMPC), palmitic acid (PA), and dipalmitoylphosphatidylcholine (DPPC). We apply the same measurement method to Tween 80, which has been shown to form insoluble layers at fluid-fluid interfaces.¹¹

4.2 MATERIALS

Palmitic acid of 99% purity, semisynthetic 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) of $\geq 99\%$ purity, and the nonionic surfactant polyoxyethylene glycol sorbitan monooleate (Tween 80) were purchased from Sigma-Aldrich and used as received. 1,2-Dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) of $>99\%$ purity was purchased from Avanti Polar

Lipids, Inc. and used as received. DPPC and DMPC were stored at -20°C . Crystalline sodium chloride (NaCl) of $\geq 99\%$ purity was purchased from Fisher Scientific. Isopropanol for solution preparation and ethanol (ACS grade) for cleaning were purchased from Pharmco-AAPER and used without further purification. Deionized (DI) water from a Barnstead UV Ultrapure II purification system was used in the fluid exchange procedure and in preparing Tween 80 solutions. The pH of the water was 5.8 after one hour in ambient conditions using an Accumet AR50 pH meter (Fisher Scientific).

DMPC, DPPC, and palmitic acid were dissolved in a measured volume of isopropanol at concentrations ranging from 0.01 – 10 mg/mL and stored at room temperature for less than a week before use. A 1.5 μM Tween 80 solution was prepared from the dilution of a 3 mM stock solution prepared by adding a measured mass of Tween 80 to DI water. NaCl was baked at a temperature of 380°C for 4 hours to remove any impurities before a known mass was added to DI water to prepare a 0.5 M NaCl solution.

4.3 METHODS

All experiments are performed at ambient temperature ($19 \pm 1^{\circ}\text{C}$), which is measured daily using an AcuRite digital thermometer.

4.3.1 DESCRIPTION OF MICROTENSIMETER

All measurements of surface tension, surface pressure, and dilatational modulus are performed on a device built in-house called the microtensiometer, which has been described previously in the work of Alvarez *et al.*¹² and is shown schematically in Figure 4.1. The device consists of a glass capillary filled with air inserted into a sample reservoir machined from a rigid photopolymer

(VeroWhitePlus RGD835, Stratasys) using a 3D prototyping device (Objet Desktop 30, polyjet printer). The microtensiometer reservoir consists of a well containing the sample and three ports connected to it: one port to hold the capillary, an inlet port connected to a large fluid reservoir, and an outlet port connected to a waste container. A 30 mm circular glass slide is affixed to the base of the well using Loctite® marine epoxy in order to view the capillary using bright-field microscopy. A polytetrafluoroethylene ring is fitted inside the well to prevent surfactant adsorption to the walls of the device and associated contamination issues.

A glass capillary (TW100-6 Kwik-Fil borosilicate, World Precision Instruments) is connected to a pressure transducer and hydrostatic pressure column, which is used to generate a bubble at the capillary tip and measure the pressure inside the capillary. The capillary is tapered using a micropipette puller (MicroData Instrument Inc., PMP-102) so that one end of the capillary has an inner radius ranging from 30-50 μm . The glass capillary is acid washed, then the inside is treated with a hydrophobic coating (Dynasylan SivoCLEAR, Evonik) to promote contact line pinning at the glass-air-aqueous interface. The hydrophobic coating is flowed through the capillary, and then the capillary is rinsed using acetone and DI water. The glass capillary is placed in a 60°C oven for 15-30 minutes to dry.

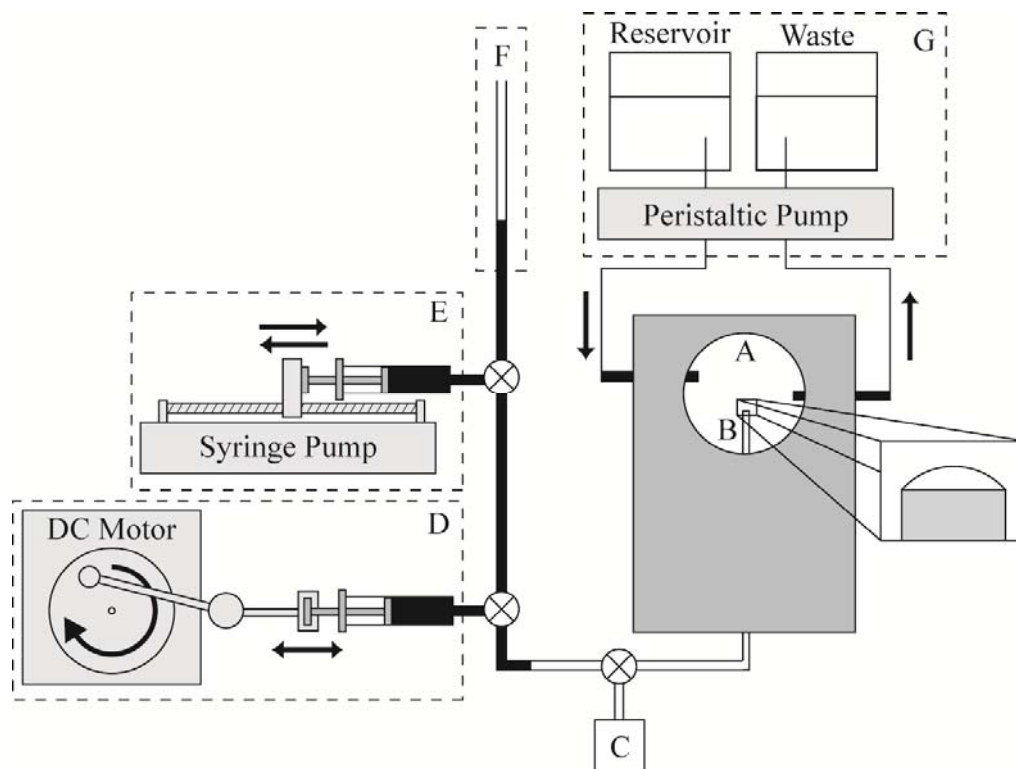


Figure 4.1 Schematic diagram of the microtensiometer and additional components used in experiments. (A) 3.5 mL sample reservoir, (B) glass capillary, (C) pressure transducer, (D) oscillating motor and piston, (E) linear compression pump, (F) hydrostatic pressure head, (G) fluid exchange system. The expanded image at lower right shows a magnified view of the capillary tip with a pinned bubble. Three-way valves are indicated with the $\otimes$ symbol. The tubing connecting the capillary to the hydrostatic pressure head is colored black in sections that are filled with water

The system used to exchange fluid in the sample reservoir of the microtensiometer is shown as Region G in Figure 4.1. The inlet port is connected to flexible tubing in a peristaltic pump (Cole-Parmer, Model#7553-30) by PTFE tubing. PTFE tubing is also used to connect the flexible tubing to the fluid reservoir (PYREX 1000 mL). The outlet port is also connected by the peristaltic pump to the waste container (PYREX 1000 mL) using PTFE tubing. The inlet and outlet tubing connections are made using polyether ether ketone (PEEK) fittings connected to threaded holes machined into the device. When the pump is

operating, the fluid in the well of the microtensiometer is replaced with the reservoir fluid at a controlled volumetric flow rate between 0.2 – 0.72 mL/min.

4.3.2 PREPARATION OF INSOLUBLE INTERFACES

Insoluble interfaces of palmitic acid, DMPC, and DPPC are generated by dissolving a known mass of the species of interest in isopropanol and filling the microtensiometer sample reservoir with the isopropanol solution. A fresh air bubble with an initially clean interface is generated. After 50 s the peristaltic pump is turned on to exchange the alcohol solution with DI water from the exchange reservoir. Immediately after the peristaltic pump is turned on, the hydrostatic pressure is manually increased at a rapid rate to prevent the bubble from retracting into the capillary. The radius of curvature of the bubble is kept large to prevent the bubble from being ejected from the capillary due to large fluctuations in the surface tension. After 15 fluid exchange residence times, calculated by dividing the volume of the reservoir by the exchange flow rate, the bubble is expanded manually to a radius of curvature close to a hemisphere. The pump is turned off after a total of 43 residence times, and the system is left to stabilize for 1000 s to allow for relaxation of the interface. Additional fluid exchange steps on the same interface are performed at a constant hydrostatic pressure.

The procedure for generating a Tween 80 coated interface is similar to that described previously.¹¹ A 1.5 μ M Tween 80 solution is added to the sample reservoir of the microtensiometer and a fresh interface is generated. When the interface has relaxed to a desired surface tension corresponding to a desired surface coverage, the peristaltic pump is turned on to exchange the Tween 80

solution in the sample reservoir with DI water. All experiments on Tween 80 in this chapter are performed at a fluid exchange rate of 0.5 mL/s. The hydrostatic pressure is kept constant during the exchange process, and the pump is stopped after 43 residence times (300 s). In some experiments examining Tween 80 interfaces, the DI water in the reservoir is replaced with a 0.5 M NaCl solution through a second fluid exchange procedure. The 0.5 M NaCl solution is flowed through the fluid reservoir at a flow rate of 0.5 mL/s for 100 s.

4.3.3 MEASURING SURFACE TENSION AND SURFACE PRESSURE

To perform surface tension measurements, a constant hydrostatic pressure head is used to pin an air bubble at the capillary tip. The small capillary tip allows for the generation of bubbles with radius of curvature from 30 to 100 μm . The pressure head is generated by a water column constructed of polyethylene tubing attached to a solenoid valve. The pressure head is measured using an Omega gauge pressure transducer (Model EW-68075-10, 0.08% accuracy) and recorded using LabView. The bubble is imaged using bright field microscopy with a Nikon T-300 inverted light microscope. Images of the bubble are collected using a digital camera (Spot RT Monochrome, Diagnostic Instruments, Inc.) and analyzed using LabView. The bubble is fit to a circle of radius $R(t)$ in real-time, and the dynamic surface tension is calculated as

$$\sigma(t) = \frac{\Delta P(t) R(t)}{2} \quad (4.1)$$

where $\Delta P(t)$ is the pressure jump across the interface and $R(t)$ is the instantaneous radius of the interface. The pressure jump is taken to be the difference between the transducer pressure reading and the hydrostatic pressure head of solution

above the capillary in the sample reservoir of the device. The hydrostatic pressure head is measured at the end of each experiment by first generating a clean air-water interface, then multiplying the difference between the measured value and the literature value for the air-water surface tension (72.8 mN/m) by $2/R$. The convention in the literature for insoluble monolayers is to report the surface pressure as

$$\Pi = \sigma_0 - \sigma(t), \quad (4.2)$$

where σ_0 is the clean surface tension of the system.

4.3.4 MEASUREMENT OF SURFACE PRESSURE AND GIBBS ELASTICITY IN STEADY ISOTROPIC COMPRESSION

The interface is compressed by linearly varying the pressure inside the capillary using a syringe pump to control the fluid volume inside the hydrostatic pressure column, shown as Region E in Figure 4.1. A three-way valve is connected in-line between the free surface at the top of the hydrostatic pressure column and a second three-way valve connecting the oscillation mechanism for small amplitude dilatation described in Section 4.3.5. The three-way valve is connected via polyethylene tubing to a 5 mL syringe containing DI water. The connection from the three-way valve to the tubing is made by Luer-Lok fitting and a 20 gauge needle, and the tubing connection to the syringe is made by a 20 gauge needle. The entire line is filled with water, and care is taken to remove any air bubbles from the line.

During the measurement, the three-way valve closes off the line to the hydrostatic pressure head and opens the line to the tubing connected to the syringe

pump. The syringe pump (BS-8000, Braintree Scientific, Inc.) varies the volumetric flow rate of water from 1 to 80 mL/hr, leading to a rate of change in the hydrostatic pressure between 1 - 100 Pa/s. The corresponding change in the radius of the bubble is imaged. The resulting instantaneous surface pressure is calculated from Equation 4.2, and the surface area is given by $A = 2\pi R \left(R - \sqrt{R^2 - R_c^2} \right)$, where R_c is the radius of the capillary.

The response of the interface depends on its mechanics. The compression rate dA/dt is a directly controlled parameter in Langmuir trough experiments and is generally kept constant during measurement of the surface pressure.¹³ The dilatation rate is the relevant rate of deformation in interfacial viscoelasticity experiments^{8, 14} and is given by

$$\dot{\delta} = \frac{1}{A} \frac{dA}{dt} = \frac{d \ln A}{dt}. \quad (4.3)$$

For a constant compression rate, the dilatation rate is negative, and the magnitude increases as surface area decreases. In the microtensiometer, the dilatation rate is determined by first calculating the surface area of the spherical cap interface using the measured radius of curvature and the known capillary radius, then performing a piecewise calculation of the slope of the natural log of the temporal surface area.

The instantaneous pressure and radius measured during compression are used to calculate the surface pressure as described in Section 3.1.2. The Gibbs elasticity,¹⁴ given by

$$E = - \frac{d\Pi}{d \ln A} \quad (4.4)$$

is a measure of the sensitivity of the surface pressure to changes in the surface concentration. E is also known as the area compressibility modulus, and the inverse of E is the compressibility of the interface commonly reported for measurements performed on a Langmuir trough.^{15, 16} The Gibbs elasticity is determined by first calculating the surface pressure and surface area at each time step, then calculating a slope based on a linear fit of surface pressure versus the natural log of the surface area. The slope is calculated in a piecewise manner similar to that used to calculate the dilatation rate. Reported error in the Gibbs elasticity is based error propagation from the measured pressure jump and radius.

4.3.5 MEASUREMENT OF DILATATIONAL MODULUS

The dilatational modulus can contain contributions from the Gibbs modulus (surface tension effects) and other intrinsic extra stresses. The total dilatational modulus can be measured independently via small amplitude oscillation of the spherical cap interface in the microtensiometer. To achieve small amplitude dilatational oscillation, the hydrostatic pressure is varied sinusoidally using a syringe connected to the oscillating motor and piston mechanism shown in Region D of Figure 4.1. The apparatus has been described in detail by Alvarez *et al.*¹⁷ The three-way valve is connected via Luer-Lok fitting to a microliter glass syringe of 50, 100, or 250 μL (Becton, Dickinson, & Co.). The amplitude of the pressure oscillation depends on the syringe size used. For the syringe sizes used here, the available pressure amplitudes are approximately 35, 70, and 180 Pa, respectively. The syringe is filled with water, and the syringe piston is attached to the moving arm of the oscillating apparatus. The motor speed

is controlled by a LabView VI to generate oscillation frequencies between 0.09 – 1.04 Hz (0.58 – 6.55 rad/s).

During oscillation of the hydrostatic pressure head, the pressure at Region C in Figure 4.1 and radius are recorded as a function of time. There is a time lag between the recording of the pressure and the recording of the radius within a time step in the LabView program. This accounted for by recording the time difference between the recording of the pressure and radius for a given time step. The oscillatory data are analyzed in MATLAB using fast Fourier transform techniques¹⁸ to determine whether higher harmonics are present in the measured oscillation of the radius as well as the calculated surface area. The amplitudes of the higher harmonics must remain less than 10% of the amplitude of the primary harmonic for the small amplitude assumption to be valid. If this requirement is met, the amplitude and phase shift from the pressure and radius signals are used to calculate the in-phase component, E' , and the out-of-phase component, E'' , that yield the complex dilatational modulus E^* based on the theory described in Chapter 3. We report these values in terms of the magnitude of the complex modulus $|E^*| = \sqrt{E'^2 + E''^2}$ and the phase angle $\delta = \tan^{-1}(E''/E')$. The magnitude of δ can range between $\delta = 0$ when $E'' = 0$ to $\delta = \pi/2$ when $E' = 0$. Uncertainties in the magnitude of the complex modulus and the phase angle are based on a propagation of error from the measured pressure and the radius.

4.4 RESULTS

4.4.1 DEPOSITION OF FATTY ACID AND PHOSPHOLIPID LAYERS USING FLUID EXCHANGE

Fatty acids and phospholipids are deposited at an air-water interface in the microtensiometer by solvent exchange from isopropyl alcohol to DI water. During the fluid exchange procedure for PA, DPPC, and DMPC, the surface tension dynamics are not clearly resolved due to refractive index differences between water and isopropanol. The initial surface tension between air and the isopropanol solution with dissolved fatty acid or phospholipid is 21.5 ± 0.5 mN/m, which agrees with the literature value of 21.74 mN/m for a clean air-isopropanol interface.¹⁹ No dynamics are observed between the point when a clean air-isopropanol solution interface is generated and when the solvent exchange procedure is started. Depending on the initial concentration of fatty acid or phospholipid dissolved in isopropanol and the fluid exchange speed, a nonzero value of the surface pressure may be obtained once the procedure is complete. A fresh air-water interface generated after the fluid exchange procedure is complete exhibits a clean surface tension value of 72.8 mN/m for 1000 s, indicating that any surface-active species remaining in the reservoir upon removing the initial solution are present in negligible concentration.

Figure 4.2 shows the resulting surface pressure as a function of initial concentration of dissolved species in isopropanol for an exchange flow rate of 0.5 mL/s. Because the interface is always expanded to approximately the same surface area after the exchange is completed, the surface pressure indicates the

number of moles of material spread at the air-water interface. For all three surface-active species, the surface pressure increases with increasing concentration. For concentrations greater than 1 mg/mL, the surface-active species falls out of solution rapidly, and large aggregates are observed in the fluid reservoir.

Palmitic acid approaches a maximum surface pressure of 9.6 ± 0.4 mN/m as the initial concentration increases. The asymptotic value of the surface pressure agrees with the equilibrium spreading pressure of 9.7 mN/m at 20°C reported by Boyd and Schubert.²⁰ The surface pressure at equilibrium does not increase past this value with the availability of more palmitic acid because at this value the monolayer remains in equilibrium with the crystal phase.¹⁵ The surface pressure for palmitic acid is zero for concentrations less than 0.05 mg/mL, indicating that the amount of palmitic acid adsorbed at the interface after fluid exchange is too low to measure.

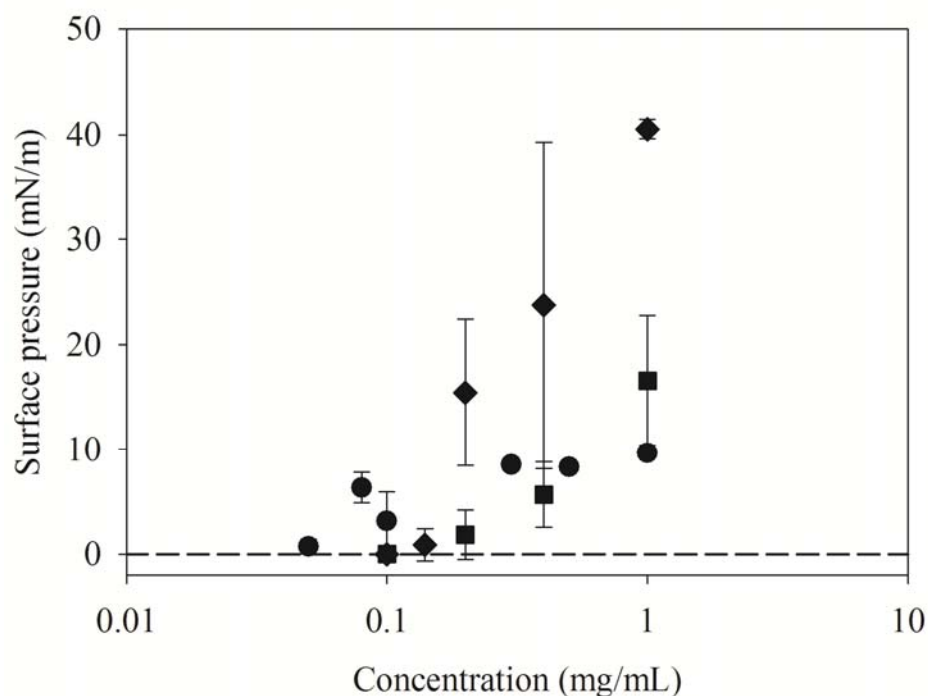


Figure 4.2. Effect of initial concentration of fatty acid or phospholipid dissolved in isopropanol on the surface pressure achieved after fluid exchange for (◆) DMPC, (●) PA, and (■) DPPC. The dashed line denotes zero surface pressure. Error bars correspond to the standard deviation based on three experiments.

Both DPPC and DMPC exhibit an increase in the surface pressure for increasing concentrations in isopropanol, indicating that more material is adsorbed to the interface. For concentrations less than 0.1 mg/mL, there is no observable surface pressure after the fluid exchange procedure. For DPPC, the initial surface pressure increases from zero to 16.6 ± 6.2 mN/m over the concentration range considered. This value is well below the collapse pressure of 60 to 70 mN/m observed for DPPC on a DI water subphase at 20°C measured on a Langmuir trough.¹⁶

The initial surface pressure of DMPC increases from zero surface pressure at a concentration of 0.1 mg/mL in isopropanol to 40.5 ± 0.9 mN/m at a

concentration of 1 mg/mL. DMPC is observed to transition to a condensed phase²¹ or undergo collapse of the monolayer²² at a surface pressure of approximately 40 mN/m in a Langmuir trough. The large error bars on the surface pressure values obtained for DMPC at bulk concentrations of 0.2 and 0.4 mg/mL, as well as for DPPC at 1 mg/mL, reflect the sensitivity of surface pressure to changes in surface concentration of phospholipid at these conditions.

The effect of the fluid exchange rate on the initial surface pressure is shown in Figure 4.3 for three different initial bulk concentrations of palmitic acid. The initial surface pressure after fluid exchange increases with increasing volumetric flow rate for concentrations of 0.05 and 0.2 mg/mL. At a concentration of 0.01 mg/mL, there is no measureable surface pressure for palmitic acid even at a higher flow rate of 0.72 mL/s. At the lowest flow rate, fluid exchange for 43 residence times does not rinse all of the isopropanol out of the fluid reservoir, which is shown by the nonzero surface pressure calculated based on a clean air-water interface. The excess isopropanol in the bulk at the low exchange flow rate is confirmed by performing a second fluid exchange at a volumetric flow rate of 0.5 mL/s. The surface pressure obtained after this second rinse is zero, as shown by the open symbols in Figure 4.3. The surface pressure of the interfaces generated at flow rates of 0.5 and 0.72 mL/s does not change when subject to a second fluid exchange.

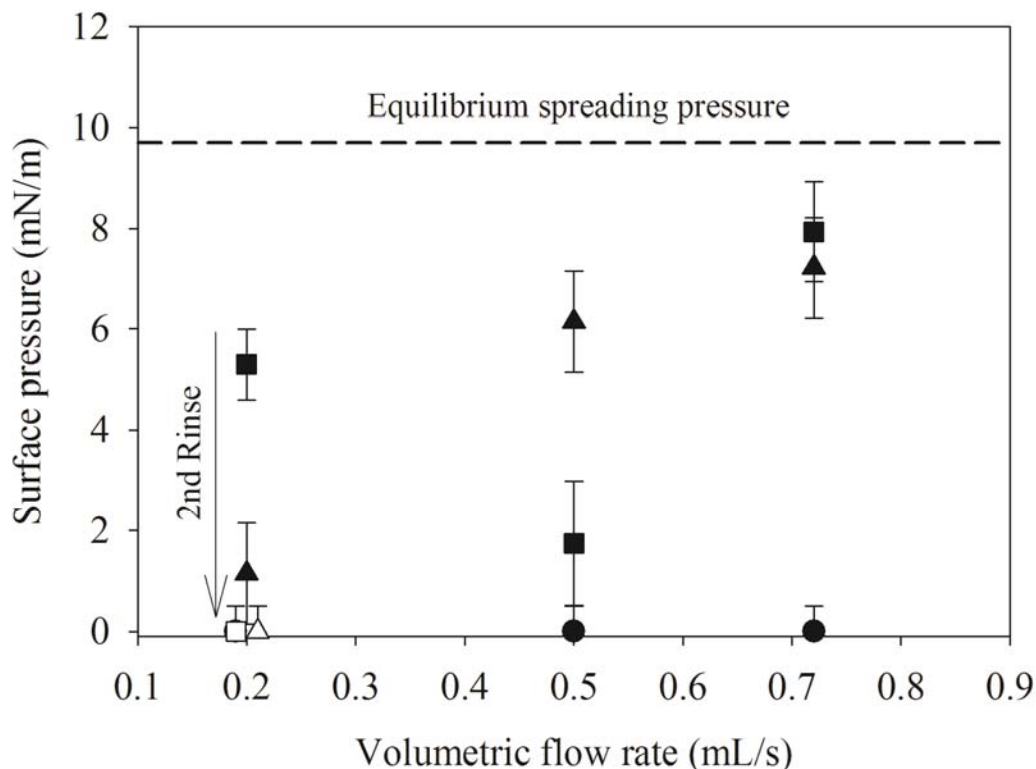


Figure 4.3. Effect of fluid exchange rate on the initial surface pressure. Symbols correspond to three different concentrations at (●) 0.01, (■) 0.05, and (▲) 0.2 mg/mL in isopropanol. Filled points correspond to the surface pressure after a single rinse, open symbols correspond to a second rinse with DI water. The horizontal dashed line indicates the equilibrium spreading pressure for palmitic acid at 20°C. Error bars represent uncertainty from propagation of error.

4.4.2 DMPC COMPRESSION ISOTHERM AND MODULUS

A DMPC coated interface is compressed from different initial surface pressures, and the resulting surface pressure as a function of surface area is shown in Figure 4.4a. Horizontal error bars indicate the uncertainty in the surface area due to a propagation of error in the capillary radius and the radius of curvature of the interface, and the uncertainty in the surface pressure is smaller than the symbol size. The capillary radius for these experiments is $35.9 \pm 0.1 \mu\text{m}$, meaning that the maximum possible surface area range is between $4050 \mu\text{m}^2$ for a flat

interface at the capillary tip and $8100 \mu\text{m}^2$ when the bubble is a hemisphere. The surface area range of $4500 - 6500 \mu\text{m}^2$ probed in the experiment is less than the total available range due to optical resolution limits on the droplet curvature at low surface areas. In addition, the bubble is prevented from ejecting at high surface areas when the bubble forms a hemispherical shape.

For each data set, the interface is compressed due to a hydrostatic pressure decrease of 10 Pa/s , which leads to a surface area decrease. The surface pressure increases as the surface area decreases, indicating an increase in the concentration of DMPC at the interface. The dilatation rate for each curve is not constant but varies between -1×10^{-3} and $-3 \times 10^{-3} \text{ s}^{-1}$ during the experiment. For the two largest initial surface pressures shown, the surface pressure deviates significantly as the interface is compressed below $5350 \mu\text{m}^2$. The surface pressure of 35 mN/m at which the deviation occurs is near the transition state or collapse pressure of DMPC of approximately 40 mN/m .

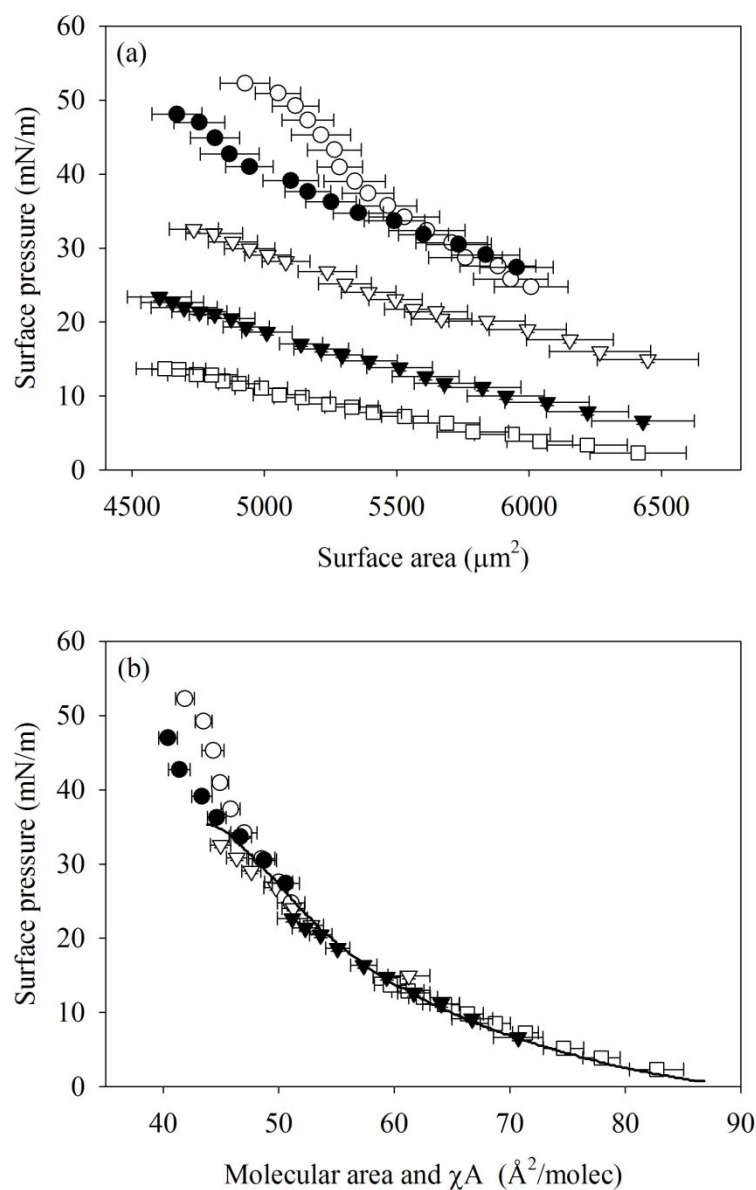


Figure 4.4. Surface pressure of DMPC as a function of (a) the surface area of the spherical cap interface, and (b) the scaled surface area. The initial surface pressures are ($\square$) 2.5 mN/m, ($\blacktriangledown$) 6.5 mN/m, (∇) 15 mN/m, ($\circ$) 25 mN/m, and ($\bullet$) 27.5 mN/m. The solid line in Figure 4.4b is the DMPC isotherm reported by Kubo *et al.*²² measured at 20°C on a water subphase in a Langmuir trough. Horizontal error bars represent uncertainty in the radius of curvature and capillary radius. Vertical error bars estimated from uncertainty in the radius and pressure are within the symbol size.

A direct comparison between the measured surface pressure-area curve and the isotherm reported from a Langmuir trough can be performed by introducing a horizontal shift of the measured surface pressure-area curves. The shift is obtained by multiplying each surface pressure-area curve by a constant χ such that the measured curve overlaps the isotherm. When the data can be shifted to overlay an isotherm measured at the same experimental conditions, the inverse of χ is equivalent to the number of molecules at the interface. The resulting collapse of the data to the isotherm for DMPC is shown in Figure 4.4b. There is good agreement in the overlap of the individual surface pressure-area curves and good agreement with the isotherm data measured on a Langmuir trough at surface pressures below 35 mN/m. There is a significant deviation in the measured data for surface pressures greater than 35 mN/m. The isotherm of DMPC depends strongly on temperature below 21°C for a molecular area of less than 50 Å²/molecule.²³

The dilatational modulus for DMPC as a function of frequency is shown for four different surface pressures in Figure 4.5. The value of $|E^*|$ for all four surface pressures is nearly independent of oscillation frequency over the experimental range available on the microtensiometer. The magnitude of $|E^*|$ at a given frequency increases with increasing surface pressure, up to $\Pi = 25.9$ mN/m, above which the magnitude of the modulus slightly decreases. The phase angle remains low for all four surface pressures, indicating that the out-of-phase component of the modulus is small or unresolved for DMPC in these experiments. At $\Pi = 7.3$ mN/m, the phase angle decreases with increasing oscillation

frequency. The values for the phase angle measured here are significantly different from the measurements of Wilke *et al.*,²⁴ who measured the dilatational properties of DMPC on a Langmuir trough at a temperature of 23°C. From their reported E' and dilatational viscosity ($\eta_d = E''/\omega$), the phase angle should be approximately 1.33 at a surface pressure of 10 mN/m for an oscillation frequency of 0.57 rad/s; however, their reported temperature is close to the phase transition temperature of 24°C for DMPC.²⁵ Because we are operating below the phase transition temperature, the interface is expected to behave more like a solid.

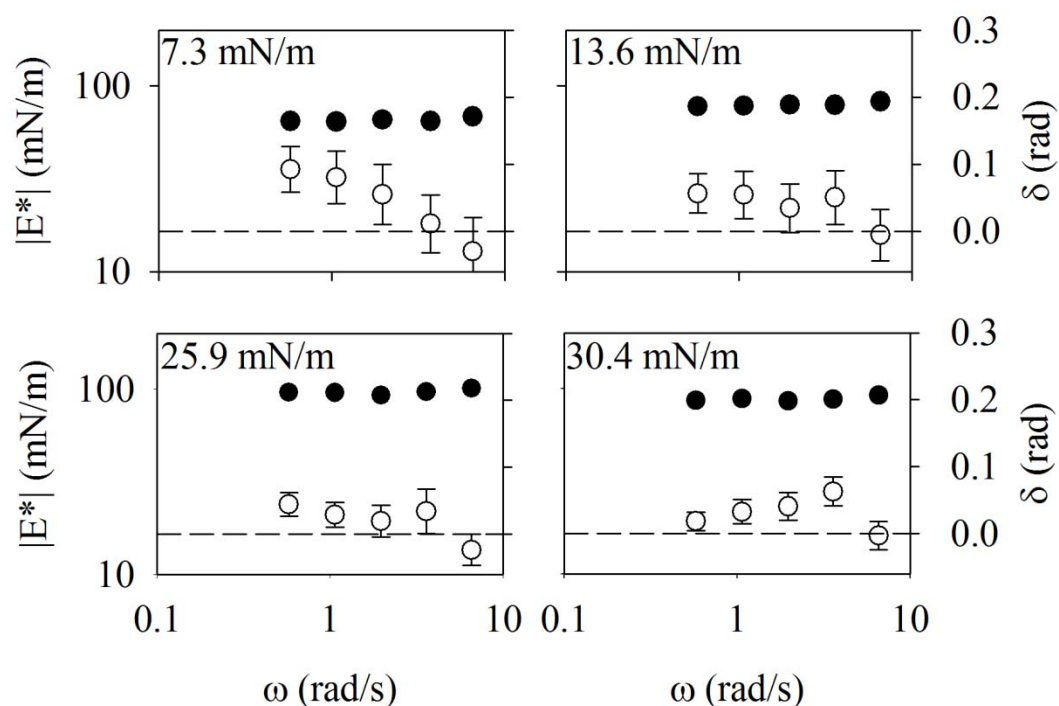


Figure 4.5. Dilatational modulus of DMPC versus angular frequency ω at surface pressures indicated in the upper right of each plot. The modulus is plotted in terms of (●) $|E^*|$ plotted on the left axis and (○) δ plotted on the right axis. The dashed line indicates the zero value for the phase angle in each plot. The scaling of the axes is the same for all plots.

From Chapter 3, the real part of the modulus for ideal Langmuir monolayers is equivalent to the Gibbs elasticity E at a given surface pressure. Figure 4.6 compares E and E' measured at a frequency of 1.06 rad/s as a function of surface pressure. The two quantities agree well over the measured range of surface pressures up to 40 mN/m. These observations suggest that any contribution to the total dilatational stress arising from intrinsic rheology is negligible. For surface pressures greater than 40 mN/m, the Gibbs elasticity decreases due to a collapse of the monolayer and E' continues to increase. Well beyond the collapse pressure for the monolayer, we no longer expect the surface to behave as an ideal Langmuir monolayer.

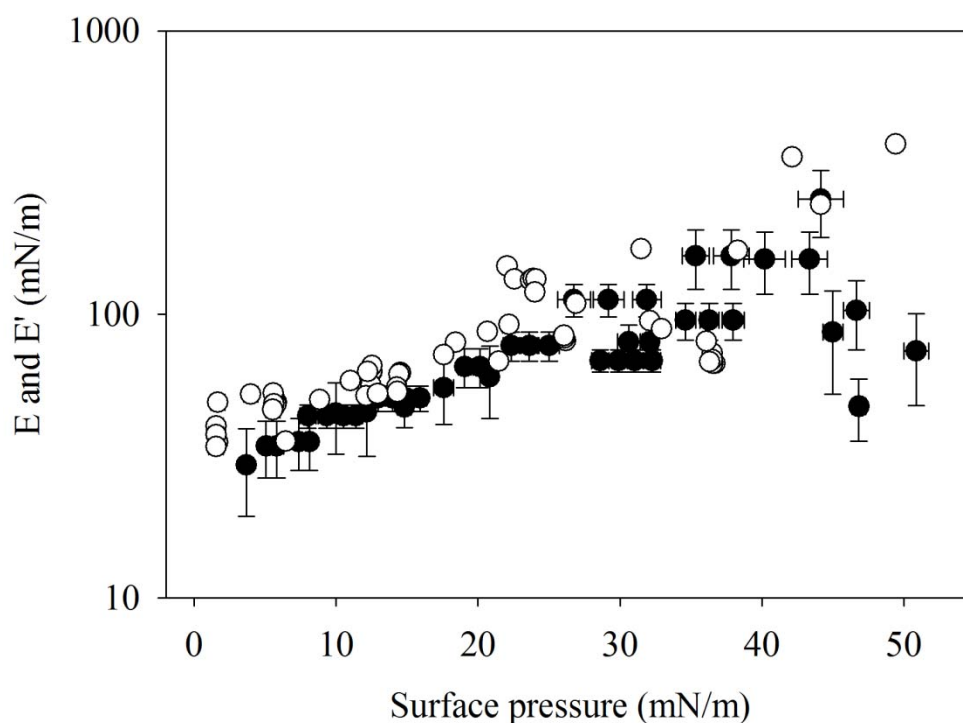


Figure 4.6. A comparison of (●) the Gibbs elasticity E and (○) the in-phase component of the dilatational modulus E' over the measured range of surface pressures for DMPC.

4.4.3 PALMITIC ACID COMPRESSION ISOTHERM AND MODULUS

Results from compression experiments for an interface with adsorbed palmitic acid are shown in Figure 4.7a. For initial surface pressures greater than the equilibrium spreading pressure, the surface pressure-area curves depend on dilatation rate. This can be seen from a comparison of the surface pressures for the interface compressed at a rate of $-2 \times 10^{-4} \text{ s}^{-1}$ from 8.5 mN/m versus the interface compressed at $-1 \times 10^{-2} \text{ s}^{-1}$ from 9.7 mN/m. When compressed at a slower dilatation rate, the interface reaches lower surface pressures compared with rapid compression. This observation agrees with previous reports on palmitic acid monolayers,²⁶ although another study reports no changes in the isotherm with compression rate until the collapse pressure is reached.²⁷ Because this deviation occurs at a surface pressure greater than the equilibrium spreading pressure, this deviation is most likely due to a competition between the dilatation rate of the interface and the rate of formation of palmitic acid crystals, which would decrease the monolayer concentration at the interface. At the highest surface pressure and fastest initial dilatation rate, there is a distinct change in slope at 25 mN/m, beyond which the surface pressure rises sharply until it collapses at 52 mN/m. We also observe a decrease in the dilatation rate from $-1 \times 10^{-2} \text{ s}^{-1}$ to $-3 \times 10^{-3} \text{ s}^{-1}$ above this kink in the surface pressure-area curve while keeping the pressure head decrease constant. This change in slope is attributed to a transition from a liquid-condensed phase to an incompressible solid-like phase.²⁸

The horizontally shifted data for palmitic acid shown in Figure 4.7b indicates good agreement between the microtensiometer surface pressure-area

curve and the isotherm measured on a Langmuir trough when the dilatation rate is fast enough to overcome the collapse of the monolayer. Based on the compression rate given by Lipp *et al.*,²⁸ the dilatation rate for the isotherm is on the order of $-1 \times 10^{-3} \text{ s}^{-1}$. When the interface is compressed at the slower dilatation rate of $-2 \times 10^{-4} \text{ s}^{-1}$, the curve cannot be shifted to the isotherm using a constant value for χ . In that case, the data is shifted so that the initial surface pressure lies on the isotherm.

A higher dilatation rate shows that the insoluble palmitic acid layer on the microtensiometer reproduces the transition between the liquid-condensed phase and the solid-like phase in both the surface pressure, where the transition is observed, as well as the sharp change in the slope. The value of χ^{-1} for these interfaces is approximately equivalent to the number of molecules at the interface except for the data measured from the initial surface pressure of 9.7 mN/m. Because this value started at the equilibrium spreading pressure, the monolayer could be in equilibrium with the crystalline phase of palmitic acid, meaning that the total number of molecules at the interface could be significantly higher than predicted. In this case, χ^{-1} is an estimate of the minimum amount of palmitic acid that is present at the interface.

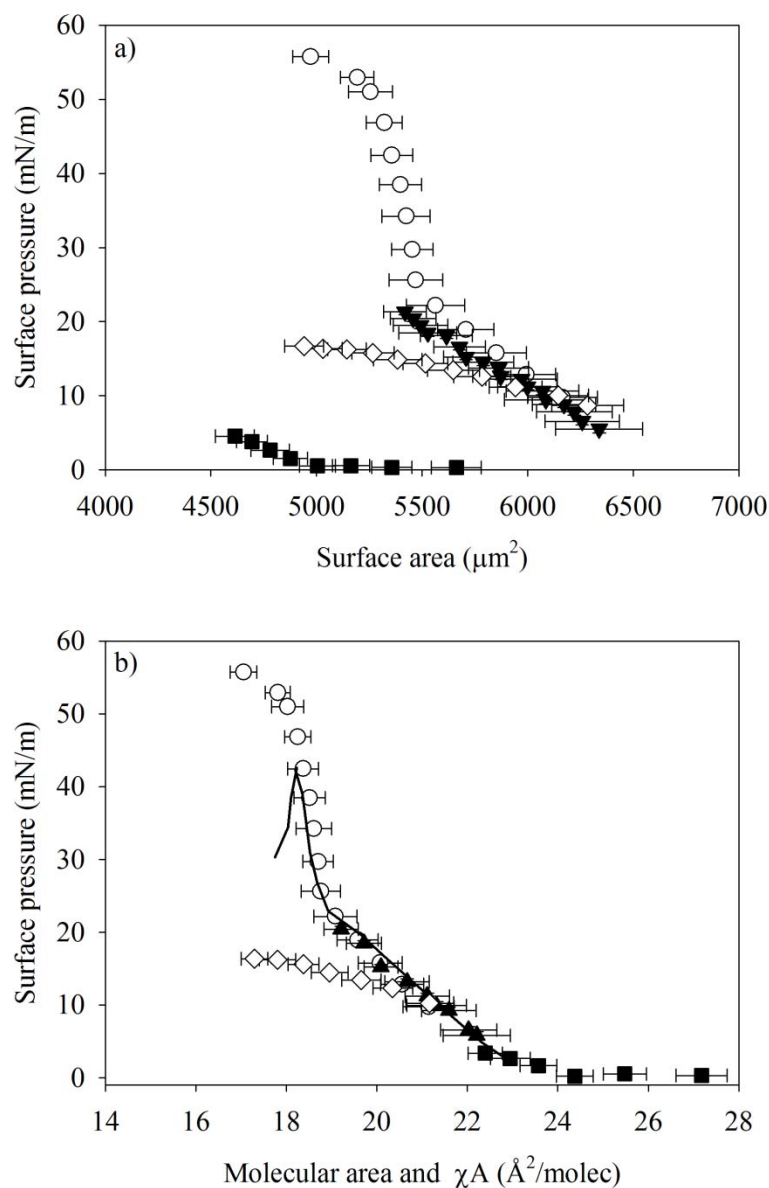


Figure 4.7. Surface pressure of palmitic acid versus (a) the surface area of the spherical cap interface, and (b) the surface area scaled by χ . The initial surface pressures and initial dilatation rates are (■) 0 mN/m and $-3 \times 10^{-3} \text{ s}^{-1}$, (▼) 5.5 mN/m and $-3 \times 10^{-3} \text{ s}^{-1}$, (◇) 8.5 mN/m and $-2 \times 10^{-4} \text{ s}^{-1}$, (○) 9.7 mN/m and $-1 \times 10^{-2} \text{ s}^{-1}$. The solid line in Figure 4.7b is the palmitic acid isotherm reported by Lipp *et al.*²⁸ measured on a water subphase at 16°C.

Figure 4.8 shows the dilatational modulus measured for palmitic acid at four different surface pressures. Measurements over the frequency range were only made for surface pressures below the equilibrium spreading pressure; above that value, the surface pressure and surface area decreased over the time period of the oscillatory experiment (~5 minutes). For example, after compression to an initial surface pressure of 15 mN/m, the surface pressure decreased 2 mN/m and the surface area decreased $70 \mu\text{m}^2$ over a period of one minute.

For the four dilatational measurements shown, the magnitude of the modulus strongly depends on the surface pressure of the oscillation. The magnitude of the modulus is nearly independent of oscillation frequency, although there is a slight increase in $|E^*|$ as the frequency increases. The phase angle decreases as the surface pressure increases, reaching negative values at the highest measured surface pressure of 9.5 mN/m. A phase angle less than zero corresponds to a negative value for E'' , which has been observed in dilatational measurements for palmitic acid monolayers performed by Giermanska-Kahn *et al.*²⁹ It is important to note that their measurements observe a negative value for the out-of-phase component of the modulus over the entire measured surface pressure range for palmitic acid. This is not consistent with the observations presented here.

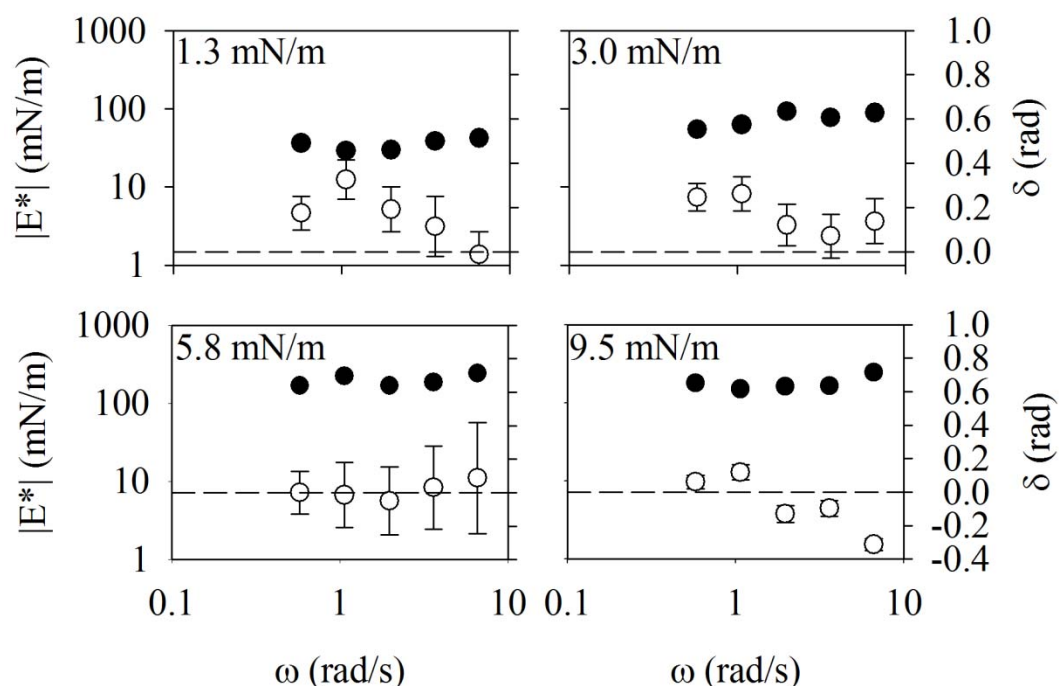


Figure 4.8 Dilatational modulus of palmitic acid versus angular frequency ω at surface pressures indicated in the upper right of each plot. The modulus is plotted in terms of (●) $|E^*|$ plotted on the left axis and (○) δ plotted on the right axis. The scaling of the ω and $|E^*|$ axes is the same for all plots. The scaling for δ is the same within each row of plots. The dashed line indicates the zero value for the phase angle in each plot.

A comparison of the Gibbs elasticity obtained from the surface-pressure area measurements and the in-phase part of the modulus is shown in Figure 4.9. The Gibbs elasticity was calculated only for the surface pressure-area measurements that could be adequately fit to the palmitic acid isotherm of Lipp *et al.* Measurements of the dilatational modulus are performed at a frequency of 1.06 rad/s for a period of approximately one minute, suggesting that measurements performed above the equilibrium spreading pressure have a nonzero stress and strain relaxation during the time period of the measurement. Reported values for E' are plotted at the average surface pressure over which the dilatational measurement was performed. Despite the stress and strain relaxation, the

measured value of E' agrees with the calculated Gibbs elasticity for a palmitic acid layer at surface pressures both above and below the equilibrium spreading pressure. Both E and E' quickly plateau to a value close to 100 mN/m at low surface pressures until the transition to a solid-like interface at $\Pi = 25$ mN/m. Above this transition point the Gibbs elasticity reaches a value of 760 mN/m before collapse. Values for E' could not be obtained above the transition pressure due to the decrease in the surface pressure immediately after the dilatation was stopped.

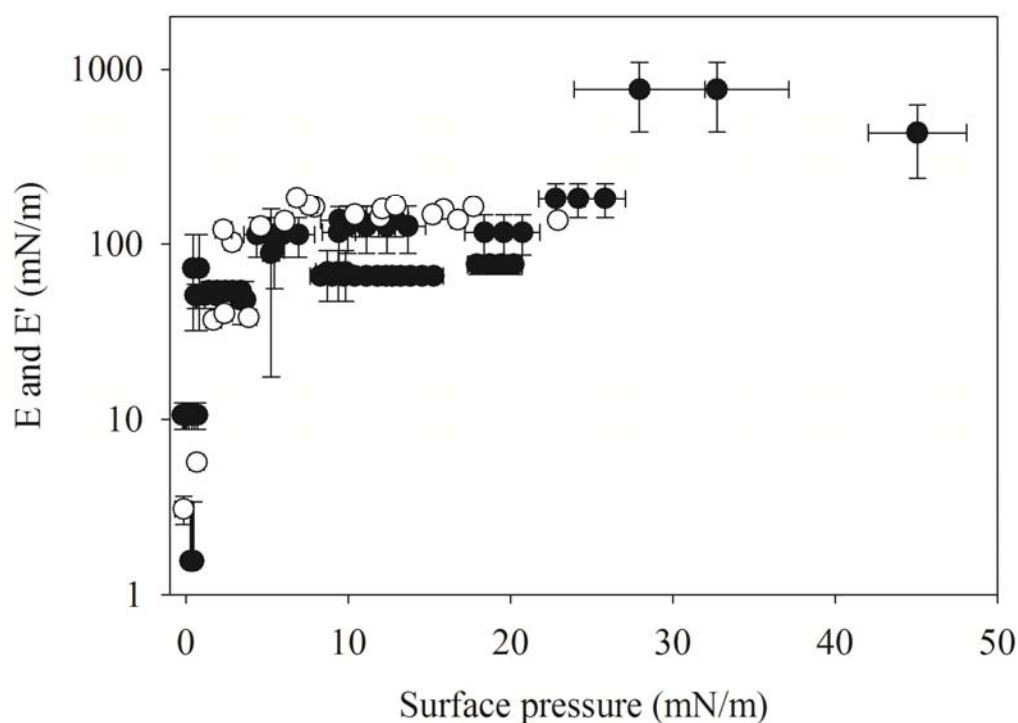


Figure 4.9. A comparison of (●) the Gibbs elasticity E and (○) the in-phase component of the dilatational modulus E' over the measured range of surface pressures for palmitic acid.

4.4.4 DPPC COMPRESSION ISOTHERM AND MODULUS

The Π - A measurements shown in Figure 4.10a for interfaces containing a deposited amount of DPPC again show the expected trend in the surface pressure as the surface area decreases. There is a distinct change in the slope of the isotherm near 12 mN/m, which is consistent with a transition from a liquid expanded-liquid condensed coexistence region to a liquid condensed phase.^{30, 31} For a constant hydrostatic pressure head decrease of 10 Pa/s, the dilatation rate below 12 mN/m is approximately $-1 \times 10^{-3} \text{ s}^{-1}$, whereas the dilatation rate for greater than 12 mN/m is slightly lower at $-6 \times 10^{-4} \text{ s}^{-1}$. A second slope change is observed above a surface pressure of 55 mN/m, which we attribute to a collapse of the DPPC layer at the interface.

Figure 4.10b shows the horizontally shifted Π - A data compared with the isotherm reported by Kim *et al.*³¹ measured on a Langmuir trough. When shifted to the isotherm, the microtensiometer data agrees well with the expected relationship between surface pressure and molecular area in the three different regions of the isotherm: the liquid expanded region below $\Pi = 6 \text{ mN/m}$, the liquid expanded-liquid condensed coexistence region between $6 < \Pi < 12 \text{ mN/m}$, and the liquid condensed region for $\Pi > 12 \text{ mN/m}$. A phase coexistence region is observed at surface pressures between $8 < \Pi < 12 \text{ mN/m}$, which is slightly above the coexistence region shown for the isotherm of Kim *et al.*³¹ Despite this, the measurement is within the full range of phase coexistence regions reported in the literature of 5 mN/m ³² to 10 mN/m .³³ A phase coexistence region for DPPC is not reported in the literature when using either a pendant drop apparatus^{34, 35} or a

constrained sessile drop.³⁶ The slope of the isotherm in the liquid condensed region above 12 mN/m is larger than that reported on a Langmuir trough. Although the compression rate for the isotherm shown in Figure 4.10b is not reported by Kim *et al.*,³¹ DPPC is known to exhibit a steeper slope in the liquid condensed region when compressed at a high rate.³⁷

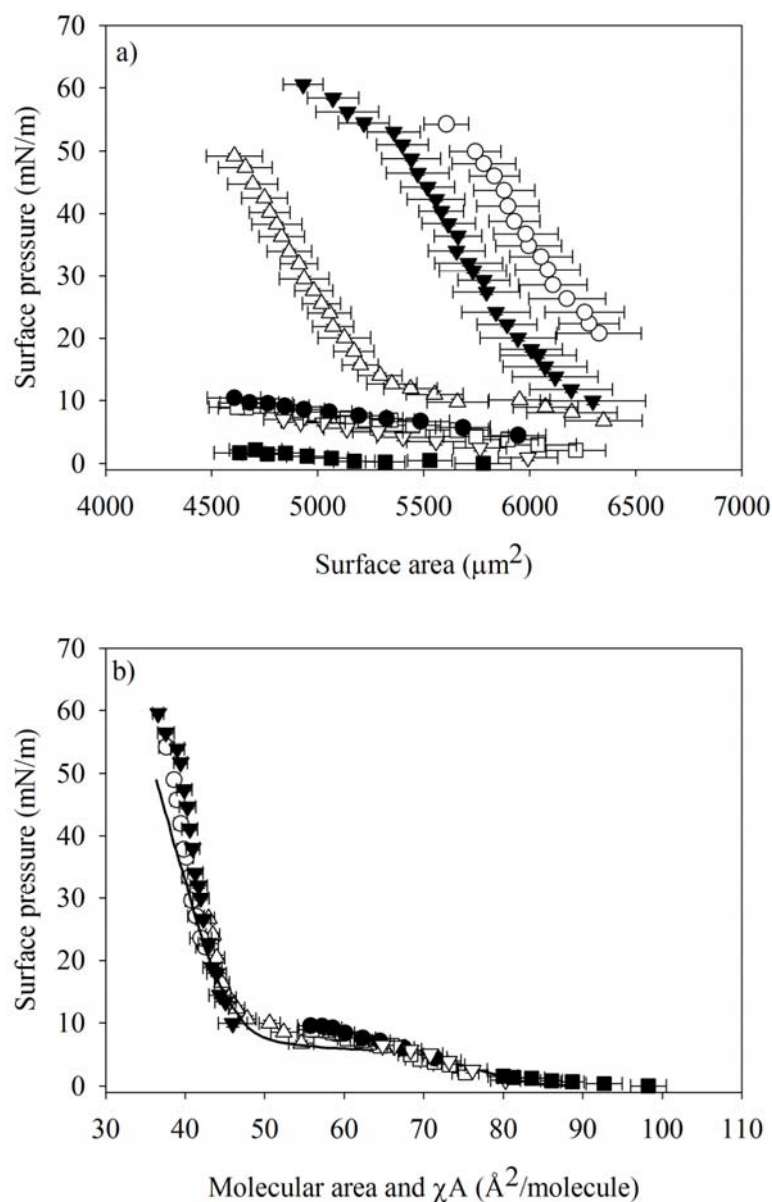


Figure 4.10. Surface pressure of DPPC versus (a) the surface area of the spherical cap interface, and (b) the surface area scaled by χ . The initial surface pressures are (■) 0 mN/m, (∇) 1 mN/m, ($\square$) 2 mN/m, (●) 4.5 mN/m, ($\triangle$) 7 mN/m, ($\blacktriangledown$) 10 mN/m, ($\circ$) 20.5 mN/m. The solid line in Figure 5.7b is a DPPC isotherm from the work of Kim *et al.*²⁹ measured on a water subphase at $21 \pm 1^\circ\text{C}$.

The dilatational measurements performed for DPPC layers at different surface pressures shown in Figure 4.11 indicate the frequency dependence of the modulus in the liquid expanded, coexistence, and liquid condensed regions of the isotherm. At all surface pressures, $|E^*|$ is nearly independent of oscillation frequency within the measured range, but the magnitude depends on the surface pressure. The magnitude of the phase angle increases as the surface pressure increases from zero in the liquid expanded region to low nonzero values in the coexistence and liquid condensed regions of the isotherm. The largest values of the phase angle are observed at 7.6 and 10 mN/m, when the DPPC layer is at the coexistence region. The phase angle values are also larger at slower oscillation frequencies. In the liquid expanded region the phase angle does not show a strong frequency dependence, reaching nonzero values below 0.2 rad.

Prior studies on the dilatational rheology of DPPC monolayers spread on a Langmuir trough show a similar dependence of the modulus on the surface pressure in the liquid expanded and liquid condensed regions.^{38, 39} In the phase coexistence region, Arriaga *et al.*³⁸ observe that the magnitude of the modulus and the dilatational viscosity depend on frequency within the experimental range of $3 \times 10^{-3} - 3 \times 10^{-1}$ Hz. We do not observe a similar frequency dependence in our data where the frequency ranges overlap.

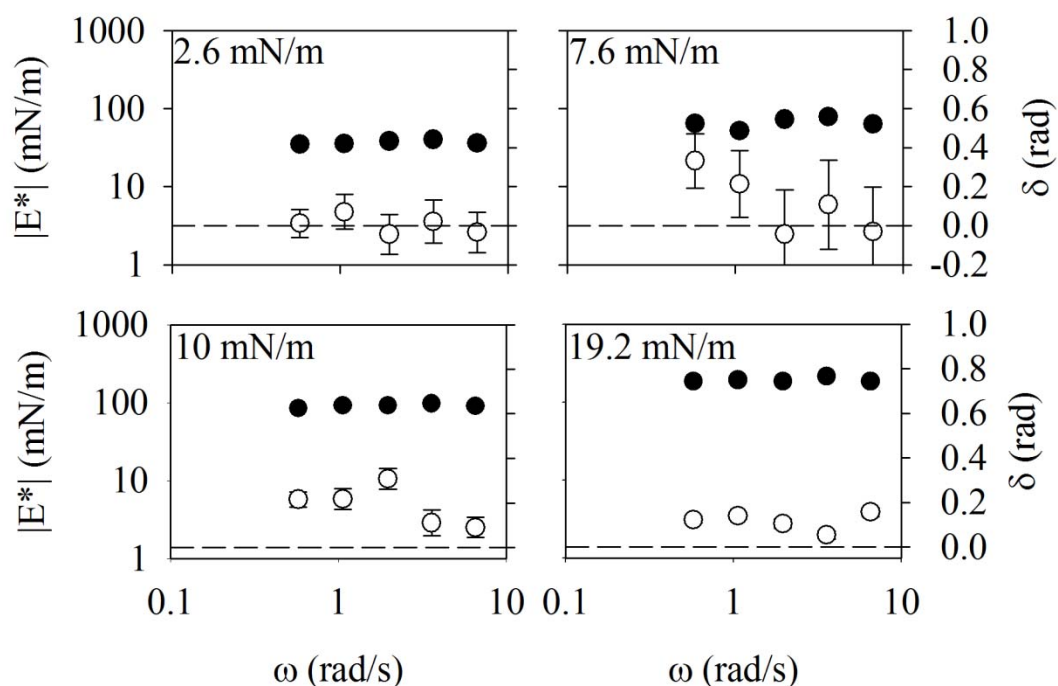


Figure 4.11. Dilatational modulus of DPPC versus angular frequency ω at surface pressures indicated in the upper right of each plot. The modulus is plotted in terms of (●) $|E^*|$ plotted on the left axis and (○) δ plotted on the right axis. The scaling of the ω and $|E^*|$ axes is the same for all plots. The scaling for δ is the same within each row of plots. The dashed line indicates the zero value for the phase angle in each plot.

A comparison of E' measured at 1.06 rad/s and the Gibbs elasticity E for a DPPC layer at the air-water interface is shown in Figure 4.12. The three regions of the isotherm are evident in the measure of the Gibbs elasticity. At surface pressures below the liquid expanded-liquid condensed coexistence region, both E and E' attain values close to 40 mN/m. Above the coexistence region, both the Gibbs elasticity and the in-phase part of the modulus increase to a values close to 160 mN/m, then continue to rise with the surface pressure to a maximum value of 390 mN/m before the DPPC interface collapses. Within the coexistence region, the Gibbs elasticity obtains a value of 21 – 28 mN/m. This is approximately half

the measured value of the in-phase part of the dilatational modulus in this region, which ranges from 35 – 75 mN/m as the surface pressure increases. A difference in magnitude between the Gibbs elasticity and the dilatational modulus has been reported previously for DPPC measured on a Langmuir trough.³⁸ The explanation proposed by Arriaga *et al.* is that the liquid condensed regions of the interface dispersed in a compressible liquid expanded phase act as solid grains and resist a decrease in surface area when compressed at a high rate.

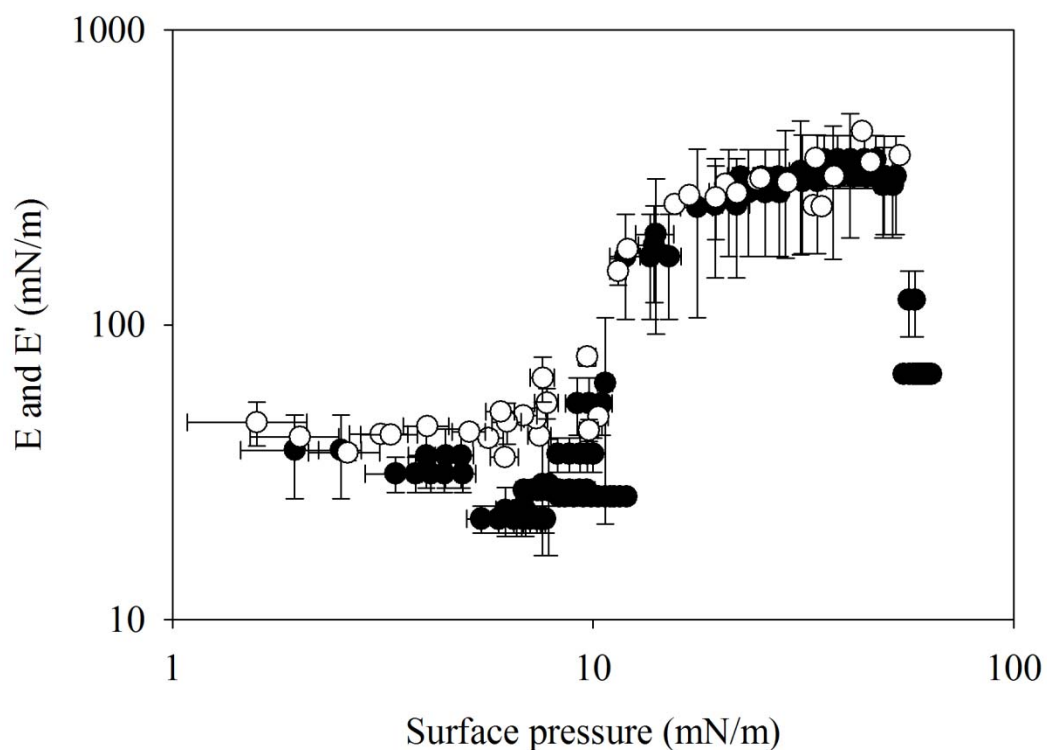


Figure 4.12. A comparison of (●) the Gibbs elasticity E and (○) the in-phase component of the dilatational modulus E' over the measured range of surface pressures for DPPC.

4.4.5 TWEEN 80 COMPRESSION ISOTHERM AND MODULUS

The capabilities of the microtensiometer in measuring surface pressure-area curves and the dilatational modulus for well-known insoluble interfaces can also be applied to probe the dilatational properties of Tween 80, which has been shown by Reichert and Walker¹¹ to form insoluble layers. Because Tween 80 is soluble in DI water, we can monitor the dynamic surface tension due to surfactant adsorption, which allows us to rinse the interface with DI water at a known surface pressure. Surface tension dynamics for Tween 80 during adsorption to an air-water interface and exchange with DI water are shown in Figure 4.13. The dynamics for all curves are similar from the generation of a clean interface at time $t=0$ until the initiation of the exchange period. During this period, the bulk concentration of Tween 80 is reduced from 1.5 μM to approximately zero. This is confirmed by generating a fresh air bubble after fluid exchange has been completed and observing no change in the surface tension over a period of 1000 s. Similar to the work of Reichert and Walker,^{11, 40} the fluid exchange does not cause the surface tension to rise back to the clean air-water surface tension of 72.8 mN/m, which is expected for soluble surfactants.

The dynamics immediately following fluid exchange depend on the surface tension at the time that fluid exchange began. Above a critical surface tension, the surface tension decreases by approximately 2 mN/m before reaching a constant value. This decrease in the surface tension is attributed to increased mass transport at the initial times of the exchange period due to increased convection in the reservoir, which enhances the mass transfer rate of surfactant to the interface.

The surface tension reaches a constant value approximately 40 s after the initialization of the exchange period. Below a critical value for the surface tension, the surface tension rises to a constant value during the fluid exchange process that is below the clean air-water surface tension value. Our results agree well with the observations of Reichert and Walker.^{11, 40} The nonzero value of the surface pressure for these interfaces indicates that an insoluble component of Tween 80 has remained at the air-water interface to form an insoluble layer.

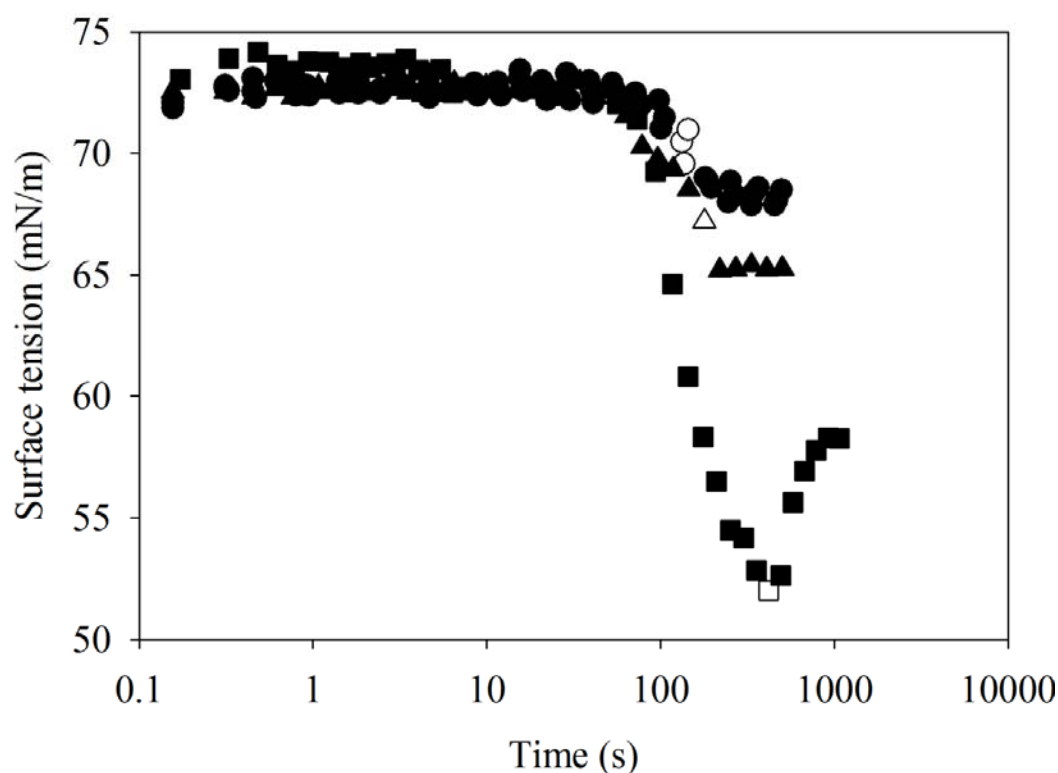


Figure 4.13. Surface tension dynamics for a 1.5 μM Tween 80 during surfactant adsorption and wash-out. The final surface pressure for each run is (●) 4 mN/m, (▲) 7.5 mN/m, and (■) 14.5 mN/m. The open symbol in each curve indicates the time when the wash-out procedure was started. Three measurements of the dynamics to $\Pi = 4$ mN/m are shown to indicate reproducibility.

The Tween 80 interfaces generated by the fluid exchange procedure are insoluble in the aqueous phase and can be subjected to both isotropic compression and small-amplitude dilatational rheological measurements to probe interfacial mechanics. Figure 4.14a shows the measured surface pressure under isotropic compression for four separate interfaces containing the insoluble component of Tween 80 with no excess surfactant in the aqueous phase. The interfaces are compressed starting from the largest measured surface area at a constant rate of change in the hydrostatic pressure head of -10 Pa/s , leading to an average dilatation rate for these interfaces between $0.001 - 0.003 \text{ s}^{-1}$.

All four compression isotherms for the insoluble component of Tween 80 at an air-DI water interface exhibit an increase in the surface pressure as the surface area decreases. The total change in the surface pressure over the surface area range is approximately 3 mN/m for each curve. A collapse pressure of 17 mN/m is observed for the compression at the largest starting surface pressure, beyond which the surface pressure decreases despite continued compression of the interface.

The presence of Tween 80 in oil-water emulsions is observed to influence the measured zeta potential of the oil droplets,⁴¹⁻⁴³ suggesting that there is an accumulation of charge at the interface due to the surfactant. To test this hypothesis, compression experiments were performed on interfaces where the DI water subphase was exchanged with a 0.5 M NaCl solution to screen any charge effects. The compression isotherms shown in Figure 4.14a show no significant deviation from the isotherms performed on a DI water subphase, indicating that

the insoluble component of Tween 80 does not exhibit a significant charge repulsion at air-water interfaces.

Tween 80 is known to degrade over time in both aqueous solution and the purified liquid.^{44, 45} Products of the various degradation processes include the primary fatty acid constituents: oleic, linoleic, palmitic, and stearic acids. Since Tween 80 could solubilize these materials and deposit them at the interface, it is important to show whether the insoluble component of Tween 80 remaining after the fluid exchange procedure is due primarily to fatty acids at the interface. Similar to the compression isotherms of the fatty acid and phospholipid layers studied in this chapter, we can shift the surface pressure-area data using constant χ values and directly compare with isotherms for the primary fatty acids^{28, 46-48} from literature as shown in Figure 4.14b. Although the measured data can be shifted to a single “master” curve, the data cannot be fit to a specific fatty acid isotherm. An alternate explanation for the observed surface pressure-area relationship is due to poly(ethylene oxide) (PEO) chains that comprise the Tween 80 head group. Although it is water soluble, PEO is also known to form insoluble monolayers at the air-water interface.⁴⁹⁻⁵¹ The compression data for Tween 80 is not expected to match a linear PEO chain isotherm due to differences in the polymer structure.

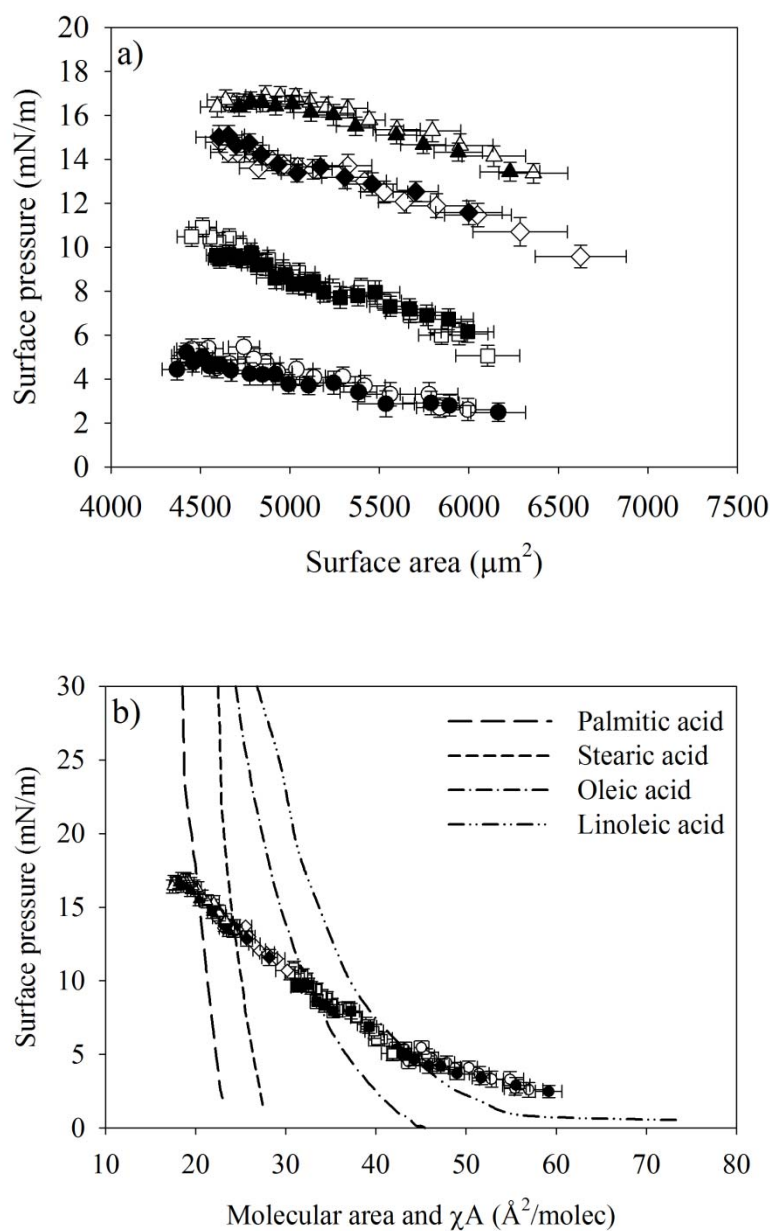


Figure 4.14. Compression measurements for the insoluble component of Tween 80 at an air-water interface. (a) Surface pressure versus the surface area of the spherical cap bubble. Different shape symbols indicate runs at different starting surface pressures. Unfilled points were performed with 0.5 M NaCl in the water subphase. (b) The same data as in (a) collapsed to a single line by scaling the surface area by χ . The data is plotted with isotherms of four major fatty acids present in Tween 80.

Measurements of the dilatational modulus performed on the insoluble component of Tween 80 are shown in Figure 4.15. The magnitude of the dilatational modulus is observed to be constant with respect to surface pressure, oscillation frequency, and the addition of salt for the experimental conditions we examined. The phase angle is approximately zero in these experiments, indicating that E'' is negligible. This dynamic response is unlike that observed for PEO monolayers⁵² or fatty acid layers. The lack of frequency dependence means that the modulus value is determined by the slope of the surface pressure-area isotherm. The results of these measurements are different from the dilatational modulus for insoluble Tween 80 layers at oil-water interfaces,¹¹ however those measurements were subject to a time lag between pressure and radius measurements for which we have since accounted.

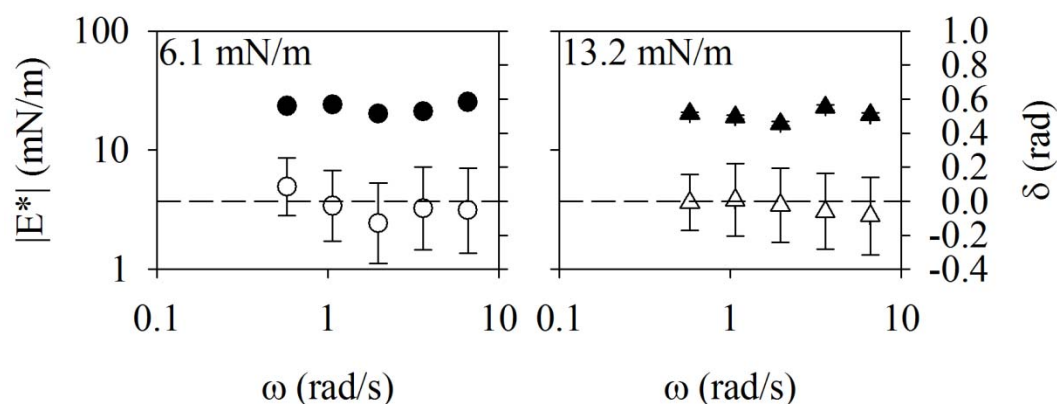


Figure 4.15. Dilatational modulus of Tween 80 versus angular frequency ω at surface pressures indicated in the upper right of each plot. Filled symbols denote the value of $|E^*|$ plotted on the left axis and open symbols denote δ plotted on the right axis. The left plot is measured on a DI water subphase, and the right plot is measured on a 0.5 M NaCl subphase. The scaling of the ω , $|E^*|$, and δ axes is the same for both plots. The dashed line indicates the zero value for the phase angle in each plot.

A comparison of the Gibbs elasticity and E' measured at 1.06 rad/s at different surface pressures confirms that the two values are equal over the surface pressure range considered. The initial value of the modulus starts close to 10 mN/m, but quickly rises to a constant value of approximately 15 mN/m for most of the surface pressure range. Neither the Gibbs elasticity nor the in-phase part of the modulus is affected by the addition of 0.5 M NaCl to the subphase.

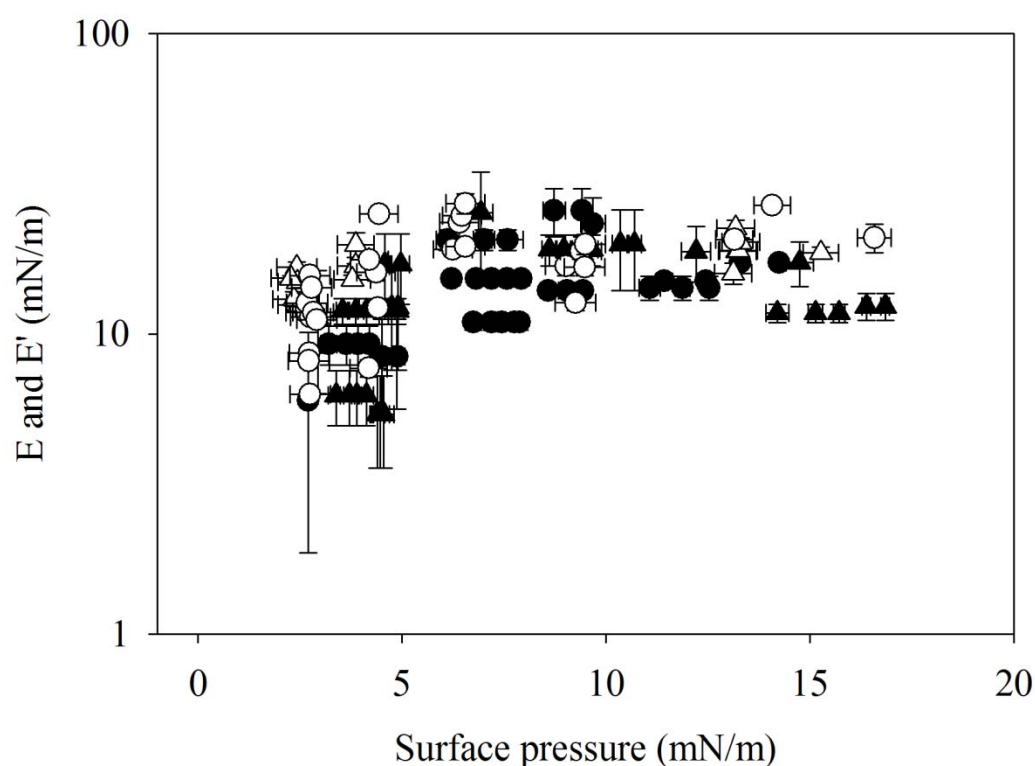


Figure 4.16. A comparison of ($\bullet$, $\blacktriangle$) the Gibbs elasticity E and ($\circ$, $\triangle$) the in-phase component of the dilatational modulus E' over the measured range of surface pressures for Tween 80. Circular symbols are measured on a DI water subphase, triangular symbols are measured on a 0.5 M NaCl subphase.

4.4 DISCUSSION

The three water-insoluble materials placed at the air-water interface in the microtensiometer are common substances used to generate Langmuir monolayers. This allows for a direct comparison between the observed surface phenomena on the microtensiometer with more conventional measurement methods.

Because DMPC is in a liquid expanded phase at 20°C, the isotherm shown in Figure 4.4b contains no distinguishing characteristics that can assist in shifting the data to the isotherm. Despite this, we see excellent agreement when using a constant χ value for the individual Π - A measurements. We cannot directly compare our measurements of the dilatational modulus to values previously obtained on a Langmuir trough due to temperature differences between the two systems. The agreement between the Gibbs elasticity and the in-phase component of the modulus indicates that the dilatational measurement is correct.

The palmitic acid isotherm exhibits a dilatation rate dependence not observed in either of the phospholipids. The interface on the microtensiometer must be compressed at dilatation rates faster than those imposed on a Langmuir trough in order to reproduce the characteristic features of the isotherm. It is important to note that the microtensiometer does not control surface area or surface pressure at the interface, which can lead to different observed collapse dynamics. For example, a palmitic acid interface compressed in a Langmuir trough above the equilibrium spreading pressure and held at a constant surface area exhibits a decrease in the surface pressure due to the formation of crystals. If the palmitic acid interface were compressed above the equilibrium spreading

pressure and then the hydrostatic pressure were held constant, the palmitic acid would also form crystals, leading to a decrease in surface pressure. Based on Equations 4.1, 4.2, and the equation for the surface area of a spherical cap, a decrease in the surface pressure will increase the radius of curvature while simultaneously decreasing the surface area. This surface area decrease will increase both the surface monolayer concentration and the surface pressure, meaning that the monolayer collapse at the microtensiometer interface will proceed until either the equilibrium spreading pressure is reached or the spherical cap interface is flat at the capillary tip. This insight into the operation of the microtensiometer means that an interface compressed above the equilibrium spreading pressure due to a constant decrease in the hydrostatic pressure head will most likely have two contributions to a decrease in the surface area: one due to the hydrostatic pressure head change, and one due to decrease in the surface pressure.

Measurements of the dilatational modulus for palmitic acid made on the microtensiometer differ significantly from those made on a planar interface during capillary wave excitation. The measurements made on the Langmuir trough were performed by the electrocapillary method at an oscillation frequency of 800 Hz,²⁹ which is two orders of magnitude larger than in our experiments. The dilatational modulus for palmitic acid at $\Pi = 9.5$ mN/m shows a negative phase angle ($E'' < 0$), which is an unphysical result. Because our measurement is so close to the equilibrium spreading pressure, it is difficult to determine whether this negative value for E'' is due to a transition between phases, as suggested by Giermanska-

Kahn *et al.*,²⁹ or due to a superposition of an oscillatory measurement with a stress (surface pressure) or strain (surface area) relaxation. Negative shear modulus values are not uncommon in the rheology literature when a fluid is subject to oscillatory shear flow superposed on steady flow.^{53, 54}

The Π - A measurements for the DPPC monolayer are in good agreement with isotherms measured on a Langmuir trough interface, capturing the liquid expanded, liquid condensed, and phase coexistence regions of the isotherm. The observation of a liquid expanded – liquid condensed coexistence region at the spherical cap interface contradicts previous measurements made on a pendant drop apparatus that do not observe this transition.^{9, 35} It has been hypothesized that the millimeter-scale radius of curvature of the pendant drop affects domain formation; however, we observe this transition with a radius of curvature 2-3 orders of magnitude smaller than pendant drop measurements. In a pendant drop device, the free surface will take the path of least resistance to accommodate a change in the volume of the droplet. It is known that both shear and dilatational stresses will affect the response of a pendant drop.¹⁰ Based on the low interfacial shear modulus of DPPC ($\sim \mu\text{N/m}$)³¹ compared to the dilatational modulus we expect the interface to more readily exhibit shear deformations to change the shape of the interface rather than expand or compress the surface area.

The dilatational measurements for DPPC do not agree directly with measurements made on a Langmuir trough using an oscillatory barrier. We attribute this to the mixed shear and dilatational flow present on a Langmuir trough during uniaxial deformation.⁸ The comparison of the Gibbs elasticity with

the in-phase component of the modulus in the phase coexistence region shows that there is an extra surface stress due to the intrinsic mechanical properties of the interface, as opposed to stresses due only to surface tension effects as described in the previous chapter.

The measurements performed on the Tween 80 interface indicate that the measured insoluble component is not due solely to fatty acids present in the surfactant. This does not rule out possible interaction between Tween 80 and fatty acids on the interface. Both the surface pressure and dilatational modulus are independent of salt concentration in the bulk phase.

Based on these results, the fluid exchange procedure described in this chapter is successful in generating insoluble surfactant layers at the microtensiometer bubble interface. Although a rigorous model describing the transport of surface-active species to the interface during the fluid exchange procedure is outside the scope of this work, we have shown that both the initially dissolved concentration of material in isopropanol and the fluid exchange flow rate can be used to control the amount of material adsorbed to the interface. Increasing the surfactant concentration increases the amount of material in the reservoir available for adsorption to the air-water interface during the fluid exchange procedure. Fluid flow is known to increase the flux of soluble surfactants to a bubble interface in the microtensiometer due to convective mass transport.⁵⁵ We expect that the increased convection at higher flow rates also increases the flux of insoluble materials to the interface during the fluid exchange procedure.

The miscibility of the initial fluid in the microtensiometer reservoir with the exchanged fluid is a key component of this procedure. If two immiscible or slightly miscible fluids such as chloroform and water are used, the fluids will emulsify in the reservoir. A second criterion for the fluid phases is that the first phase must be able to dissolve enough of the surfactant to deposit a substantial amount at the interface during the exchange procedure. In this chapter we have used isopropanol and water as the two phases; however, other water-soluble solutes can be used. Although we have assumed that all isopropanol is removed from the reservoir, it is possible that there could be some residual isopropanol due to either dead space in the microtensiometer reservoir or isopropanol vapor partitioning into the air bubble phase inside the capillary. The 1000 s waiting period after the fluid exchange procedure allows time for vapor diffusion into the capillary as well as isopropanol evaporation from the aqueous phase.

The system described here requires approximately 3 mL of a surfactant solution at low (mg/mL) concentrations. This is significantly more than the amount of solution ($\sim\mu\text{L}$) deposited at a Langmuir trough interface in the same concentration. The benefits of this measurement include the small amount of subphase solution necessary to run the experiment as well as the ability to change concentration or pH easily. This is achieved simply by using the peristaltic pump connected to a reservoir of the desired solution. The total experimental time is reduced when measuring the effect of subphase compositions on the response of complex insoluble interfaces.

A possible source of error in measurements on the microtensiometer is the presence of surface-active contaminants. These materials could change the response of the interface to compression as well as lower the collapse pressure of the interface. An issue that is specific to insoluble layers is film leakage at high surface pressures, where surfactant can spread onto solid surfaces in contact with the interface. This tends to occur at surface tensions below 5 mN/m, which we have avoided in our experiments.

Isotherms can depend strongly on conditions such as subphase pH, temperature, and spreading solvent. For this reason, the χ value used to shift microtensiometer experiments to isotherms from the literature is not an exact measure of the number of molecules at the interface. Shifting the *II-A* data to a single curve indicates self-consistency in the data by showing that the initial surface pressure achieved through the fluid exchange procedure is equivalent to the surface pressure measured during a compression of the interface. This is true even if the data cannot be fit to an isotherm. We shift the curve to an isotherm to show that the measurement is both self-consistent and able to reproduce characteristics of isotherms measured on common measurement apparatuses.

The fact that the microtensiometer only generates dilatational deformations greatly simplifies the analysis of measurements where interfacial rheology is expected to contribute to the measured interfacial stress. Both Langmuir trough and pendant drop/bubble experiments result in a combination of shear and dilatational deformation, which can make the analysis of surface pressure-area isotherms and dilatational modulus measurements difficult. The

isotropic compression and expansion of the interface performed on the microtensiometer provides a method to measure purely dilatational stress-strain relationships.

4.5 SUMMARY

This chapter provides a method to generate insoluble interfaces in the microtensiometer and confirms that the interfaces generated by this method are equivalent to those measured on standard measurement systems. The amount of insoluble surfactant added to the interface can be controlled by varying either the initial dissolved concentration of surfactant or the subphase exchange flow rate. The resulting interface can be subjected to both isotropic and oscillatory deformation due to a change in the hydrostatic pressure head of the system.

In the cases of palmitic acid, DMPC, and DPPC, we have shown that our measurements reproduce results observed in the literature. Our results also benefit from a purely dilatational compression and oscillation of the interface, which allow for a simplified analysis compared to the mixed dilatation and shear observed on both Langmuir trough and pendant drop apparatuses. The success of our experimental methods on commonly-studied insoluble interfaces has allowed us to probe the properties of the insoluble components of Tween 80. The isotherm and dilatational modulus indicate that the surface properties of Tween 80 are not strongly dependent upon isotropic compression or oscillatory dilatation. These results show that the microtensiometer can be used to measure the surface properties of insoluble materials.

1. Goerke, J., Pulmonary surfactant: functions and molecular composition. *Biochimica et Biophysica Acta (BBA)-Molecular Basis of Disease* **1998**, 1408, (2), 79-89.
2. Stefaniu, C.; Brezesinski, G.; Möhwald, H., Langmuir monolayers as models to study processes at membrane surfaces. *Advances in colloid and interface science* **2014**.
3. Wüstneck, R.; Perez-Gil, J.; Wüstneck, N.; Cruz, A.; Fainerman, V.; Pison, U., Interfacial properties of pulmonary surfactant layers. *Advances in colloid and interface science* **2005**, 117, (1), 33-58.
4. Ushikubo, F.; Cunha, R., Stability mechanisms of liquid water-in-oil emulsions. *Food Hydrocolloids* **2014**, 34, 145-153.
5. Decesari, S.; Facchini, M.; Mircea, M.; Cavalli, F.; Fuzzi, S., Solubility properties of surfactants in atmospheric aerosol and cloud/fog water samples. *Journal of Geophysical Research: Atmospheres (1984–2012)* **2003**, 108, (D21).
6. Petkov, J. T.; Gurkov, T. D.; Campbell, B. E.; Borwankar, R. P., Dilatational and shear elasticity of gel-like protein layers on air/water interface. *Langmuir* **2000**, 16, (8), 3703-3711.
7. Malcolm, B., Aspects of Langmuir trough design in relation to the study of molecular monolayers of polymers and condensed films. *Thin Solid Films* **1989**, 178, (1), 17-25.
8. Verwijlen, T.; Imperiali, L.; Vermant, J., Separating viscoelastic and compressibility contributions in pressure-area isotherm measurements. *Advances in colloid and interface science* **2013**.
9. Li, J.; Miller, R.; Vollhardt, D.; Weidemann, G.; Möhwald, H., Isotherms of phospholipid monolayers measured by a pendant drop technique. *Colloid and Polymer Science* **1996**, 274, (10), 995-999.
10. Yeung, A.; Zhang, L., Shear effects in interfacial rheology and their implications on oscillating pendant drop experiments. *Langmuir* **2006**, 22, (2), 693-701.
11. Reichert, M. D.; Walker, L. M., Interfacial Tension Dynamics, Interfacial Mechanics, and Response to Rapid Dilution of Bulk Surfactant of a Model Oil–Water-Dispersant System. *Langmuir* **2013**, 29, (6), 1857-1867.
12. Alvarez, N. J.; Walker, L. M.; Anna, S. L., A microtensiometer to probe the effect of radius of curvature on surfactant transport to a spherical interface. *Langmuir* **2010**, 26, (16), 13310-13319.

13. Kaganer, V. M.; Möhwald, H.; Dutta, P., Structure and phase transitions in Langmuir monolayers. *Reviews of Modern Physics* **1999**, 71, (3), 779.
14. Edwards, D. A.; Brenner, H.; Wasan, D. T., *Interfacial Transport Processes and Rheology*. Butterworth-Heineman: 1991.
15. Gaines, G. L., *Insoluble monolayers at liquid-gas interfaces*. 1966.
16. Duncan, S. L.; Larson, R. G., Comparing experimental and simulated pressure-area isotherms for DPPC. *Biophysical journal* **2008**, 94, (8), 2965-2986.
17. Alvarez, N. J.; Anna, S. L.; Saigal, T.; Tilton, R. D.; Walker, L. M., Interfacial dynamics and rheology of polymer-grafted nanoparticles at air–water and xylene–water interfaces. *Langmuir* **2012**, 28, (21), 8052-8063.
18. Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P., *Numerical Recipes in C: The Art of Scientific Computing*. Cambridge University Press: 1992.
19. Vazquez, G.; Alvarez, E.; Navaza, J. M., Surface tension of alcohol water+ water from 20 to 50. degree. C. *Journal of chemical and engineering data* **1995**, 40, (3), 611-614.
20. Boyd, G.; Schubert, J., Energy relations in unimolecular film formation: the spreading of cetyl alcohol and palmitic acid on aqueous surfaces. *The Journal of Physical Chemistry* **1957**, 61, (10), 1271-1275.
21. Gaboriaud, F.; Golan, R.; Volinsky, R.; Berman, A.; Jelinek, R., Organization and structural properties of Langmuir films composed of conjugated polydiacetylene and phospholipids. *Langmuir* **2001**, 17, (12), 3651-3657.
22. Kubo, I.; Adachi, S.; Maeda, H.; Seki, A., Phosphatidylcholine monolayers observed with Brewster angle microscopy and π -A isotherms. *Thin Solid Films* **2001**, 393, (1), 80-85.
23. Li, M.; Retter, U.; Lipkowski, J., Kinetic studies of spreading DMPC vesicles at the air-solution interface using film pressure measurements. *Langmuir* **2005**, 21, (10), 4356-4361.
24. Wilke, N.; Vega Mercado, F.; Maggio, B., Rheological properties of a two phase lipid monolayer at the air/water interface: effect of the composition of the mixture. *Langmuir* **2010**, 26, (13), 11050-11059.
25. Caffrey, M., *LIPIDAT: a database of thermodynamic data and associated on lipid mesomorphic and polymorphic transitions*. CRC Press: 1993.

26. Heikkilä, R. E.; Kwong, C. N.; Cornwell, D. G., Stability of fatty acid monolayers and the relationship between equilibrium spreading pressure, phase transformations, and polymorphic crystal forms. *Journal of lipid research* **1970**, 11, (3), 190-194.
27. Albrecht, O., Experimental study of the stability and metastability of palmitic acid. *Thin Solid Films* **1989**, 178, (1), 93-101.
28. Lipp, M. M.; Lee, K.; Waring, A.; Zasadzinski, J. A., Fluorescence, polarized fluorescence, and Brewster angle microscopy of palmitic acid and lung surfactant protein B monolayers. *Biophysical journal* **1997**, 72, (6), 2783-2804.
29. Giermanska-Kahn, J.; Monroy, F.; Langevin, D., Negative effective surface viscosities in insoluble fatty acid monolayers: Effect of phase transitions on dilational viscoelasticity. *Physical Review E* **1999**, 60, (6), 7163.
30. Miñones Jr, J.; Rodríguez Patino, J.; Conde, O.; Carrera, C.; Seoane, R., The effect of polar groups on structural characteristics of phospholipid monolayers spread at the air–water interface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2002**, 203, (1), 273-286.
31. Kim, K.; Choi, S. Q.; Zasadzinski, J. A.; Squires, T. M., Interfacial microrheology of DPPC monolayers at the air–water interface. *Soft Matter* **2011**, 7, (17), 7782-7789.
32. Borissevitch, G. P.; Tabak, M.; Oliveira, O. N., Interaction of dipyrindamole with lipids in mixed Langmuir monolayers. *Biochimica et Biophysica Acta (BBA)-Biomembranes* **1996**, 1278, (1), 12-18.
33. Bordini, F.; De Luca, F.; Cametti, C.; Naglieri, A.; Misasi, R.; Sorice, M., Interactions of mono- and di-sialogangliosides with phospholipids in mixed monolayers at air-water interface. *Colloids and Surfaces B: Biointerfaces* **1999**, 13, (3), 135-142.
34. Jyoti, A.; Prokop, R.; Li, J.; Vollhardt, D.; Kwok, D.; Miller, R.; Möhwald, H.; Neumann, A., An investigation of the compression rate dependence on the surface pressure-surface area isotherm for a dipalmitoyl phosphatidylcholine monolayer at the air/water interface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1996**, 116, (1), 173-180.
35. Anton, N.; Pierrat, P.; Lebeau, L.; Vandamme, T. F.; Bouriart, P., A study of insoluble monolayers by deposition at a bubble interface. *Soft Matter* **2013**, 9, (42), 10081-10091.

36. Saad, S. M.; Policova, Z.; Acosta, E. J.; Neumann, A. W., Axisymmetric Drop Shape Analysis– Constrained Sessile Drop (ADSA-CSD): A Film Balance Technique for High Collapse Pressures. *Langmuir* **2008**, 24, (19), 10843-10850.
37. Crane, J. M.; Hall, S. B., Rapid compression transforms interfacial monolayers of pulmonary surfactant. *Biophysical journal* **2001**, 80, (4), 1863-1872.
38. Arriaga, L. R.; López-Montero, I.; Ignés-Mullol, J.; Monroy, F., Domain-growth kinetic origin of nonhorizontal phase coexistence plateaux in langmuir monolayers: compression rigidity of a Raft-like lipid distribution. *The Journal of Physical Chemistry B* **2010**, 114, (13), 4509-4520.
39. Lucero Caro, A.; Rodríguez Niño, M. R.; Rodríguez Patino, J. M., The effect of pH on surface dilatational and shear properties of phospholipid monolayers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2008**, 327, (1), 79-89.
40. Reichert, M. D. Using Microscale Interfaces to Connect Transport Dynamics, Interfacial Mechanics, and Coalescence Behavior for a Model Oil-Dispersant-Aqueous System. Dissertation, Carnegie Mellon University, Pittsburgh, 2013.
41. Hsu, J.-P.; Nacu, A., Behavior of soybean oil-in-water emulsion stabilized by nonionic surfactant. *Journal of colloid and interface science* **2003**, 259, (2), 374-381.
42. Stalidis, G.; Avranas, A.; Jannakoudakis, D., Interfacial properties and stability of oil-in-water emulsions stabilized with binary mixtures of surfactants. *Journal of colloid and interface science* **1990**, 135, (2), 313-324.
43. Avranas, A.; Stalidis, G., Interfacial properties and stability of oil-in-water emulsions stabilized with binary mixtures of surfactants: II. Effect of a cationic surfactant on a nonionic surfactant stabilized emulsion. *Journal of colloid and interface science* **1991**, 143, (1), 180-187.
44. Donbrow, M.; Azaz, E.; Pillersdorf, A., Autoxidation of polysorbates. *Journal of pharmaceutical sciences* **1978**, 67, (12), 1676-1681.
45. Kerwin, B. A., Polysorbates 20 and 80 used in the formulation of protein biotherapeutics: structure and degradation pathways. *Journal of pharmaceutical sciences* **2008**, 97, (8), 2924-2935.
46. Mao, G.; VanWyck, D.; Xiao, X.; Mack Correa, M. C.; Gunn, E.; Flach, C. R.; Mendelsohn, R.; Walters, R. M., Oleic acid disorders stratum

- corneum lipids in Langmuir monolayers. *Langmuir* **2013**, 29, (15), 4857-4865.
47. Tomoaia-Cotișel, M.; Mocanu, A.; Lupea, M.; Chifu, E., Insoluble mixed monolayers: III. The ionization characteristics of some fatty acids at the air/water interface. *Journal of colloid and interface science* **1987**, 117, (2), 464-476.
 48. Pal, P.; Nandi, D.; Misra, T. N., Immobilization of alcohol dehydrogenase enzyme in a Langmuir-Blodgett film of stearic acid: its application as an ethanol sensor. *Thin Solid Films* **1994**, 239, (1), 138-143.
 49. Shuler, R.; Zisman, W. A., Study of the behavior of polyoxyethylene at the air-water interface by wave damping and other methods. *The Journal of Physical Chemistry* **1970**, 74, (7), 1523-1534.
 50. Kuzmenka, D. J.; Granick, S., Collapse of poly (ethylene oxide) monolayers. *Macromolecules* **1988**, 21, (3), 779-782.
 51. Kawaguchi, M.; Komatsu, S.; Matsuzumi, M.; Takahashi, A., Concentration dependence of surface pressure of polyether monolayers at the air-water interface. *Journal of colloid and interface science* **1984**, 102, (2), 356-360.
 52. Kawaguchi, M.; Sauer, B. B.; Yu, H., Polymeric monolayer dynamics at the air/water interface by surface light scattering. *Macromolecules* **1989**, 22, (4), 1735-1743.
 53. Doi, M.; Edwards, S., Dynamics of concentrated polymer systems. Part 4.—Rheological properties. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics* **1979**, 75, 38-54.
 54. Anderson, V.; Pearson, J.; Sherwood, J., Oscillation superimposed on steady shearing: Measurements and predictions for wormlike micellar solutions. *Journal of Rheology (1978-present)* **2006**, 50, (5), 771-796.
 55. Alvarez, N. J.; Vogus, D. R.; Walker, L. M.; Anna, S. L., Using bulk convection in a microtensiometer to approach kinetic-limited surfactant dynamics at fluid–fluid interfaces. *Journal of colloid and interface science* **2012**, 372, (1), 183-191.

CHAPTER 5

PROBING TIMESCALES FOR COLLOIDAL PARTICLE ADSORPTION USING SLUG BUBBLES IN A MICROCHANNEL

5.1 INTRODUCTION

Particle stabilized emulsions and foams are used in the generation of many functional materials, including colloidosomes,¹ porous ceramic and polymer monoliths,² and liquid marbles.³ Droplet-stabilizing colloidal particles that catalyze reactions at oil-water droplet interfaces have also been suggested as an efficient method of biofuel conversion.⁴ In all of these cases, control of the average size and size distribution of the particle-stabilized bubbles and drops, as well as their degree of particle surface coverage, is desirable. The generation of particle-stabilized emulsions involves the dispersion of one fluid phase into a second continuous liquid phase, which requires the breakup of large droplets into smaller ones through agitation. During this process, significant transport phenomena occur at different length and time scales: the breakup of the dispersed phase, the adsorption of particles to the newly generated clean interface, and the coalescence of droplets due to collisions. Particle adsorption will stabilize droplets against coalescence in the emulsion generation process, but only after a stabilizing coverage of colloidal particles has had enough time to adsorb to the interface.⁵

Because it is not possible to separate the breakup, transport, and coalescence mechanisms in bulk emulsification processes such as high-shear homogenization or sparging, the relationship between the bulk particle

concentration and the resulting dispersed phase droplet size cannot be decoupled.⁶ Although simple relationships exist to determine the average droplet size,^{6, 7} these relationships are unable to account for changes in the resulting particle-stabilized emulsion microstructure due to changes in particle shape,⁸ pH,⁹ salt concentration,¹⁰ or the presence of surfactant.¹¹ One promising solution to this problem is to use microfluidic droplet generation strategies that allow for independent control of the droplet size and the amount of time between droplet formation and subsequent droplet-droplet interactions. Microfluidic methods have been used previously in the generation of highly monodisperse particle-stabilized bubbles and droplets. Various methods of particle loading onto the fluid interface have been invoked: hydrodynamic focusing prior to droplet break-off,¹² convection-diffusion processes within the continuous phase,¹³⁻¹⁵ and convection-diffusion processes within the dispersed phase.¹⁶ Although these methods have been successfully implemented to generate particle-stabilized bubbles and drops, the timescales for particle adsorption in microfluidic devices is still not well understood. Priest and Whitby have suggested that particles will adsorb faster to droplets confined in microfluidic channels due to the presence of a thin film between the droplet interface and the microchannel wall.¹⁷ Mulligan and Rothstein estimate that the timescales for adsorption of particles to droplets will be on the order of seconds based on diffusion timescales estimated using micron length scales.¹³ In order for microfluidic strategies to be successfully implemented in the generation of particle-stabilized emulsions and foams, the adsorption

dynamics must be quantified in terms of the bubble and channel properties, and the particle characteristics.

In this chapter we will examine the dynamics of particle adsorption to bubbles in surface-active particle suspensions confined within a rectangular microfluidic channel. Large bubbles with undeformed radii much larger than either cross-sectional dimension of the microfluidic channel will form long slug bubbles, necessitating the formation of thin film regions along the walls of the microchannel, and open corner regions available for “leaking” fluid flow around the bubble.¹⁸ To study particle adsorption in microfluidic channels, it is imperative that the surface-active particle suspensions are stable against flocculation. The systems that we study in this chapter are aqueous suspensions of colloidal silica and the cationic surfactant CTAB. These suspensions exhibit excellent stability against flocculation and have been characterized previously in terms of bulk emulsion and foam stability¹⁹⁻²¹ and interfacial rheology.^{20, 22}

During particle adsorption, the bubbles generated in the nanoparticle-surfactant suspension exhibit unique shapes and dynamics that are not commonly observed in less confining geometries. For bubbles traveling at velocities characteristic of microfluidic flows, the particle transport is dominated by convection around the bubble. Using our experimental observations, we develop a simple transport model to explain the bubble dynamics that result from particle adsorption to slug bubbles. The model relies on particle transport only in the region of the curved end caps, and argues that depletion effects can have a detrimental effect on particle adsorption to the bubble interface. Our model shows

good agreement with the measured shape changes that we hypothesize are a result of the growth of a particle-stabilized region along the bubble as it translates along the microchannel. The model can be used to predict the channel lengths necessary to generate particle-stabilized bubbles.

5.2 MATERIALS AND METHODS

The experiments were performed in a microfluidic device fabricated in poly(dimethylsiloxane) (PDMS; Dow Sylgard 184) using standard soft lithography methods.²³ In the device, shown in Figure 5.1, bubbles are generated at a T-junction with the aqueous continuous phase pumped into the main inlet at a constant flow rate using a programmable syringe pump (Harvard Apparatus PHD2000) and nitrogen gas pumped into the side inlet by a constant pressure supplied by a nitrogen tank and regulator (ControlAir, Inc. T550X Miniature EIA). The channels are sealed by treating the surface of the device with air plasma (Harrick Plasma PDC-32G) and bringing it into contact with another plasma treated PDMS slab. In order to retain the hydrophilicity of the channel walls imparted by the plasma exposure, the channels are immediately filled with deionized (DI) water (resistivity 18.2 M Ω cm; Barnstead) after bonding and stored immersed in DI water until use.

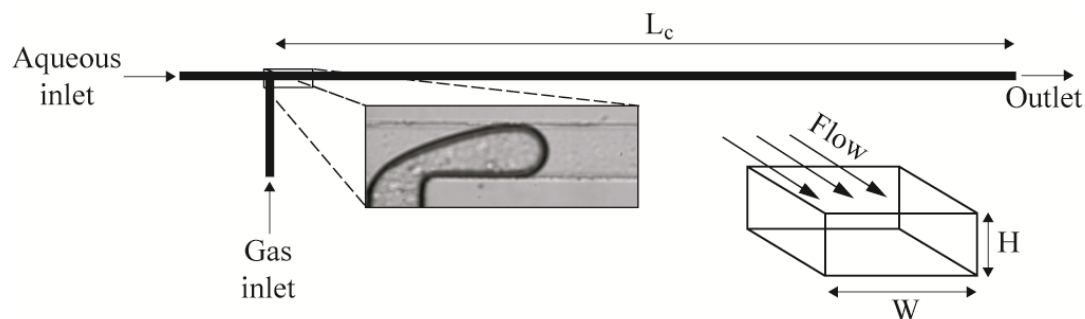


Figure 5.1. Schematic diagram of the microfluidic device. The inset image shows a nitrogen bubble extending into the main channel prior to pinch-off. The channel width W is $142\ \mu\text{m}$. The distance from the T-junction to the device outlet L_c is $57\ \text{mm}$, and the channel depth is $42\ \mu\text{m}$ as shown in the bottom-right corner of the diagram.

The continuous phase fluids used are (i) deionized (DI) water, DI water with suspended pure Ludox AM-30 (6 nm nominal particle radius; Sigma Aldrich), (iii) DI water with dissolved cationic surfactant cetyltrimethylammonium bromide (CTAB; CMC $0.9\ \text{mM}$; BDH), and (iv) aqueous suspensions of CTAB and Ludox. The pure Ludox system is diluted from the initial manufacturer-supplied concentration of $30\ \text{wt}\%$ to $2\ \text{wt}\%$ by gently adding DI water with a micropipette, then sonicating the suspension for 30 minutes in an ultrasonic bath (American Beauty S-5500) to disperse the particles. The CTAB is used as received, and pure surfactant solutions are prepared at concentrations of $0.21\ \text{mM}$ and $90\ \text{mM}$. A particle suspension of $2\ \text{wt}\%$ Ludox and $0.21\ \text{mM}$ CTAB is generated by dropwise dilution of a $4\ \text{wt}\%$ solution of Ludox particles with a $0.42\ \text{mM}$ CTAB solution. The holding vial is gently shaken in between the addition of more surfactant solution to prevent silica from precipitating out of solution. A $10\ \text{wt}\%$ Ludox and $0.21\ \text{mM}$ CTAB solution is prepared by dropwise dilution of a $30\ \text{wt}\%$ Ludox solution with a $0.29\ \text{mM}$

CTAB solution using a similar procedure with shaking in between surfactant addition. After the desired concentrations of Ludox and CTAB are reached, the solutions are sonicated for 30 minutes. In what follows, we will refer to a suspension of y wt% Ludox and 0.21 mM CTAB as “ y wt% silica-CTAB”, where y corresponds to the weight percent of Ludox (silica) in the bulk suspension. For a CTAB molecule headgroup area of $\sim 0.59 \text{ nm}^2$ (measured using the Langmuir-Blodgett technique)²⁴ and a nanoparticle surface area of $\sim 220 \text{ m}^2/\text{g}$, the available nanoparticle surface area for surfactant adsorption is 30 times the total headgroup area in the surfactant solution for the 2 wt% silica-CTAB suspension and over 200 times the total headgroup area in the 10 wt% silica-CTAB suspension. This leads to effectively all of the positively charged surfactant adsorbing to the surface of the negatively charged nanoparticles, a state which has been confirmed through surface tension measurements of the supernatant obtained after ultracentrifugation of CTAB and silica nanoparticle suspensions.²⁰ Attempts to prepare a 10 wt% silica-CTAB suspension with the same CTAB-to-silica area ratio as the 2 wt% silica-CTAB suspension result in severe precipitation immediately after the addition of the surfactant, and therefore this composition is not used. The final surfactant concentration necessary to achieve this silica-to-CTAB area ratio is 1.57 mM, which is above the CMC and has been shown previously to lead to serious flocculation of nanoparticles in bulk solution.^{19, 22} After waiting 12 hours to allow the surfactant to populate the silica surface, the 2 wt% silica-CTAB suspension is diluted with DI water to achieve particle concentrations of 0.2 wt% and 1 wt%, referred to throughout the Chapters 5 and 6

as “0.2 wt% silica-CTAB” and “1 wt% silica-CTAB”, respectively. All solutions are sonicated immediately after dilution, as well as immediately before each experiment in order to break up any aggregates formed. Due to the low volume fractions of particles used in this study, the viscosity of the particle suspensions without CTAB is not expected to vary significantly from pure water. The silica-CTAB suspensions are not expected to show a viscoelastic response at the particle and surfactant concentrations studied, with viscosities that are not expected to vary significantly from pure water.²⁵

The surface tension of each suspension is tested using a microtensiometer apparatus for which the details are described in detail elsewhere.²⁶ Briefly, the apparatus consists of a glass capillary with a tip radius between 10 – 50 μm inserted into a well containing a surfactant solution that is open to the atmosphere. A bubble with an initially clean interface is generated at the end of the capillary using a constant pressure head that is monitored using a pressure transducer (0 – 5 psi, Cole Parmer). The bubble forms a spherical cap shape pinned at the end of the capillary with a radius of curvature that depends only on the pressure jump across the interface and the interfacial tension through the Laplace equation. By observing the radius of curvature using a bright field microscope (Nikon T-300) and a digital camera (Diagnostic Instruments Spot RT Monochrome), we calculate the surface tension as a function of time for each of our systems. Data from bubble generation is acquired every 0.16 s for the first 5 s to capture the initial dynamics. After the first 5 s, data is collected every second to assess long-time surface tension dynamics. For the silica-CTAB suspensions, the solution is

sonicated for 30 minutes before each measurement to ensure reproducibility in the dynamic curves. For pure DI water and the 2 wt% silica suspension without CTAB, we obtain equilibrium surface tensions of 71.43 ± 0.13 mN/m and 71.64 ± 0.15 mN/m respectively, meaning that the silica nanoparticles without surfactant do not significantly alter the interfacial tension. This is shown in Figure 5.2 by a plot of the dynamic surface tension of the 2 wt% silica suspension, which does not change over a period of 10^3 s. The surface tension of the 0.21 mM CTAB solution without silica decreased over a period of 10^3 seconds to a surface tension of 55.23 ± 0.15 mN/m as shown in Figure 5.2, while the 90 mM CTAB solution without silica (not shown in Figure 5.2) exhibits very fast surfactant dynamics such that the surface tension reaches an equilibrium value of 34.02 ± 0.18 mN/m in less than 0.1 s. The dynamics of the silica-CTAB suspensions (Figure 5.2) are significantly slower than the pure CTAB solutions. The 0.2 wt% silica-CTAB suspension reaches an equilibrium surface tension of 62.00 ± 0.14 mN/m at 4×10^3 s. The 1, 2, and 10 wt% silica-CTAB solutions did not reach equilibrium values for the surface tension after 10^4 s. The 1 and 2 wt% silica-CTAB solutions reach similar surface tension values of 63.11 ± 0.20 mN/m and 62.69 ± 0.24 mN/m, respectively. The measured surface tension of the 10 wt% silica-CTAB suspension after 10^4 s is 59.88 ± 0.12 mN/m. This is significantly lower than the surface tension measured in similar systems after 3×10^3 s in a pendant bubble apparatus²⁰ or 300 s in a du Noüy ring tensiometer,¹⁹ suggesting that the depletion of CTAB from the bulk solution due to adsorption at the nanoparticle surface significantly increases the amount of time necessary to reach an equilibrium

surface tension in particle-surfactant systems. The surface tension dynamics of the silica-CTAB suspensions are not monotonic with respect to concentration; however, we have not used salt in these experiments to screen out charge effects, which can affect both the cationic surfactant adsorption dynamics²⁷ and particle adsorption dynamics.⁵ The dynamics will also be affected by bulk concentration of nanoparticles as well as the number of CTAB molecules adsorbed at the particle surface. Although the dynamics are complex, the silica-CTAB system takes a significant amount of time to adsorb to the air-water interface under the stagnant conditions in the microtensiometer, compared to the pure surfactant case.

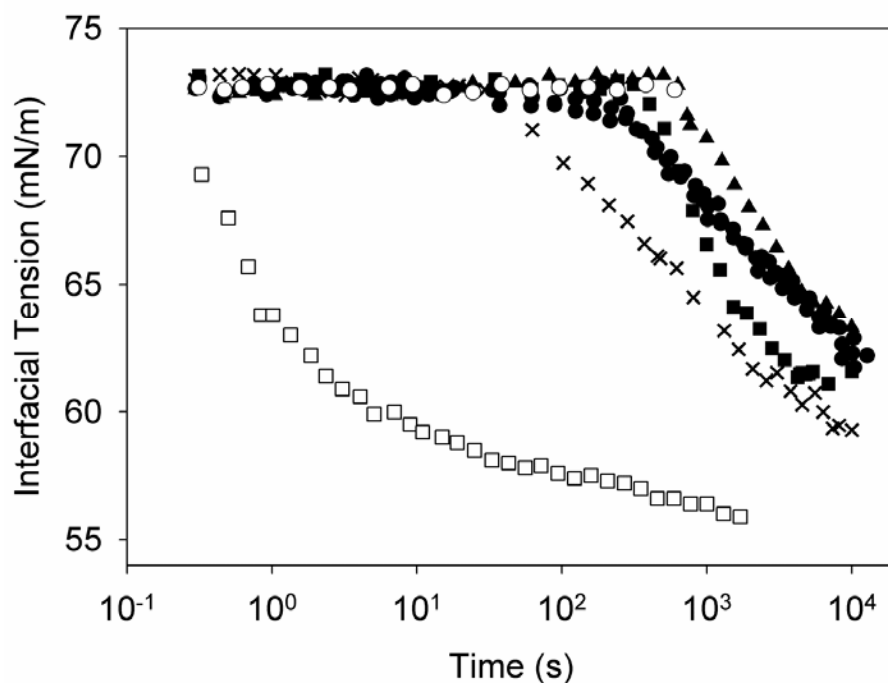


Figure 5.2. Dynamic surface tension measurements for (○) 2 wt% silica suspension, (□) 0.21 mM CTAB solution, and (■) 0.2wt%, (▲) 1 wt%, (●) 2 wt%, and (×) 10 wt% silica-CTAB suspensions. Three repeated experiments for the 2 wt% silica-CTAB suspension are shown to indicate the representative repeatability for each system.

Prior to the start of each microfluidic experiment, the continuous phase fluid is passed through the microchannels for five minutes to bring the concentration in the microchannels to the bulk concentration. Then, the nitrogen is connected at an initial inlet pressure of 10 kPa and gradually increased until bubbles are generated at the T-junction. The flow rate and pressure are tuned to allow only one bubble to be generated and flow down the microchannel at a time to avoid interactions between bubbles. The relevant experimental conditions studied in this chapter include continuous phase volumetric flow rates $0.42 < Q < 1.67$ mL/hr and gas pressures $10 < p_g < 35$ kPa. The bubbles are observed in bright field imaging mode on a Nikon Ti-U microscope and bubble dynamics are

recorded using a high speed camera (Phantom v9.1). Videos are recorded at several positions along the microchannel, and the resulting images are analyzed using either MATLAB's Image Processing Toolbox or ImageJ. A defect in the microfluidic device 40 mm downstream of the T-junction affected the motion of bubbles downstream of the defect, so analysis of bubble shape and velocity is only performed in the first 80% of the channel length. Figure 5.3 shows an example of an altered bubble shape at 50 mm. We used only non-wetting bubbles exhibiting smooth, reproducible motion for the experiments described in this chapter. Error bars and uncertainty in reported bubble measurements represent the standard deviation of measurements of five bubbles.

5.3 RESULTS

5.3.1 EXPERIMENTAL OBSERVATIONS

The experimental setup in Figure 5.1 is used to generate bubbles that are larger than the width of the microchannel. Because we require that only one bubble travels along the microchannel during the experiment, the continuous phase flow rate and the pressure must be balanced so that the additional pressure drop that arises from the bubble in the channel is greater than the gas pressure at the T-junction. In all experiments where the gas phase does not wet the channel walls, the bubbles generated at the T-junction form slugs that are lubricated by a thin film of liquid between the bubble interface and the channel walls. Bubbles generated in the 0.21 mM CTAB solution and the 0.2 wt% silica-CTAB suspension wetted the channel walls, leading to added resistance from moving contact lines and a lack of reproducibility. For the bubbles generated in DI water,

the 2 wt% silica suspension without surfactant, the 90 mM CTAB solution, and the 1 wt%, 2 wt%, and 10 wt% silica-CTAB suspensions, the confined bubble shape fills the channel with a thin fluid film between the flat bubble interface and the side walls of the channel. The bubble motion is smooth and continuous along the entire microchannel from the T-junction to the outlet (Figure 5.3), and the measurements are reproducible, as indicated by the relatively small error bars shown in the subsequent graphs quantifying bubble size and velocity.

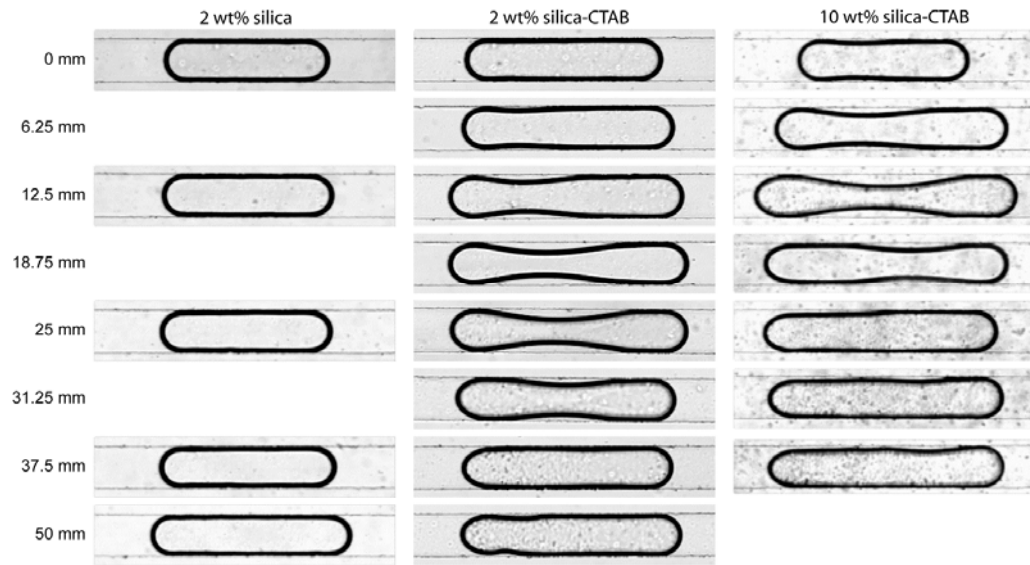


Figure 5.3. Representative bright-field images of the bubbles traveling along the microchannel at several distances downstream of the T-junction, shown in the left column. In all images, the direction of flow is from left to right. The channel width in all images is 142 μm .

As bubbles approach the end of the microchannel, they lengthen due to the compressibility of the gas phase and the decreasing pressure along the length of the microchannel. The pressure difference Δp between the pressure at some position x along the axis of the rectangular microchannel and the pressure at the

microchannel exit p_0 (approximately atmospheric pressure) depends on the channel geometry and the volumetric flow rate of fluid as

$$\Delta p = p(x) - p_0 = \frac{12\mu Q(L_c - x)}{HW^3} \left[1 - \frac{192W}{\pi^5 H} \tanh\left(\frac{\pi H}{2W}\right) \right]^{-1} \quad (5.1)$$

where W , H , and L_c are the microchannel width, height, and length, respectively, μ is the viscosity of the aqueous phase fluid, and Q is the volumetric flow rate of the continuous phase. Assuming that the bubble does not contribute appreciably to the resistance, the pressure decreases linearly along the microchannel. The pressure inside the bubble will be greater than the pressure in the fluid surrounding the bubble due to the Laplace pressure, which is on the order of 2 kPa for the hydraulic radius and surface tensions in the experiment. This is negligible compared to the absolute pressure inside the microchannel and is neglected in the bubble length calculation. Since nitrogen acts as an ideal gas and because the microchannel cross section is constant, Boyle's law predicts that the initial bubble length L_i and the length of the bubble L at some position x along the microchannel are related to the initial absolute pressure $p_i = p(x = 0)$ and the pressure at position x by

$$p_i L_i = p(x) L(x) \quad (5.2)$$

For the bubbles generated in the 2 wt% silica suspension, the bubble length is expected to grow by 15% after a distance $x = 50$ mm, which is consistent with the length growth observed for this system in Figure 5.3.

Bubbles generated in the silica-CTAB suspensions exhibit significantly different bubble shapes than the single component systems. At some distance x

downstream of the T-junction, these bubbles form a two-lobed structure connected by a thinner neck region. The neck propagates forward as the bubble travels along the microchannel. In some cases, the two-lobed bubble shape relaxes to fill the microchannel cross-section, adopting a more uniform shape. Representative images of bubbles exhibiting this necking transition are shown in Figure 5.3 at several positions along the microchannel. Due to the formation of the neck region, the length of the bubbles initially increases much faster than the rate of gas expansion from the pressure decrease along the microchannel as shown in Figures 5.4a and 5.4b.

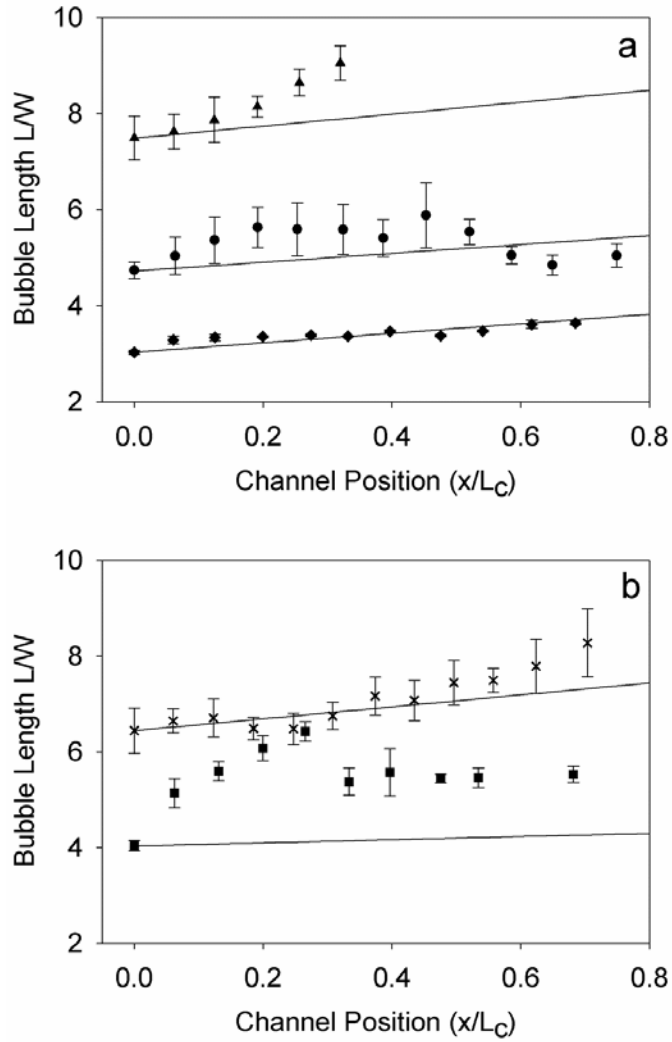


Figure 5.4. Bubble length as a function of position in the microchannel for (a) different bubble velocities generated in the 2 wt% silica-CTAB suspension (($\blacktriangle$) 2 wt% silica-CTAB suspension, $Q = 0.85$ mL/hr; ($\bullet$) 2 wt% silica-CTAB suspension, $Q = 1.00$ mL/hr; ($\blacklozenge$) 2 wt% silica-CTAB suspension, $Q = 1.67$ mL/hr) and (b) bubbles generated in different concentrations of the particle-surfactant suspension (($\times$) 1 wt% silica-CTAB suspension, $Q = 1.00$ mL/hr; ($\blacksquare$) 10 wt% silica-CTAB suspension, $Q = 1.00$ mL/hr.) Lines are bubble length predictions based on equations (5.2) and (5.3). The experimental data for ($\blacktriangle$) ends abruptly due to bubble break up, shown in Figure 5.6.

Measurements of the location of the neck midpoint a along the bubble show that the neck first appears on the bubble a distance of one channel width W from the bubble rear after the bubble has travelled a short distance downstream of

the T-junction. As the bubble translates along the microchannel, the neck moves forward on the bubble toward the leading edge until the ratio of the neck position to the total bubble length L is greater than 0.5, after which time the necked region relaxes to fill the channel cross section. The location of the neck is measured as function of bubble position along the channel for all experiments that exhibit neck formation. Plotting the neck position scaled by the constant channel width (Figure 5.5a) shows that the neck region always first appears at a distance equal to one channel width downstream of the rear of the bubble. The channel position at which the neck is first observed occurs at larger distances downstream of the T-junction as the flow rate increases. The neck propagates forward along the bubble until one of three outcomes occurs. These outcomes are most easily seen by rescaling the neck location with the instantaneous bubble length, which changes along the channel as shown in Figure 5.4b. The first possible outcome is that the neck position surpasses half of the bubble length and the neck relaxes to fill the channel cross section. After this point no neck is observed, which we show in Figure 5.5(b) as a neck position of $a/L = 1$ for bubbles generated in the 2 wt% silica-CTAB suspension at a flow rate of 1 mL/hr (●) and bubbles generated in the 10 wt% silica-CTAB suspension at 0.42 mL/hr (■). The second possibility is that the neck persists until the bubble exits the microchannel, which is observed for bubbles generated in the 2 wt% silica-CTAB suspension at a flow rate of 1.67 mL/hr (◆) and bubbles generated in the 1 wt% silica-CTAB suspension at 1 mL/hr (✕). A third possibility, which occurs for bubbles generated in 2 wt% silica-CTAB and $Q = 0.85$ mL/hr (▲), is that the neck region thins and becomes

unstable, leading to bubble break up. An example is shown in the image sequence in Figure 5.6. After bubble break-up, both bubble sections continue to travel along the microchannel. The bubble that formed from the rear of the larger bubble does not relax to a shape that fills the walls of the microchannel, and travels in a deformed shape until it reaches the microchannel outlet. The front bubble forms a new necked region that begins to propagate forward along the bubble until the bubble reaches the device outlet.

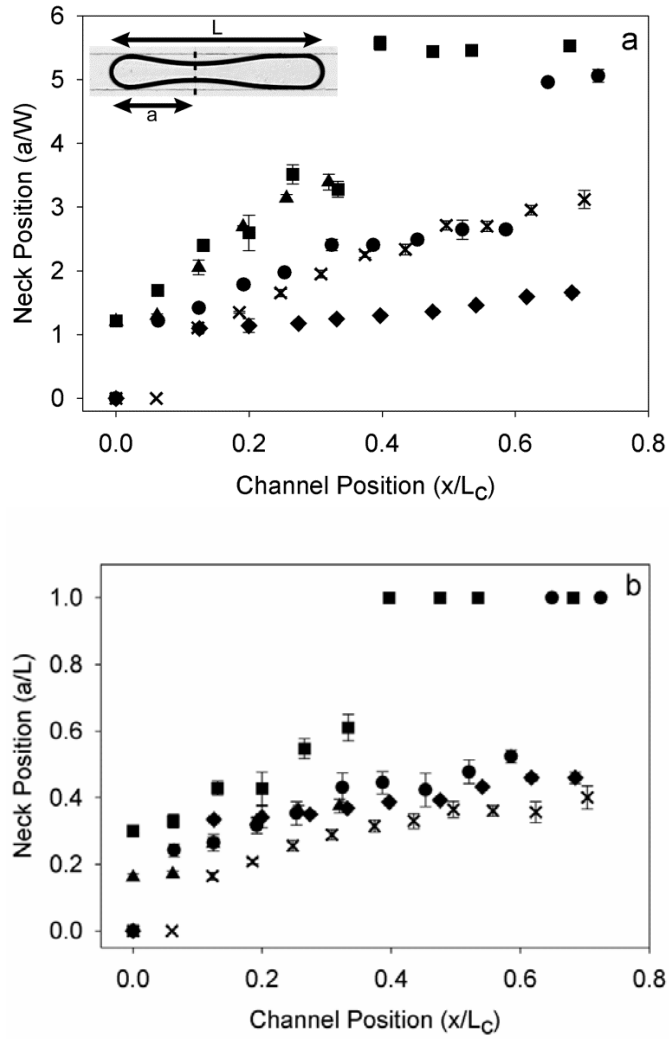


Figure 5.5. Distance of the midpoint of the neck from the rear of the bubble as a function of the normalized bubble position within the channel. (a) The location normalized by the width W of the microchannel and (b) the location normalized by the instantaneous length of the bubble L for: (▲) 2 wt% silica-CTAB suspension, $L_i/W = 7.49 \pm 0.46$, $Q = 0.85$ mL/hr; (●) 2 wt% silica-CTAB suspension, $L_i/W = 4.72 \pm 0.10$, $Q = 1.00$ mL/hr; (◆) 2 wt% silica-CTAB suspension, $L_i/W = 3.031 \pm 0.042$, $Q = 1.67$ mL/hr; (×) 1 wt% silica-CTAB, $L_i/W = 6.44 \pm 0.47$, $Q = 1.00$ mL/hr; (■) 10 wt% silica-CTAB, $L_i/W = 4.72 \pm 0.10$, $Q = 1.00$ mL/hr.

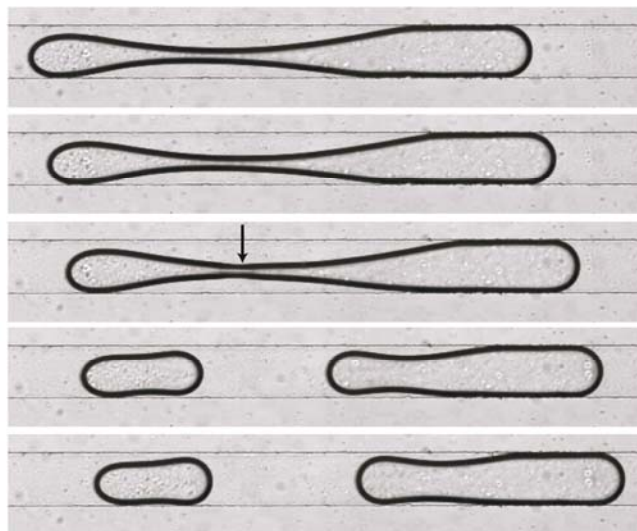


Figure 5.6. Successive images of a bubble generated in the 10 wt% silica-CTAB suspension at $Q = 0.85$ mL/hr ($L_i/W = 4.72 \pm 0.10$) breaking up during the necking process in a microchannel. The arrow indicates the location of the neck breakup. The time step between images is 1.8 ms. The channel width is 142 μm .

In cases where the neck relaxes before the bubble has exited the microchannel, the bubble forms a slug shape that does not always remain in contact with the channel walls. This can be seen in the images for both the 2 wt% silica-CTAB and the 10 wt% silica-CTAB solutions in Figure 5.3, in comparison to the bubble generated in the silica suspension without surfactant. These deformations only appear after the bubble has experienced the necking transition. Bubbles that complete the necking transition are stable against coalescence outside the microchannel and retain an elongated shape, shown in Figure 5.7. These shapes are significantly different from those of the stable bubbles generated in the 90 mM CTAB solution, which form spherical bubbles that arrange in a hexagonal close packed layer (Figure 5.7). Bubbles generated in DI water and 2 wt% silica without surfactant are not stable against coalescence outside the microchannel.

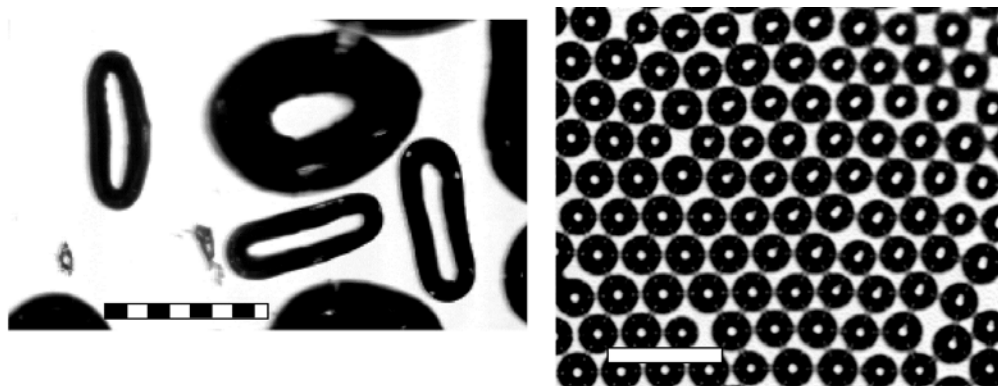


Figure 5.7. Images of stable bubbles produced in the microfluidic channel. The bubbles produced in a 2 wt% silica-CTAB suspension (left image, scale bar 200 μm) show elongated shapes outside of confinement, compared with the stable spherical bubbles produced in a 90 mM CTAB solution (right image, scale bar 250 μm).

In all experiments, the observed bubble velocity U is less than the average continuous phase fluid velocity V , which is calculated from the volumetric flow rate Q supplied by the syringe pump divided by the cross-sectional area of the microchannel $A_c = WH$. Because only a single bubble travels along the microchannel during an experiment, the additional gas flow rate is not expected to factor appreciably into the average fluid velocity. Observations²⁸ and analytical considerations¹⁸ demonstrate that long bubbles traveling in Newtonian fluids with uniform interfacial boundary conditions through rectangular channels exhibit a constant velocity independent of position in the microchannel. In the present experiments, bubbles generated in DI water and in the 2 wt% silica suspension without surfactant exhibit a constant velocity along the entire length of the channel. The observed bubble velocity is less than the average velocity of the continuous phase fluid, as shown in Figure 5.8. In our experiments, the continuous phase flow rate and the bubble length are coupled due to the

requirement that only one bubble is present in the microchannel. The bubble velocities reported are the average of the front and rear velocities of the bubble, which are within measurement error of each other at each channel position. When generated in the silica-CTAB suspensions, the bubbles exhibit a decrease in the average velocity that accompanies the necking transition. The bubble velocities normalized by the average fluid velocity for both necking and non-necking cases are shown in Figure 5.8 as a function of the channel position x normalized by the total channel length L_c . Bubbles that flow through the silica-CTAB suspension exhibit an initially constant velocity that begins to decrease after the neck region has formed.

5.3.2 PARTICLE ADSORPTION MODEL AND ANALYSIS

The important distinction between colloidal silica with and without dissolved CTAB present in the suspending medium is that the adsorption of the cationic surfactant to the negatively-charged nanoparticle surface alters the wettability of the nanoparticle, promoting its adsorption to the liquid-fluid interface, as discussed previously by a number of authors for oil-water systems²⁹⁻³¹ as well as air-water interfaces.³¹ The addition of CTAB below the CMC will generally increase the contact angle of the initially hydrophilic silica particles at the air-water interface, which increases the amount of energy necessary for a particle to desorb from the interface to a magnitude far above the thermal energy of the system.³² A high surface concentration of nanoparticles that require a large amount of energy to desorb will jam at the interface, forming a solid-like layer that resists a decrease in the interfacial area.³³ The relaxation of bubbles from the

elongated slug to a sphere requires a decrease in the interfacial area, which can only occur if the already densely packed nanoparticles are expelled from the interface. The persistent nonspherical shapes of the bubbles produced in the silica-CTAB suspension that appear after the bubbles exit the microchannel (Figure 5.7) are consistent with the irreversible adsorption of nanoparticles at high surface concentrations. Since the bubbles are generated rapidly at the T-junction, the interface is expected to be free of particles at the upstream end of the microchannel. This suggests that adsorption of CTAB-covered nanoparticles to the bubble interface occurs within the residence time of the bubble in the microchannel, and that the unique bubble dynamics exhibited in these suspensions is a direct result of nanoparticle adsorption.

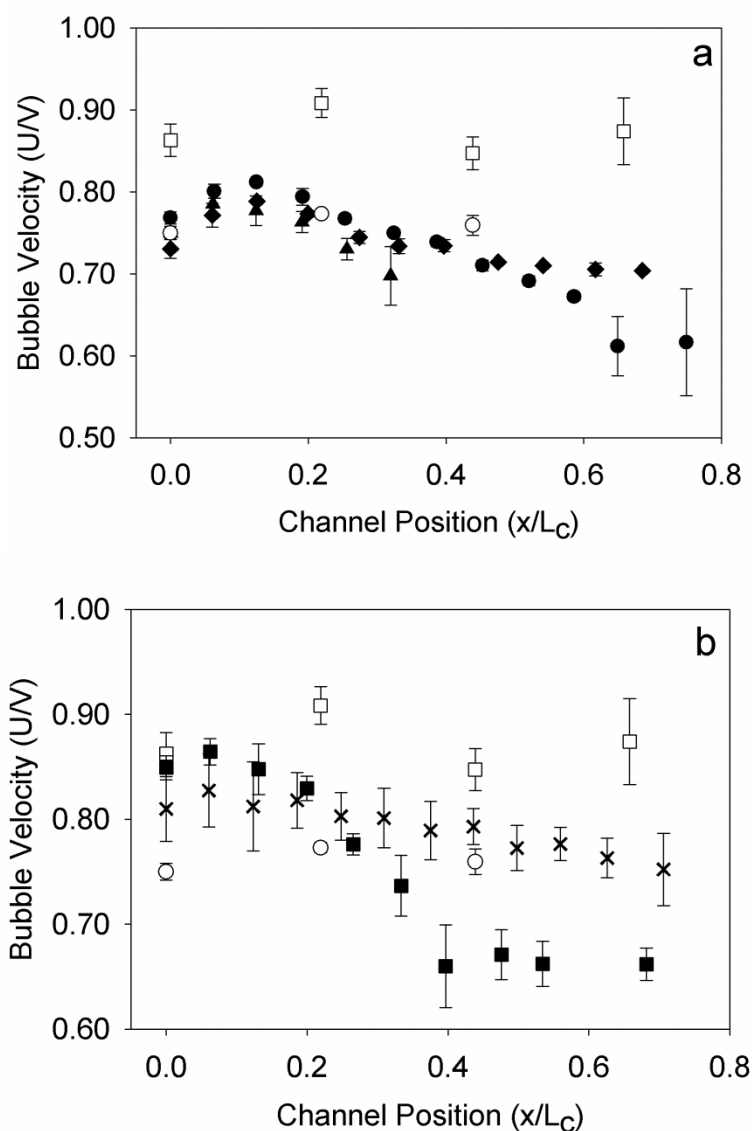


Figure 5.8. Bubble velocities for various (a) bubble lengths and (b) silica-CTAB concentrations: (○) DI water, $L_i/W = 6.19 \pm 0.23$, $Q = 0.70$ mL/hr; (□) 2 wt% silica suspension, $L_i/W = 3.895 \pm 0.092$, $Q = 0.90$ mL/hr; (▲) 2 wt% silica-CTAB suspension, $L_i/W = 7.49 \pm 0.46$, $Q = 0.85$ mL/hr; (●) 2 wt% silica-CTAB suspension, $L_i/W = 4.72 \pm 0.10$, $Q = 1.00$ mL/hr; (◆) 2 wt% silica-CTAB suspension, $L_i/W = 3.031 \pm 0.042$, $Q = 1.67$ mL/hr; (×) 1 wt% silica-CTAB, $L_i/W = 6.44 \pm 0.47$, $Q = 1.00$ mL/hr; (■) 10 wt% silica-CTAB, $L_i/W = 4.72 \pm 0.10$, $Q = 1.00$ mL/hr. The DI water and 2 wt% silica suspension velocities are included in both graphs to emphasize the velocity changes that occur in the presence of silica-CTAB suspensions.

Confined gas bubbles can be subject to a range of forces that affect the bubble shape and dynamics due to channel geometry, continuous phase flow, or interfacial phenomena. Bubbles moving through constrictions in pores will form a gas neck surrounded by an outer fluid annulus that can induce bubble pinch-off,³⁴ and bubble breakup in T-junctions is a common microfluidic method of bubble splitting.³⁵ These geometric obstructions are not present in the current experiments. Bubble breakup occurs in straight capillaries when the surface tension forces at the rear of the bubble cannot balance the viscous stresses, and a viscous fluid jet penetrates the trailing bubble surface.³⁶ Plateau-Rayleigh instabilities lead to undulations in thin viscous fluid films surrounding low viscosity inner phases,³⁷ but these instabilities are saturated in the presence of flow³⁸ and are not observed for the long bubbles in the pure particle suspensions or the pure surfactant solutions in our experiments. Surface tension gradients due to the presence of surfactants or temperature gradients induce Marangoni stresses at the interface that can induce motion through stagnant fluids or retard bubble trains in capillaries.³⁹ Although the cationic CTAB surfactant is present in our system, the bubbles in a surfactant system without surface-active particles do not exhibit the neck observed in our experiments. A combination of geometry, fluid flow, and surface-active species can also induce bubble shape changes and breakup when surfactant-stabilized bubbles form “tails” in an extensional flow field.⁴⁰ Particle-stabilized bubbles also experience a tail formation with bubble break up from the rear of the bubble in similar flow fields.⁴¹ Because our experiments do not exhibit the geometry to generate an extensional flow field, we

do not attribute the bubble dynamics observed in these experiments to extensional bubble deformation.

The experimental observations described above suggest the following hypothesis regarding the dynamics of nanoparticle adsorption and its effect on bubble dynamics. As shown schematically in Figure 5.9, bubbles are first generated at the T-junction with effectively zero particle coverage at the interface. As the bubbles translate along the microchannel, particles adsorb to the interface and pack at the rear of the bubble. The packed particles act as a solid layer, changing the tangential stress condition at the bubble interface from zero stress at the clean air-water interface to zero slip at the particle-covered interface, which increases the drag in the thin film near the rear of the bubble. The increased drag causes the rear of the bubble to travel at a slower velocity than the clean bubble front, causing the front and rear of the bubble to separate and form a thin neck region. The position of the neck approximately demarcates the region of the bubble that is covered by particles. However, we expect that the neck cannot form unless the viscous stress is able to overcome the capillary pressure in the rear end cap, which likely cannot occur until the radius of curvature of the neck is greater than that in the end cap, or when $a \geq W$. As particles continue to adsorb to the interface, the particle stabilized region increases in size, and the neck propagates forward. Once the capillary pressure is again able to overcome the difference in shear stress at the front and rear of the bubble, the neck expands until a more uniform slug shape is observed. The bubble travels at a slower velocity due to

added shear stress along the channel walls resulting from the solid-like adsorbed particle layer.

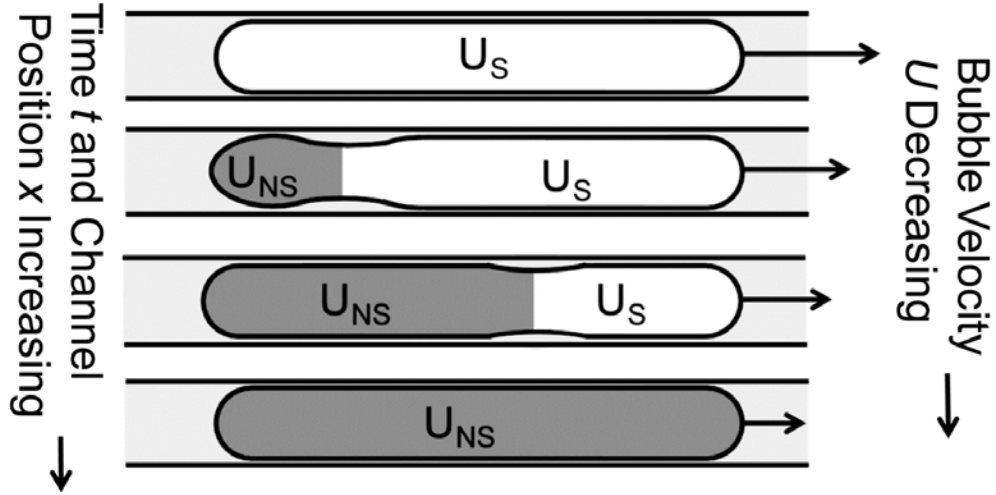


Figure 5.9. Schematic diagram of the bubble dynamics resulting from adsorption of surface-active particles. Particles adsorb and pack at the rear of the bubble, leading to a no-slip (NS) boundary condition at the rear bubble interface compared with a shear-free condition (S) at the leading edge. Added drag from the immobile interface reduces the bubble speed.

To test the plausibility of our hypothesis, we estimate the particle flux to the interface by taking into account the geometry of the bubble confined within a rectangular capillary. The shape of a confined bubble in a rectangular channel depends on the forces acting upon the interface. As in many microfluidic experiments, the Reynolds number Re comparing the relative magnitude of inertia to viscous forces is low. We define Re using the continuous phase fluid properties, the volumetric fluid flow rate, and the channel dimensions as

$$Re = \frac{2\rho Q}{\mu(W + H)} \quad (5.3)$$

Assuming the densities ρ and viscosities μ of the dilute aqueous suspensions are the same as that of water, the present experiments correspond to $0.85 < Re < 2.9$.

At these low values, the bubble shape deviates a negligible amount from flow at $Re = 0$ in circular capillaries,⁴² and we assume that this approximation is also applicable in rectangular microchannels. For low Reynolds number flows, the shape and dynamics of bubbles in rectangular channels has been studied by Wong *et al.*,^{18, 43} who determined that the dominating force balance is between viscous stresses acting on the interface and capillary pressure. The ratio of these two effects is estimated by the capillary number. For bubbles, the capillary number Ca depends on the bubble velocity, the viscosity of the external fluid, and the surface tension σ ,

$$Ca = \frac{\mu U}{\sigma}. \quad (5.4)$$

For our experiments, $3 \times 10^{-4} < Ca < 1 \times 10^{-3}$, indicating that, in the absence of surface-active particle adsorption, surface tension forces determine the bubble shape in the microchannel.

The shape of a bubble confined in a rectangular channel affects the fluid motion around the interface as well as the location of the bubble interface where most of the particle adsorption occurs. At low values of Ca the bubble shape has three distinct regions, illustrated schematically in Figure 5.10: the rounded end caps at the front and rear of the bubble, the thin lubricating films along the four walls of the channel with film thickness δ , and the four corner regions with a radius of curvature R . The cross-sectional shape of the bubble in the rectangular capillary resembles a rectangle with rounded end corners. Because the thickness of the lubricating film is typically much smaller than the smallest channel

dimension, $\delta \ll H$, we can immediately apply a simple geometric approximation to determine the bubble perimeter P_b

$$P_b \approx 2(H + W + (\pi - 4)R) \quad (5.5)$$

and the cross-sectional area of the bubble A_b

$$A_b \approx HW + (\pi - 4)R^2. \quad (5.6)$$

Estimating the work required to displace a meniscus in a wedge⁴⁴ reveals that for small capillary numbers, $Ca \ll 1$, the mean radius of curvature of the bubble is given by the simple expression

$$R = \frac{A_b}{P_b}. \quad (5.7)$$

Solving equations (5.5) – (5.7) simultaneously, we obtain an expression for the radius of curvature in the corners as a function of the channel geometry

$$R = \frac{H + W - \sqrt{H^2 + (\pi - 2)HW + W^2}}{4 - \pi}. \quad (5.8)$$

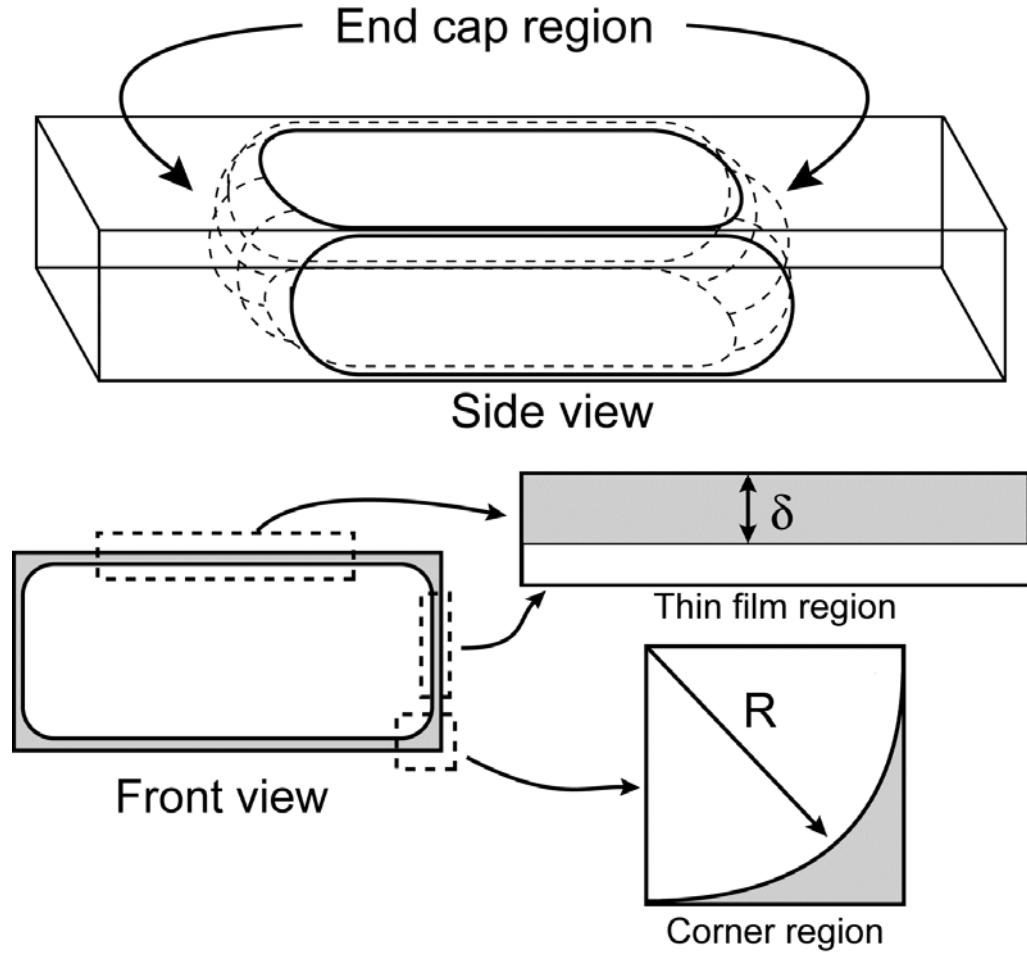


Figure 5.10. Schematic diagram of the shape of a long bubble confined within a rectangular capillary at low Re and Ca . The three distinct regions of the bubble interface include the end cap region, the thin film region, and the corner region.

For a clean bubble with a mobile or stress-free interface in a rectangular channel, the thickness of the lubricating film is a complex function of the capillary number, the channel geometry, and the position along the length of the bubble that must be integrated numerically.⁴³ We estimate the film thickness using

$$\delta = 0.643(3Ca)^{2/3} R \quad (5.9)$$

which corresponds to the maximum film thickness for a bubble in a rectangular capillary.⁴³ The presence of a packed particle layer at the interface will render the bubble surface immobile, leading to a no-slip boundary condition at the surface. To estimate the thickness of the lubricating film region in the immobilized region, we use Bretherton's analysis of the film thickness surrounding a bubble with a no-slip interface in an axisymmetric capillary,⁴⁵ which has the same scaling as in equation (5.9) but is reduced in magnitude by a factor of $2^{-1/3}$. We use this estimate since the film thickness for immobile interfaces in rectangular microchannels has not been analyzed in the literature.

The mass flux j of particles to the interface per unit area is related to the number flux ϕ by the mass of a spherical colloidal silica nanoparticle of radius r_p ,

$$\phi = \frac{3j}{4\pi\rho_p r_p^3} \quad (5.10)$$

where ρ_p is the nanoparticle density. We assume that particles that adsorb to the interface immediately form a hexagonal close-packed structure at the interface, shown schematically in Figure 5.11. As particles adsorb to the interface the surface area A of the bubble that is stabilized by this layer increases. If there are repulsive interparticle interactions on the interface, there may be an effective equilibrium spacing ε between the particles (Figure 5.11). The rate of particle-covered area growth dA/dt is given by the product of the effective particle cross-sectional area at the interface, the packing density of circles in a hexagonal lattice ($\pi\sqrt{3}/6$), and the number flux of particles j multiplied by the surface area

available for particle flux, A_{flux} . Combining this product with equation (5.10) yields

$$\frac{dA}{dt} = \frac{3\sqrt{3}}{2\pi\rho_p} \frac{(r_p + \varepsilon)^2}{r_p^3} jA_{flux}. \quad (5.11)$$

For long bubbles, the majority of the area growth will occur in the axial direction. Neglecting the end cap regions, the particle-stabilized area is given by the perimeter of the bubble times the length of the bubble stabilized by particles,

$$A = aP_b \quad (5.12)$$

If we neglect the change in the perimeter that occurs in the neck region of the bubble, then the perimeter is constant, allowing us to combine equations (5.11) and (5.12) to obtain an expression for the rate of growth da/dt of the particle-stabilized length of the bubble,

$$\frac{da}{dt} = \frac{3\sqrt{3}}{2\pi\rho_p} \frac{(r_p + \varepsilon)^2}{r_p^3} \frac{jA_{flux}}{P_b}. \quad (5.13)$$

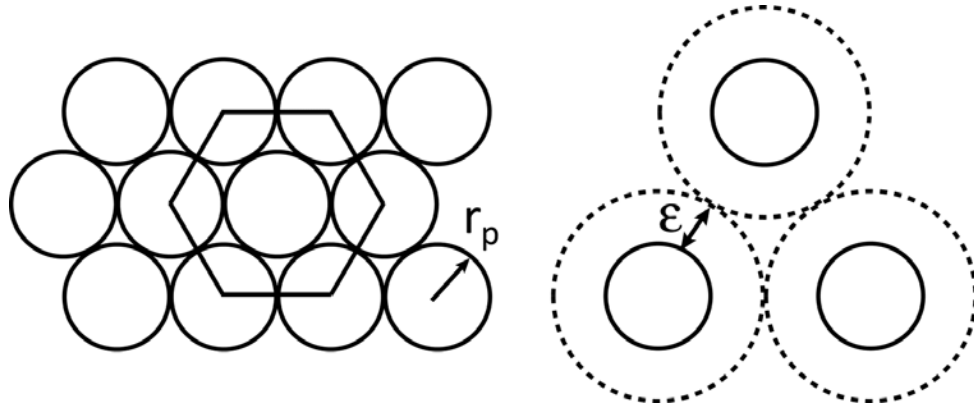


Figure 5.11. Schematic diagram of the assumed particle arrangement at the air-water interface. The particles are assumed to form a hexagonally close packed structure with no spacing between the particles (left), or there can be uniform spacing between particles that results in an effective packing radius of $r_p + \varepsilon$.

The rate of mass flux to the interface depends on the flow field around the bubble in the rectangular microchannel. Experimentally, the bubble is observed to move at a velocity that is less than the average fluid velocity at all points along the channel. In the fixed reference frame of the bubble, the particle suspension flows past the bubble in the direction from rear to front with an approximate velocity of $V - U$. Although clean bubbles in rectangular capillaries exhibit velocities approximately 5% greater than the average fluid velocity for our measured capillary numbers,¹⁸ the presence of surface-active components increases the rigidity of the interface and results in bubbles that travel slower than the average fluid velocity in rectangular channels.²⁸ Particles can potentially adsorb to the interface in the three distinct regions shown in Figure 10: the curved end caps of the bubble, the thin film region along the walls of the channel, or the open region for fluid flow that is present in the microchannel corners.

The mass flux to the interface depends on the Peclet number Pe , which estimates the rate of particle convection near the interface to the rate of particle diffusion. The Peclet number in our system in the fixed bubble reference frame is

$$Pe = \frac{(V - U)\ell}{D}, \quad (5.14)$$

where ℓ is the characteristic length scale in the relevant region of the interface and $D = kT / 6\pi\mu r_p$ is the diffusivity of a particle based on Stokes-Einstein diffusion.⁴⁶ In the end cap region, the relevant length scale is the hydraulic radius of the microchannel,

$$R_h = \frac{HW}{H + W} \quad (5.15)$$

which leads to Peclet numbers in the end cap regions of the order of $Pe_{cap} \sim 10^4$. The open area for flow in the corners is calculated based on the static shape of the bubble interface in the rectangular geometry. The characteristic length scale in that region is the largest distance between the bubble interface and the microchannel walls, which is $0.414R$, leading to Peclet numbers in the corner region that are of the order of $Pe_{cor} \sim 10^3 - 10^4$. In the thin film region, the characteristic length scale is the film thickness δ . Given characteristic capillary numbers, the thickness of the film ranges from 200-500 nm, leading to Peclet numbers of the order of $Pe_{film} \sim 10^2$.

At large Peclet numbers, $Pe \gg 1$, a concentration boundary layer forms near the interface. Particles must diffuse across the boundary layer thickness δ_b in order to adsorb to the fluid interface. Within the boundary layer, we assume that Fick's law governs the particle flux to the interface:

$$j = -D\nabla C \quad (5.16)$$

where C is the particle mass concentration in the continuous phase liquid, which can vary with position. We can estimate the particle flux to the interface by first assuming that once a particle is adsorbed to the interface, it is immediately convected along the interface away from the region immediately adjacent to the boundary layer. Thus we assume that the mass concentration of particles at the interface is zero. If we then assume that the concentration gradient is approximately linear across the boundary layer thickness, we obtain an approximation for the concentration gradient of

$$\nabla C \approx \frac{-C_\infty}{\delta_b}. \quad (5.17)$$

The bulk mass concentration C_∞ for a dilute suspension of particles is the product of the particle mass fraction x_p and the aqueous suspension density ρ_f .

In the end cap region we estimate the boundary layer thickness assuming uniform flow past a rigid sphere of radius r for $Pe \gg 1$ and $Re < 1$. The resulting boundary layer thickness is given by⁴⁷

$$\delta_{b,cap} \approx \left(\frac{4}{3Pe} \right)^{1/3} r \quad (5.18)$$

We assume a rigid spherical boundary as opposed to an inviscid bubble due to the presence of nanoparticles at the interface, which causes the interface to act as a solid surface. In the lubricating films and the corners, the average boundary layer thickness δ_b within the thin film of thickness δ along a bubble of length L is given by

$$\delta_{b,film} \approx \frac{\delta^{2/3}}{Pe^{1/3}} L^{1/3} \quad (5.19)$$

which is approximated from the boundary layer that arises in flow between two flat plates.⁴⁸ For the experimental microchannel geometry with hydraulic radius of 32 μm , the boundary layer thickness in the end cap region is of the order of $\delta_{b,cap} \sim 0.1 - 1 \mu\text{m}$. For characteristic values of the film thickness and the Peclet number, and assuming a bubble length of 500 μm , the minimum estimated boundary layer thickness in the lubricating film is $\delta_{b,film} = 600 \text{ nm}$, which exceeds the film thickness itself. In order to estimate the boundary layer thickness in the corner region, we replace the film thickness δ in equation (5.19) with the largest cross-sectional dimension of the corner channels of $0.414R$ to obtain a boundary layer thickness in the corners of the order of $\delta_{b,cor} \sim 1 \mu\text{m}$.

A comparison of the characteristic geometric length scales with the boundary layer thicknesses in each region of the bubble suggests that the corner and thin film regions can become depleted of particles, dramatically decreasing the rates of particle adsorption in those regions. We can estimate the effects of particle depletion from the bulk by using a depletion number S_d , which determines the effect of a finite volume V_D on the observed equilibrium transport to an interface of area A_D .^{49,50}

$$S_d = \frac{A_D \delta_b}{V_D} \quad (5.20)$$

where we have replaced the adsorption depth in the case of zero flow with the mass transfer boundary layer thickness. For $S_d \ll 1$, the volume of fluid in the region can be treated as an infinite reservoir, but as S_d approaches unity, a lower equilibrium surface concentration is observed. Depletion from the bulk has two effects that decrease the total particle mass flux to the interface: 1) it lowers the observed equilibrium surface concentration and 2) it slows particle transport dynamics to interfaces. In the thin film region, the ratio of the available surface area to the volume of fluid in the thin film is $1/\delta$, yielding depletion numbers always greater than unity. The total available area for particle adsorption in the corner regions is $2\pi RL$ and the available corner volume is $(1-\pi/4)R^2L$, meaning that the depletion number in the corner region is always less than 0.5. From these estimates, we expect that adsorption will be dominated by the transport of particles to the end cap region, and that depletion effects will prevent adsorption in the thin film and to a lesser extent, the corner regions along the length of the bubble.

To test the idea that depletion controls the rates of transport in the thinnest regions, we model the adsorption to the bubble interface assuming that particle adsorption is occurring (without depletion effects) in only one region of the confined bubble interface at a time. The equation for the particle flux j in the thin film region is calculated by combining equations (5.16), (5.17), and (5.19). The available area for particles to adsorb to the interface is equal to the bubble perimeter (minus the length of the bubble interface in the corner regions) multiplied by the length of the bubble segment that is not stabilized by particles ($L - a$). Applying these equations to equation (5.13) yields a first order ordinary differential equation in time. Assuming that the instantaneous bubble length is approximately equal to the final bubble length L_f , we can integrate the equation and solve for the instantaneous neck position a as a function of time t :

$$a_{film} = L_f \left(1 - \exp \left(-\frac{t}{t_{film}} \right) \right) \quad (5.21)$$

where the time constant t_{film} is

$$t_{film} = \frac{4\pi^2}{\sqrt{3}} \frac{\mu\rho_p}{kT\rho_f} \frac{r_p^4}{(r_p + \varepsilon)^2} \frac{1}{x_p} \frac{P_b}{P_b - 2\pi R} \frac{\delta^{2/3} L_f^{1/3}}{Pe_{film}^{1/3}}. \quad (5.22)$$

An equation similar to (5.21) can be derived for the corner regions. The flux in the corners is modeled by equations (5.16), (5.17), and (5.19) where the film thickness is replaced by $0.414R$. For a total available area for particle adsorption of $2\pi R(L - a)$, we once again integrate equation (5.13) to obtain an equation for the growth of the particle stabilized length a_{cor} due to a particle flux in the corner region that is of a similar form to equation (5.21), where t_{film} is replaced by

$$t_{cor} = \frac{4\pi^2}{\sqrt{3}} \frac{\mu\rho_p}{kT\rho_f} \frac{r_p^4}{(r_p + \varepsilon)^2} \frac{1}{x_p} \frac{P_b}{2\pi R} \frac{(0.414R)^{2/3} L_f^{1/3}}{Pe_{cor}^{1/3}}. \quad (5.23)$$

In the case where the flux is to the rear end cap, the available area for particle flux is the surface area of the rear end cap $2\pi R_h^2$, which is a constant independent of the length of the particle-stabilized region a . Applying equations (5.16), (5.17), and (5.18) to model the flux to the end cap region and integrating equation (5.13), we find that under these conditions the length of the particle-stabilized region grows linearly with time:

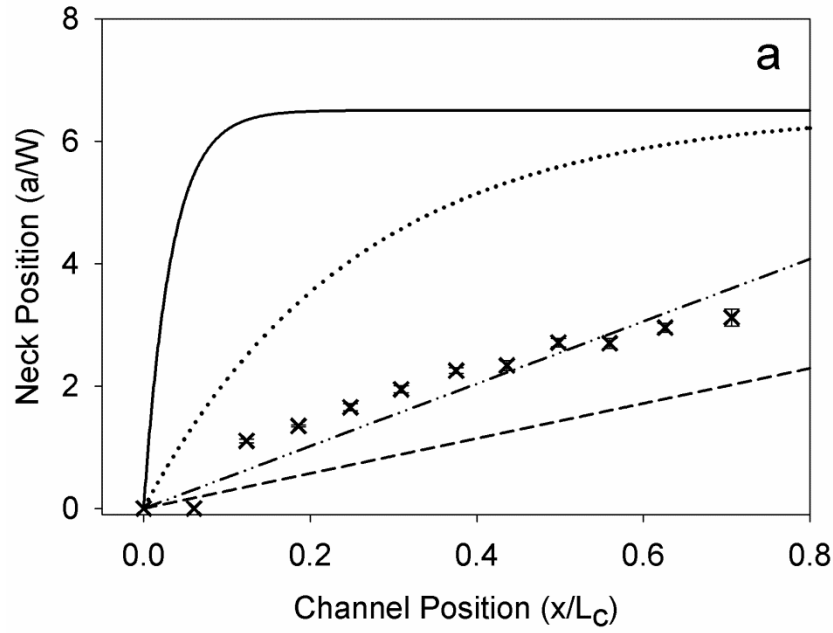
$$a_{cap} = L_f t_{cap}^{-1} t = L_f \left(\frac{4\pi^2}{\sqrt{3}} \frac{\mu\rho_p}{kT\rho_f} \frac{r_p^4}{(r_p + \varepsilon)^2} \frac{1}{x_p} \frac{P_b L_f}{2\pi R_h} \left(\frac{4}{3Pe_{cap}} \right)^{1/3} \right)^{-1} t. \quad (5.24)$$

Figure 5.12 shows the results of the three models compared with experimental data at three different concentrations of the silica-CTAB suspensions. Because the model does not incorporate the growth of the bubble length in the channel, we have scaled the observed position of the neck with the channel width. The models predict the rate of particle adsorption measured by the location of the neck at a given bubble position along the microchannel. The models cannot predict the conditions necessary for the neck region to initially form or relax at the end of the necking transition since they do not account for the stresses acting on the bubble. For all concentrations, the linear growth rate predicts the propagation rate of the neck the most accurately, with the particle flux models in the thin film and corner regions overpredicting the rate of particle adsorption. The only way that the fast rates of particle adsorption predicted by the

timescales in equations (5.22) and (5.23) could not have an effect on the total rate of adsorption in the microchannel is if the depletion of particles from the thin film and corner regions slowed the adsorption rate in those areas. From this, we conclude that depletion effects are preventing fast adsorption rates in the thin film and corner regions.

The particle flux in the thin film is the fastest of the three regions, with complete bubble coverage occurring at very short distances downstream of the T-junction. The particle flux in the corners is slower than in the thin film, with the neck length again predicted to decay exponentially to the overall bubble length. The particle flux to the end cap region is linear with respect to time, and the resulting growth of the particle-stabilized region is much slower than the other two regions. By using values corresponding to the experimental conditions in equations (5.21) through (5.24), the only free parameter is ε , the effective particle spacing on the air-water interface. Increasing the effective spacing on the bubble interface decreases the number of particles necessary to grow the particle-stabilized region by a given amount, therefore increasing the rate of neck growth. Increasing the bulk particle concentration x_p decreases the timescales for complete adsorption in equations (5.22), (5.23), and (5.24). Experimentally, the rate of adsorption is observed to increase with increasing silica weight fraction, as shown in Figure 5.12. The effective value of the particle spacing ε that yields the best agreement with the observed neck propagation rate for the 1 wt% silica-CTAB suspension is $\varepsilon = 2$ nm, which leads to an effective particle packing radius on the interface of $\varepsilon + r_p = 8$ nm. The observed duration of the neck propagation period

in the 2 wt% silica-CTAB suspension agrees exceptionally well with the growth rate predicted by equation (5.24) with zero effective particle spacing. In the case of the 10 wt% silica-CTAB suspension, all three models overpredict the rate of neck growth, even in the case when the silica particles are close packed at the interface ($\varepsilon = 0$).



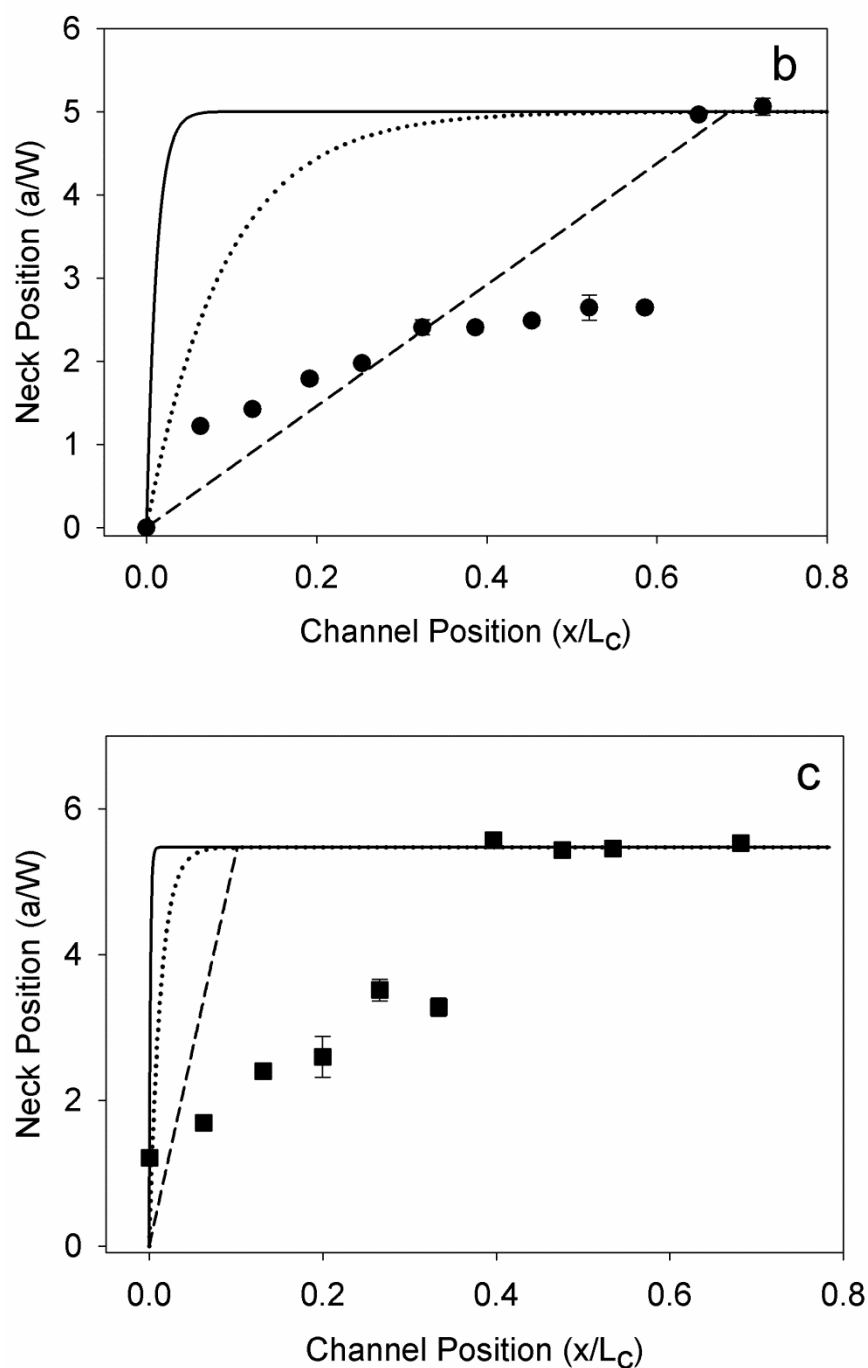


Figure 5.12. Comparison of the models for particle flux to the bubble interface in the thin film (—), the channel corner ($\cdots$), and the end cap region with particle spacing $\varepsilon = 0$ (-- --). Also shown is the rate of growth of the neck region for the end cap model with particle spacing $\varepsilon = 2$ nm ($\text{--}\cdots\text{--}$). These models are compared with experimental data for bubbles generated in a silica-CTAB suspension at (a) 1 wt%, (b) 2 wt%, and (c) 10 wt% silica. The volumetric flow rates are $Q = 1$ mL/hr for the 2 wt% and 1 wt% solutions, and $Q = 0.42$ mL/hr for the 10 wt% solution.

The initial lengths of the bubbles are (a) $L_i/W = 4.72 \pm 0.10$, (b) $L_i/W = 6.44 \pm 0.47$, and (c) $L_i/W = 4.72 \pm 0.10$.

The models cannot account for either the initial appearance of the neck position at approximately one channel width from the rear of the bubble, or the subsequent relaxation of the neck once it has reached a point beyond the half length of the bubble, because equations (5.21), (5.23), and (5.24) do not account for the balance of the shear stress and the surface tension at the bubble interface. The bubble in the 1 wt% silica-CTAB suspension forms a neck that propagates forward on the bubble faster than the linear model with close packing, $\varepsilon = 0$, but the model fits well to the experiments with a spacing of $\varepsilon = 2$ nm. This suggests that the surface concentration of particles that equilibrate at the interface depends on bulk concentration, which is consistent with previous observations for nanoparticles adsorbing to static fluid-fluid interfaces.⁵¹ One explanation for the apparent decreased rate of particle adsorption compared with predictions at the high silica weight fraction of 10 wt% is the possible formation of silica aggregates. From equations (5.22) – (5.24), and recalling the dependence of the Peclet number in equation (5.14) on the particle radius through Stokes-Einstein diffusivity, the adsorption timescales (assuming $\varepsilon = 0$) scale with the particle radius as $r_p^{5/3}$. An increase in the average particle radius will significantly slow the rate of adsorption, which can ultimately lead to bubbles generated at the microchannel outlet that have fewer particles at the interface than expected and an increased susceptibility to coalescence.

The decrease in the bubble velocity is closely linked to the neck propagation, and therefore the particle adsorption to the bubble surface. The presence of a close-packed layer of particles at the air-water interface will significantly affect the response of that interface to deformation and shear. Experimental studies of the interfacial shear viscosity of polystyrene particles at air-water interfaces show a sharp increase in the surface viscosity for high particle surface packing.⁵² A similar condition occurs at the air-water interface of the bubble in the microchannel, where the packing of nanoparticles at the bubble interface gives rise to an effective surface viscosity at the interface. The additional shear stress that arises due to the presence of this layer increases the pressure drop across the length of the bubble due to shear stress in the thin film region that is normally not present in the case of clean bubbles with shear-free interface conditions.

The velocity of clean bubbles in rectangular channels has been determined analytically using a “leaky piston” model, wherein the largest wall shear stresses are present in the transition region between the rounded end caps and the thin film region.¹⁸ Because the clean bubble has a shear stress-free interface, there is zero additional shear stress in the thin film and corner regions along the length of the channel for small values of the capillary number. If particles are adsorbed at the interface, there will be an additional shear stress at the channel walls, increasing the pressure drop across the bubble.

Using asymptotic analysis, Lac and Sherwood estimated that the pressure drop per unit length ΔP along viscous droplets confined in round capillaries is

linearly dependent upon the droplet velocity and will exceed the pressure drop across the end cap regions.⁵³ In rectangular channels, this increase in pressure due to the packed particle layer at the interface will drive more fluid through the corner regions of the bubble, decreasing the bubble velocity. This argument is consistent with the experimental velocity values shown in Figure 8. The observed decrease is not perfectly linear, which could be a result of the presence of the thinner necked region, in which the shear stresses at the wall are not as significant as in the particle-stabilized thin film region, decreasing the overall pressure drop driving fluid flow through the corners.

Although we assume that the particles adsorb at the rear of the bubble and are swept toward the front during particle adsorption due to the bubble traveling slower than the average fluid velocity, we cannot explain why the particles do not continue to convect along the surface to form a close-packed layer at the front of the bubble. A similar effect has been observed experimentally for surfactants adsorbing to confined fluid interfaces in rectangular microchannels,⁵⁴ where the surfactant concentration propagates forward from the rear of the bubble. Based on fluorescence measurements, there is a clear distinction in these experiments between the surfactant-rich bubble rear and the relatively clean bubble front during the initial times in the surfactant adsorption process. In some studies of axisymmetric core-annular flows, the inner fluid can form a periodic, axisymmetric “bamboo” wave structure at the fluid-fluid interface.⁵⁵ In the case where the outer fluid is less viscous than the inner fluid, a pressure gradient that extends radially outward from the inner core can arise that favors recirculation of

the annular fluid.⁵⁶ Although the outer aqueous fluid in our experiments is much more viscous than the inviscid gas bubble, the presence of particles at the interface increases the effective viscosity of the air-water interface. This “hardening” effect of particles at the interface may promote recirculation of the outer aqueous suspension in the thinner neck region, which would drive the particles in the neck back toward the rear of the bubble and effectively limit the region over which adsorbed particles are collected on the bubble interface.

We could not reproduce either the necking transition or the bubble velocity decrease for bubbles translating in a circular capillary. An image of a long bubble confined in a circular capillary of inner diameter 1 mm containing a 2 wt% silica-CTAB suspension is shown in Figure 5.13. The bubble does not form an observable thinner neck region at any point along the 100 mm long capillary, and the bubble velocity is not observed to decrease appreciably at any point along the channel for capillary numbers on the order of $10^{-4} - 10^{-3}$. The lack of an observed neck region in these capillaries can be explained through the available surface area to volume ratio for particle adsorption. In circular capillaries the film thickness is constant along the bubble and can be estimated using equation (5.9), where R is the radius of the capillary tube. For a tube radius of 500 μm , the thin film thickness is on the order of 1-5 μm . The depletion number for the thin film region based on this film thickness, using a boundary layer thickness estimated using equation (5.19), is of order of $S_d \sim 0.01 - 0.1$, meaning that depletion effects do not alter the rate of adsorption of particles along this thin film region. The adsorption of particles is enhanced by the lubricating

layer around the bubble, which means that a large number of particles are adsorbed to the interface a short distance after it is generated.

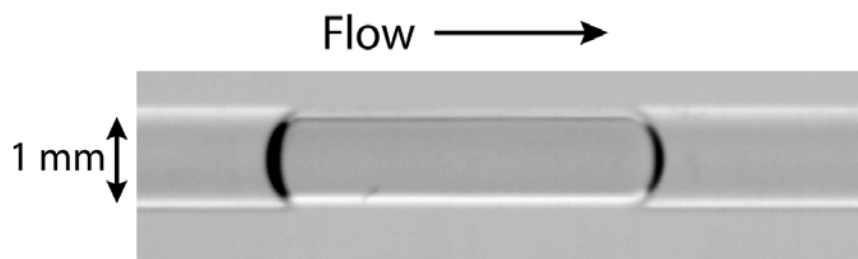


Figure 5.13. Characteristic bubble shape observed in a circular capillary when generated in a 2 wt% silica-CTAB suspension.

5.4 DISCUSSION

The particle adsorption model presented here provides a good estimate of the total timescale for particle adsorption and the resulting bubble dynamics in rectangular geometries. One important aspect that must be taken into consideration in generating particle-stabilized bubbles in microchannels is the residence time of the bubble. In cases where either the particle adsorption rate is slow or the bubble motion is fast, the bubble exits the microchannel before being completely stabilized by particles. Bubbles that exit the microfluidic device can collide with other bubbles, and those bubbles that do not have a stabilizing layer of particles adsorbed at the interface will be susceptible to coalescence. On the other hand, the knowledge of and control over the amount of particles adsorbed at the interface may lead to the continuous generation of nonspherical particle-stabilized drops and bubbles.^{15, 57}

The particle adsorption timescales observed in the microfluidic device (~ 1 s) are significantly shorter than the surface tension dynamic timescales measured

in the microtensiometer ($\sim 10^4$ s). This is due largely to the high Peclet number flows present in the microfluidic experiment, compared to the quiescent fluid in the microtensiometer with zero Peclet number. This flow decreases the mass transfer boundary layer thickness, which can decrease the diffusion timescale of surface-active species to the bubble interface by orders of magnitude.⁵⁸ The long timescales for the adsorption of the silica-CTAB mixtures to bubble interfaces under quiescent conditions are decreased by flow in the microfluidic device to the order of the residence time of the bubble in the microfluidic device.

One significant drawback in the experimental setup presented here is that the bubble length and the volumetric flow rate of the continuous phase liquid are coupled, meaning that we cannot independently study the effects of bubble length and bubble velocity on the rate of particle adsorption to the interface. This would be important in examining, for example, scaling the adsorption timescales with the Peclet number, as well as the effect of the bubble length on the rate of particle adsorption. We are also limited in the total straight length of microchannel that can be used due to the maximum size of the mold used in the soft lithography process (approximately 70 mm). Increasing the overall length by the addition of turns in the microchannel would affect the flow field around the bubble,⁵⁹ as well as the motion of particles on the bubble interface.

We have neglected microchannel roughness in our analysis, which can be on the order of microns in devices generated using similar soft lithography processes.⁶⁰ This roughness along the walls of the microchannel would increase the effective thin film thickness between the bubble and the wall in our analysis.

Assuming that the thin film thickness is equal to a moderate channel roughness of $2\text{ }\mu\text{m}$, the calculated depletion number is still greater than 0.2 for characteristic experimental conditions, meaning that depletion can still affect the rate of nanoparticle adsorption. The nanoparticle adsorption timescale for this case from equation (5.22) is still smaller than the adsorption timescale in the corner region, meaning that adsorption in the thin film would still lead to a faster neck propagation rate than that observed experimentally.

Although the model does well at predicting the neck propagation rate, the simplicity of the model limits its application to specific conditions. If the bubble size is comparable to or smaller than the larger cross-sectional microchannel dimension, then the depletion effects will not be as significant, and the rate of particle adsorption will increase. Also, it is important to note that this model assumes that a single bubble is moving through the microchannel and does not take into account the effects of bubble trains on the flow field⁶¹ or the depletion of particles from the bulk when multiple bubble interfaces are present. A significant assumption in this analysis is that the particles arrange in a hexagonal close-packed structure on the interface; however, particle-surfactant suspensions that are used to stabilize emulsions and foams formed using bulk agitation methods can form multilayers at the air-water and oil-water interface.¹⁹ Because we have broken up aggregates *via* sonication prior to each experiment, we do not expect that multilayers of particles will form until the bubble has been completely stabilized by particles, after which point the continued particle flux to the interface could allow multilayers to form. The particle shape can also affect the

rate of growth of the particle-stabilized region. Anisotropic particles would not exhibit a hexagonal close-packed structure shown in Figure 5.11, which would alter the rate of particle-stabilized area growth in equation (5.11).

The presence of the neck region in the microchannel is a unique bubble deformation that arises due to the combined effects of colloidal particle adsorption and bubble confinement. Although the neck region is less confined, meaning that depletion effects should not significantly alter the rate of transport to the interface, the neck region is surrounded on both sides with regions that can have significant depletion effects (see images in Figure 5.3). Because of this, the contribution of the neck region to the total particle adsorption rate is expected to be negligible. The transport to the interface in the neck region will not be hindered if shear stresses cause enough deformation at the interface to allow significant fluid flow around the bubble rear, as in the images of the long bubble near breakup in Figure 5.6.

5.5 SUMMARY

In this chapter we report experimental observations of unique bubble dynamics that occur during the adsorption of colloidal particles when the bubble is confined in and propagating along a rectangular microchannel. We have observed that a bubble generated in a stable suspension of colloidal silica and CTAB forms a two-lobed shape connected by a thin neck region. The formation of this neck and the commensurate decrease in the bubble velocity along the channel are presumed to occur during the dynamic adsorption of surface active colloidal particles to the moving bubble interface. Comparison with observations

of bubbles flowing through a silica suspension that is not surface active shows that the same bubble dynamics do not occur. The propagation of the neck in the direction of flow and the nonspherical bubble shapes that persist upon the bubble exiting the microchannel suggest that the silica-CTAB suspension is adsorbing to the interface in a comparable timescale to the residence time of the bubble in our microfluidic device.

To explain our experimental observations we have developed a transport model to describe the adsorption rate of particles to long confined bubbles, and we have taken initial steps to understand how the surface coverage of colloidal particles affects bubble motion in confined geometries. The small volumes of fluid that surround the bubble near the channel walls have a detrimental effect on the rate of particle adsorption in the thin film and corner regions. By estimating the particle flux to the interface using boundary layer theory and Fick's law of diffusion, we have developed a model for particle adsorption to the end cap region of the bubble, and we have shown that our model for particle adsorption agrees with our observations. In the microchannel, the dominating particle flux is at the rear of the bubble at the rounded end cap, leading to a particle-stabilized region that starts at the rear of the bubble and moves linearly with time along the bubble surface toward the front of the bubble.

1. Dinsmore, A.; Hsu, M. F.; Nikolaides, M.; Marquez, M.; Bausch, A.; Weitz, D., Colloidosomes: selectively permeable capsules composed of colloidal particles. *Science* **2002**, 298, (5595), 1006-1009.
2. Gonzenbach, U. T.; Studart, A. R.; Tervoort, E.; Gauckler, L. J., Macroporous Ceramics from Particle-Stabilized Wet Foams. *J. Am. Ceram. Soc.* **2007**, 90, (1), 16-22.
3. Aussillous, P.; Quéré, D., Liquid marbles. *Nature* **2001**, 411, (6840), 924-927.
4. Crossley, S.; Faria, J.; Shen, M.; Resasco, D. E., Solid nanoparticles that catalyze biofuel upgrade reactions at the water/oil interface. *Science* **2010**, 327, (5961), 68-72.
5. Manga, M. S.; Cayre, O. J.; Williams, R. A.; Biggs, S.; York, D. W., Production of solid-stabilised emulsions through rotational membrane emulsification: influence of particle adsorption kinetics. *Soft Matter* **2012**, 8, (5), 1532-1538.
6. Leal-Calderon, F.; Schmitt, V., Solid-stabilized emulsions. *Curr. Opin. Colloid Interface Sci.* **2008**, 13, (4), 217-227.
7. Binks, B. P.; Lumsdon, S. O., Pickering Emulsions Stabilized by Monodisperse Latex Particles: Effects of Particle Size. *Langmuir* **2001**, 17, (15), 4540-4547.
8. Madivala, B.; Vandebril, S.; Fransaer, J.; Vermant, J., Exploiting particle shape in solid stabilized emulsions. *Soft Matter* **2009**, 5, (8), 1717-1727.
9. Gonzenbach, U. T.; Studart, A. R.; Tervoort, E.; Gauckler, L. J., Tailoring the microstructure of particle-stabilized wet foams. *Langmuir* **2007**, 23, (3), 1025-1032.
10. Yang, F.; Liu, S.; Xu, J.; Lan, Q.; Wei, F.; Sun, D., Pickering emulsions stabilized solely by layered double hydroxides particles: The effect of salt on emulsion formation and stability. *J. Colloid Interface Sci.* **2006**, 302, (1), 159-169.
11. Pichot, R.; Spyropoulos, F.; Norton, I. T., O/W emulsions stabilised by both low molecular weight surfactants and colloidal particles: The effect of surfactant type and concentration. *J. Colloid Interface Sci.* **2010**, 352, (1), 128-135.
12. Subramaniam, A. B.; Abkarian, M.; Stone, H. A., Controlled assembly of jammed colloidal shells on fluid droplets. *Nat. Mater.* **2005**, 4, (7), 553-556.

13. Mulligan, M. K.; Rothstein, J. P., Deformation and Breakup of Micro-and Nano-particle Stabilized Droplets in Microfluidic Extensional Flows. *Langmuir* **2011**, 27, (16), 9760-9768.
14. Park, J. I.; Nie, Z.; Kumachev, A.; Abdelrahman, A. I.; Binks, B. P.; Stone, H. A.; Kumacheva, E., A microfluidic approach to chemically driven assembly of colloidal particles at gas-liquid interfaces. *Angew. Chem.* **2009**, 121, (29), 5404-5408.
15. Studart, A. R.; Shum, H. C.; Weitz, D. A., Arrested Coalescence of Particle-coated Droplets into Nonspherical Supracolloidal Structures†. *J. Phys. Chem. B* **2009**, 113, (12), 3914-3919.
16. Nie, Z.; Park, J. I.; Li, W.; Bon, S. A. F.; Kumacheva, E., An “inside-out” microfluidic approach to monodisperse emulsions stabilized by solid particles. *J. Am. Chem. Soc.* **2008**, 130, (49), 16508-16509.
17. Priest, C.; Reid, M. D.; Whitby, C. P., Formation and stability of nanoparticle-stabilised oil-in-water emulsions in a microfluidic chip. *J. Colloid Interface Sci.* **2011**, 363, (1), 301-306.
18. Wong, H.; Radke, C.; Morris, S., The motion of long bubbles in polygonal capillaries. Part 2. Drag, fluid pressure and fluid flow. *J. Fluid Mech.* **1995**, 292, 95-110.
19. Binks, B. P.; Rodrigues, J. A.; Frith, W. J., Synergistic Interaction in Emulsions Stabilized by a Mixture of Silica Nanoparticles and Cationic Surfactant. *Langmuir* **2007**, 23, (7), 3626-3636.
20. Ravera, F.; Santini, E.; Loglio, G.; Ferrari, M.; Liggieri, L., Effect of Nanoparticles on the Interfacial Properties of Liquid/Liquid and Liquid/Air Surface Layers. *J. Phys. Chem. B* **2006**, 110, (39), 19543-19551.
21. Hassander, H.; Johansson, B.; Törnell, B., The mechanism of emulsion stabilization by small silica (Ludox) particles. *Colloids Surf.* **1989**, 40, (0), 93-105.
22. Liggieri, L.; Santini, E.; Guzman, E.; Maestro, A.; Ravera, F., Wide-frequency dilational rheology investigation of mixed silica nanoparticle-CTAB interfacial layers. *Soft Matter* **2011**, 7, (17), 7699-7709.
23. Xia, Y.; Whitesides, G. M., Soft lithography. *Annu. Rev. Mater. Sci.* **1998**, 28, (1), 153-184.
24. Wang, W.; Gu, B.; Liang, L.; Hamilton, W. A., Adsorption and Structural Arrangement of Cetyltrimethylammonium Cations at the Silica

- Nanoparticle–Water Interface. *J. Phys. Chem. B* **2004**, 108, (45), 17477-17483.
25. Limage, S. P.; Krägel, J.; Schmitt, M.; Dominici, C.; Miller, R.; Antoni, M., Rheology and Structure Formation in Diluted Mixed Particle–Surfactant Systems. *Langmuir* **2010**, 26, (22), 16754-16761.
 26. Alvarez, N. J.; Walker, L. M.; Anna, S. L., A Microtensiometer To Probe the Effect of Radius of Curvature on Surfactant Transport to a Spherical Interface. *Langmuir* **2010**, 26, (16), 13310-13319.
 27. Svitova, T.; Wetherbee, M.; Radke, C., Dynamics of surfactant sorption at the air/water interface: continuous-flow tensiometry. *J. Colloid Interface Sci.* **2003**, 261, (1), 170-179.
 28. Fuerstman, M. J.; Lai, A.; Thurlow, M. E.; Shevkoplyas, S. S.; Stone, H. A.; Whitesides, G. M., The pressure drop along rectangular microchannels containing bubbles. *Lab Chip* **2007**, 7, (11), 1479-1489.
 29. Lan, Q.; Yang, F.; Zhang, S.; Liu, S.; Xu, J.; Sun, D., Synergistic effect of silica nanoparticle and cetyltrimethyl ammonium bromide on the stabilization of O/W emulsions. *Colloids Surf., A* **2007**, 302, (1–3), 126-135.
 30. Binks, B. P.; Whitby, C. P., Nanoparticle silica-stabilised oil-in-water emulsions: improving emulsion stability. *Colloids Surf., A* **2005**, 253, (1–3), 105-115.
 31. Maestro, A.; Guzman, E.; Santini, E.; Ravera, F.; Liggieri, L.; Ortega, F.; Rubio, R. G., Wettability of silica nanoparticle-surfactant nanocomposite interfacial layers. *Soft Matter* **2012**, 8, (3), 837-843.
 32. Binks, B. P., Particles as surfactants—similarities and differences. *Curr. Opin. Colloid Interface Sci.* **2002**, 7, (1–2), 21-41.
 33. Bala Subramaniam, A.; Abkarian, M.; Mahadevan, L.; Stone, H. A., Colloid science: Non-spherical bubbles. *Nature* **2005**, 438, (7070), 930-930.
 34. Roof, J., Snap-off of oil droplets in water-wet pores. *Soc. Pet. Eng. J.* **1970**, 10, (1), 85-90.
 35. Link, D. R.; Anna, S. L.; Weitz, D. A.; Stone, H. A., Geometrically Mediated Breakup of Drops in Microfluidic Devices. *Phys. Rev. Lett.* **2004**, 92, (5), 054503.

36. Olbricht, W. L.; Kung, D. M., The deformation and breakup of liquid drops in low Reynolds number flow through a capillary. *Phys. Fluids A* **1992**, 4, (7), 1347-1354.
37. Aul, R. W.; Olbricht, W. L., Stability of a thin annular film in pressure-driven, low-Reynolds-number flow through a capillary. *J. Fluid Mech.* **1990**, 215, 585-599.
38. Frenkel, A.; Babchin, A.; Levich, B.; Shlang, T.; Sivashinsky, G., Annular flows can keep unstable films from breakup: Nonlinear saturation of capillary instability. *J. Colloid Interface Sci.* **1987**, 115, (1), 225-233.
39. Ajaev, V. S.; Homsy, G. M., Modeling shapes and dynamics of confined bubbles. *Annu. Rev. Fluid Mech.* **2006**, 38, (1), 277-307.
40. Mulligan, M. K.; Rothstein, J. P., The effect of confinement-induced shear on drop deformation and breakup in microfluidic extensional flows. *Phys. Fluids* **2011**, 23, (2), 022004-11.
41. Mulligan, M. K.; Rothstein, J. P., Deformation and Breakup of Micro- and Nanoparticle Stabilized Droplets in Microfluidic Extensional Flows. *Langmuir* **2011**, 27, (16), 9760-9768.
42. Heil, M., Finite Reynolds number effects in the Bretherton problem. *Phys. Fluids* **2001**, 13, 2517.
43. Wong, H.; Radke, C. J.; Morris, S., J. Fluid Mech. *J. Fluid Mech.* **1995**, 292, 71-94.
44. Mason, G.; Morrow, N. R., Meniscus curvatures in capillaries of uniform cross-section. *J. Chem. Soc., Faraday Trans. I* **1984**, 80, (9), 2375-2393.
45. Bretherton, F. P., The motion of long bubbles in tubes. *J. Fluid Mech.* **1961**, 10, (02), 166-188.
46. Einstein, A., Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen. *Ann. Phys. (Berlin, Ger.)* **1905**, 322, (8), 549-560.
47. Levich, V. G.; Spalding, D. B., *Physicochemical Hydrodynamics*. Prentice-Hall Englewood Cliffs, NJ: 1962; Vol. 689.
48. Probstein, R. F., *Physicochemical Hydrodynamics*. Wiley Online Library: 1994; Vol. 833.
49. Ferri, J. K.; Kotsmar, C.; Miller, R., From surfactant adsorption kinetics to asymmetric nanomembrane mechanics: Pendant drop experiments with subphase exchange. *Adv. Colloid Interface Sci.* **2010**, 161, (1-2), 29-47.

50. Alvarez, N. J.; Walker, L. M.; Anna, S. L., A criterion to assess the impact of confined volumes on surfactant transport to liquid-fluid interfaces. *Soft Matter* **2012**, 8, (34), 8917-8925.
51. Du, K.; Glogowski, E.; Emrick, T.; Russell, T. P.; Dinsmore, A. D., Adsorption Energy of Nano- and Microparticles at Liquid-Liquid Interfaces. *Langmuir* **2010**, 26, (15), 12518-12522.
52. Reynaert, S.; Moldenaers, P.; Vermant, J., Interfacial rheology of stable and weakly aggregated two-dimensional suspensions. *Phys. Chem. Chem. Phys.* **2007**, 9, (48), 6463-6475.
53. Lac, E.; Sherwood, J. D., Motion of a drop along the centreline of a capillary in a pressure-driven flow. *J. Fluid Mech.* **2009**, 640, 27-54.
54. Baret, J.-C.; Kleinschmidt, F.; El Harrak, A.; Griffiths, A. D., Kinetic Aspects of Emulsion Stabilization by Surfactants: A Microfluidic Analysis. *Langmuir* **2009**, 25, (11), 6088-6093.
55. Joseph, D.; Bai, R.; Chen, K.; Renardy, Y., Core-annular flows. *Annu. Rev. Fluid Mech.* **1997**, 29, (1), 65-90.
56. Kouris, C.; Tsamopoulos, J., Dynamics of axisymmetric core-annular flow in a straight tube. I. The more viscous fluid in the core, bamboo waves. *Phys. Fluids* **2001**, 13, 841.
57. Pawar, A. B.; Caggioni, M.; Ergun, R.; Hartel, R. W.; Spicer, P. T., Arrested coalescence in Pickering emulsions. *Soft Matter* **2011**, 7, (17), 7710-7716.
58. Alvarez, N. J.; Vogus, D. R.; Walker, L. M.; Anna, S. L., Using bulk convection in a microtensiometer to approach kinetic-limited surfactant dynamics at fluid-fluid interfaces. *J. Colloid Interface Sci.* **2012**, 372, (1), 183-191.
59. Squires, T. M.; Quake, S. R., Microfluidics: Fluid physics at the nanoliter scale. *Rev. Mod. Phys.* **2005**, 77, (3), 977.
60. McDonald, J. C.; Duffy, D. C.; Anderson, J. R.; Chiu, D. T.; Wu, H.; Schueller, O. J. A.; Whitesides, G. M., Fabrication of microfluidic systems in poly(dimethylsiloxane). *Electrophoresis* **2000**, 21, (1), 27-40.
61. Günther, A.; Khan, S. A.; Thalmann, M.; Trachsel, F.; Jensen, K. F., Transport and reaction in microscale segmented gas-liquid flow. *Lab Chip* **2004**, 4, (4), 278-286.

CHAPTER 6**DYNAMIC PARTICLE LOADING DURING SLUG FLOW AND THE GENERATION OF MONODISPERSE BUBBLES OF NONEQUILIBRIUM SHAPES****6.1 INTRODUCTION**

Stable bubble and droplet morphologies that deviate from a spherical shape are a unique characteristic of particle-stabilized emulsions and foams. Due to the large energy of desorption required to eject a colloidal particle from a fluid-fluid interface,¹ an interface that is packed with particles will resist a decrease in the surface area. Because a relaxation from a spherical shape necessarily decreases the surface area, particle jamming at the interface causes the shape of the droplet to remain in a nonequilibrium shape. The control of droplet morphology in emulsions is important in dairy products,² pharmaceuticals,³ and materials fabrication.⁴

Nonequilibrium shapes of bubbles and drops can be generated in bulk foams and emulsions using high-shear homogenization⁵ or solvent evaporation to create droplets with buckled interfaces.⁶ In these systems, the droplet size, morphology, and particle coverage at the interface are not well-controlled. Bon *et al.*⁷ showed that nonequilibrium droplet shapes can be formed by flowing a particle-stabilized emulsion through a small capillary; however, the size and shape distribution is determined by the initial droplet size distribution. Microfluidic methods for generating particle-stabilized bubbles and drops have good control over the droplet size,^{8,9} and nonequilibrium shapes can be generated by uncontrolled partial coalescence of droplets⁸ or by templating with double

emulsions.¹⁰ In these systems, the droplets are generated using a flow-focusing mechanism in a much larger capillary so that the nonequilibrium shapes are generated from a spherical template.¹¹

Particle-stabilized droplets with an elongated shape are also desirable when generating emulsions. Cui *et al.*¹² used an electric field to deform particle-stabilized water droplets into elongated shapes. Cheng and Valenkar¹³ formed elongated particle-stabilized droplets in a spinning drop tensiometer. Both generation methods are batch methods that generate a single particle-stabilized droplet, and there is little attention given to the timescales necessary to generate these nonspherical droplets.

In this chapter, we show that particle adsorption during slug flow in a channel can be used to generate monodisperse particle-stabilized bubbles in uniform elongated shapes. We first perform a visual confirmation of particle adsorption and packing at a dispersed phase interface using latex particle adsorption to an octanol drop interface in aqueous suspension.¹⁴ Droplets are generated in both circular and square glass capillaries to observe the effect of channel cross-sectional shape on the particle packing at the interface. We then show that bubbles generated in the CTAB-silica mixture used in Chapter 5 exhibit a broad range of droplet shapes when removed from confinement. The particle adsorption timescale developed in the previous chapter is used as a characteristic timescale during bubble translation in the channel, and the relative magnitude of that timescale compared with the residence time in the channel is shown to be a key factor in the generation of stabilized bubbles. We also show secondary effects

that can increase the polydispersity in the shape of generated bubbles: the formation of bubble trains that exhibit lower particle coverage in the middle of the train, and bubble break-up at the outlet, which leads to a bidisperse distribution of bubble shapes.

6.2 MATERIALS AND METHODS

6.2.1 MATERIALS

The materials and preparation of the mixture of cetyltrimethylammonium bromide (CTAB) and colloidal silica (Ludox AM30) are described in Chapter 5. 1-Octanol (Certified) and L-lysine hydrochloride (Tissue Culture Grade) are purchased from Fisher Scientific and used as received. L-lysine hydrochloride is referred to as lysine throughout the chapter. Sulfate latex beads (8% w/v) of diameter 1.9 μm are purchased from Life Technologies.

A 0.3 %(w/v) latex suspension containing lysine is prepared by adding a known volume of the undiluted latex suspension to a lysine solution prepared using DI water from a Barnstead UV Ultrapure II purification system. The final concentration of lysine in the particle suspension is 0.017 M. Particle suspensions prepared without lysine did not adsorb to an octanol droplet interface during flow in a glass capillary.

6.2.2 MICROFLUIDIC FABRICATION

Microfluidic channels are fabricated from poly(dimethylsiloxane) (PDMS) using standard soft lithography techniques.¹⁵ The device design is shown in Figure 6.1. The continuous phase liquid is pumped into the device at a constant flow rate by a syringe pump (PHD2000 series, Harvard Apparatus) using a disposable syringe (BD Luer-Lok) with sizes ranging from 5 – 60 mL. A gas

phase fluid is pumped in at constant pressure using a pressure regulator (Hewlett-Packard, 0 – 60 psi). The inlet ports of the microfluidic device are connected to the syringe and the pressure regulator respectively by 0.030" inner diameter LDPE tubing (BB31695-PE/4, Scientific Commodities Inc.). Gas bubbles are produced at the T-junction and are observed along the downstream length of the microchannel.

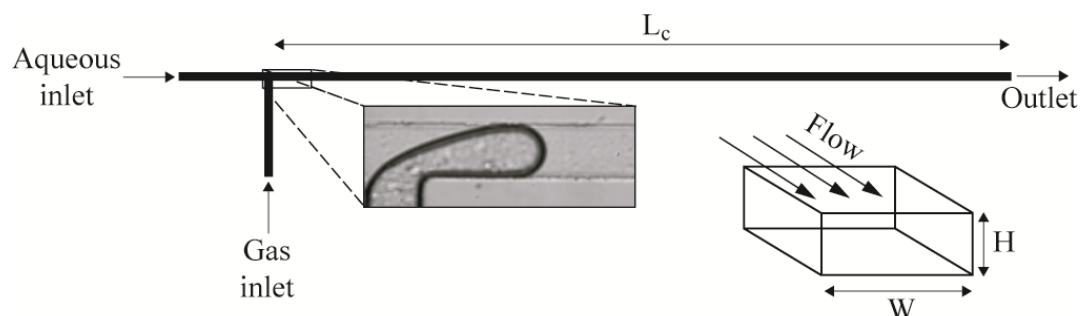


Figure 6.1. Schematic diagram of the microfluidic device. The inset image shows a nitrogen bubble extending into the main channel prior to pinch-off. The lower right shows the rectangular cross-section of the microchannel with the channel width W and height H . The distance from the T-junction to the device outlet is L_c .

6.2.2 CO-FLOW MICROCAPILLARY DEVICE

Bubbles and drops are also generated in a microcapillary device. A schematic diagram of the device is shown in Figure 6.2. A 300 μm inner diameter borosilicate glass capillary (CV3040, Vitrocom) is cleaved to a length of 3 mm and inserted into either a 580 μm inner diameter borosilicate glass capillary (1B100-6, World Precision Instruments, Inc.) or a square capillary with inner side length 500 μm (Friedrich & Dimmock, Inc.). The two capillaries are placed inside a barbed Kynar T-connector with 1/16" inner diameter (30703-70, Cole-Parmer) so that the larger capillary emerges from one end of the T-junction and the smaller capillary emerges from the other end of the T-junction. A segment of 0.8 mm

inner diameter flexible silicone tubing (Masterflex 96400-13, Cole-Parmer) is used to seal the connection between the T-junction and the larger glass capillary. Approximately 4" of 0.030" inner diameter LDPE tubing (BB31695-PE/4, Scientific Commodities Inc.) is fit over the section of smaller glass capillary emerging from the T-junction and glued in place using adhesive (Loctite Stik'n Seal Outdoor Adhesive). The adhesive also forms a seal to allow dispersed phase fluid to flow only through the smaller capillary and to prevent the continuous phase fluid from entering the tubing. A piece of 0.8 mm inner diameter flexible silicone tubing is fit over the open end of the tubing to allow for quick connection to the inner phase flow generation system.

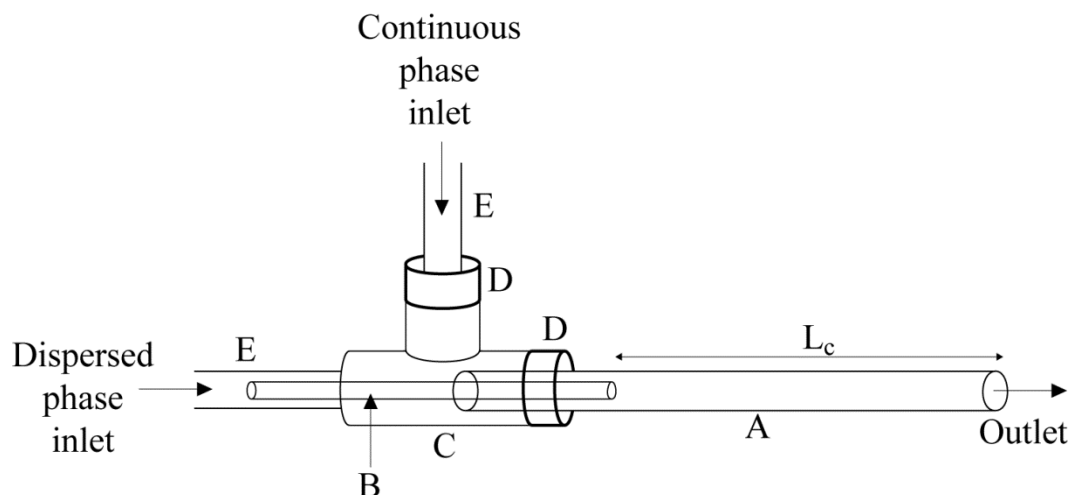


Figure 6.2. Schematic diagram of the co-flow capillary device. The major components of the device are (A) 580 μm ID circular or 500 μm square glass capillary, (B) 300 μm ID circular glass capillary, (C) barbed T-connector, (D) flexible silicone tubing, and (E) 0.030" ID LDPE tubing.

The continuous phase fluid is pumped into the device at a constant flow rate using a syringe pump (PHD2000 series, Harvard Apparatus) with a disposable syringe (BD Luer-Lok). When octanol is used as the dispersed phase

fluid, a second Harvard Apparatus syringe pump is used to control the liquid flow rate. When air is used as the dispersed gas phase, a pressure regulator is used to control the air flow into the capillary. Oil droplets or air bubbles are generated by the inner capillary and travel inside the longer glass capillary a distance L_c to the outlet. The capillary outlet is connected to a fluid reservoir containing either DI water when generating octanol drops or a CTAB-silica mixture at the same concentration as the continuous phase. The reservoir is made by boring a hole into the side of a petri dish, then inserting the capillary end through the hole. A piece of silicone tubing is used to seal the connection between the capillary and the petri dish. The reservoir is filled with enough fluid to completely submerge the capillary end.

A MotionPro X4 high-speed camera (Redlake) is used to image the devices on either a Nikon TE-2000 inverted light microscope or a Bausch & Lomb Zoom 500 stereoscope mounted on a light table (The Richards Corporation). Length scale calibration for both cameras on the inverted light microscopes is performed using a stage micrometer (Edmund Optics). A similar calibration is performed on the light table using a dot calibration target with a 2 mm dot diameter (Edmund Optics).

The various techniques for dispersed phase droplet generation and the various surface active particle systems used are summarized in Table 6.1.

Case	Apparatus	Cross-section shape	R (μm)	H (μm)	W (μm)	L_c (mm)	Inner phase	Outer phase	Particle phase	r_p (nm)	Particle conc.	C (M)
A	Capillary	Circular	580	-	-	40 – 130	Octanol	DI + lysine + latex	Latex	1000	0.3% (w/v)	0.017
B	Capillary	Square	-	500	500	130	Octanol	DI + lysine + latex	Latex	1000	0.3% (w/v)	0.017
C	Capillary	Circular	580	-	-	40 – 130	Air	DI + CTAB + silica	Silica	6	2% (w/w)	2.1×10^{-4}
D	Capillary	Circular	580	-	-	40 – 130	Air	DI + CTAB + silica	Silica	6	10% (w/w)	2.1×10^{-4}
E	Microchannel	Rectangular	-	69.9 ± 1.6	97.2 ± 3.6	50	Air	DI + CTAB + silica	Silica	6	10% (w/w)	2.1×10^{-4}
F	Microchannel	Rectangular	-	38.3 ± 1.3	95.6 ± 1.7	50	Air	DI + CTAB + silica	Silica	6	10% (w/w)	2.1×10^{-4}
G	Microchannel	Rectangular	-	30.4 ± 1.2	82.1 ± 3.3	50	Air	DI + CTAB + silica	Silica	6	10% (w/w)	2.1×10^{-4}

Table 6.1. Device geometries and fluid phase compositions for the experiments considered. Dimensions include the radius of the capillary R , square glass capillary or microfluidic channel depth H and width W , and the length between the droplet generation site and the channel outlet L_c . Relevant particle conditions include the particle radius r_p , the particle concentration, and the concentration C of L-lysine-HCl or CTAB in the outer phase.

6.3 RESULTS

6.3.1 DIRECT OBSERVATION OF PARTICLE ADSORPTION

When octanol droplets are generated continuously into a flowing latex suspension, the rear of the bubble becomes packed with particles. Droplets generated in circular capillaries form an axisymmetric packed end cap region, as shown in Figure 6.3a by the darker region at the rear of the droplet. A magnified image of the droplet interface shown in Figure 7.3c shows the front of the particle-stabilized region for a droplet at the same flow conditions. The flow rates for the inner Q_i and outer Q_o phases are given in the figure caption, and the experimental conditions are described by Case A in Table 6.1. The droplet velocity U relative to the superficial velocity U_s of the outer phase, defined as Q_o divided by the cross sectional area A of the channel, is 1.032 ± 0.019 . This means that the droplet moves faster than the outer phase fluid, which is expected for slug droplets moving in circular capillaries.^{16, 17} Fluid flow moves from the front of the dispersed phase to the rear in the droplet reference frame, indicating that particles that adsorb to the interface are also swept to the rear of the droplet.

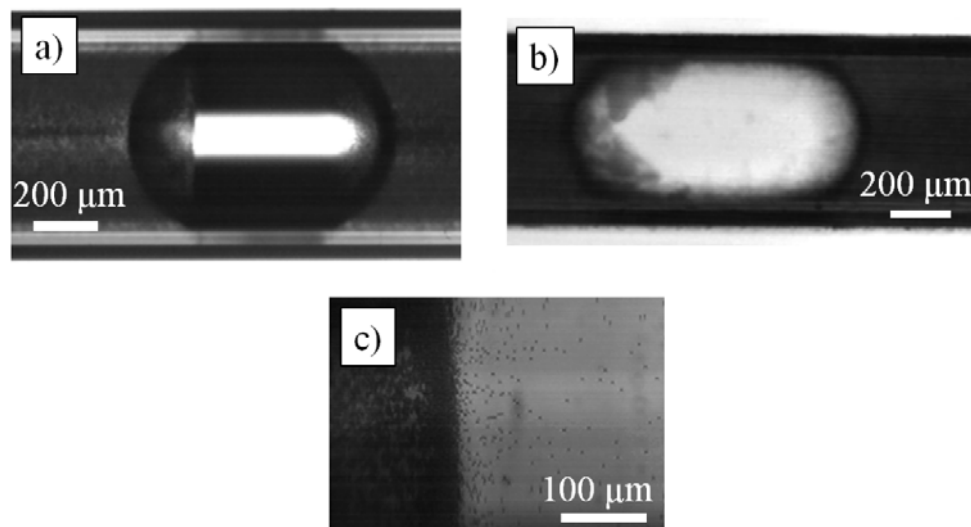


Figure 6.3. Particle packing at the interface of an octanol droplet flowing in a latex particle suspension in a (a) circular and (b) square glass capillary. Image (b) is taken through a flat face of the square capillary. Image (c) shows an image of the particles at the octanol droplet interface in the circular capillary. Droplet motion in images is from left to right. For images (a) and (c), $Q_i = 0.1$ mL/hr and $Q_o = 1$ mL/hr. For image (b), $Q_i = 0.3$ mL/hr and $Q_o = 3$ mL/hr.

Figure 6.3b shows what happens in experimental Case B when the capillary geometry is square: the particles pack unevenly toward the rear of the droplet, with more particles collecting near the corners of the channel. For these experimental conditions, the droplet velocity of 1.247 ± 0.031 mm/s is slower than the superficial outer phase velocity of 3.33 ± 0.033 mm/s. A droplet speed slower than the superficial velocity is expected for droplets in rectangular channels due to excess flow in the corners of the channel.^{18, 19} Despite the fact that the average fluid flow is from the rear of the droplet to the front in a fixed droplet reference frame, a higher concentration of particles is observed at the rear of the droplet.

The particle coverage at the rear of the droplet increases over time, as shown in Figure 6.4 for Case A. As the droplet flows in the latex suspension, the

surface area of the particle-packed rear of the bubble A_p increases. The particle stabilized area is calculated by measuring the length ℓ of the particle-covered region from the rear of the droplet to the packed front, then calculating the surface area assuming the bubble rear is a spherical cap with a radius of curvature equal to the capillary radius, given by

$$A_p = 2\pi R\ell . \quad (6.1)$$

Times are calculated based on the droplet velocity U divided by the distance downstream of the end of the inner capillary. At very short times, the droplet has a nonzero surface area stabilized by latex particles due to particle adsorption during droplet generation. The growth of the particle-stabilized region indicates that particles adsorb to the interface over time and are convected to the droplet rear due to fluid flow.

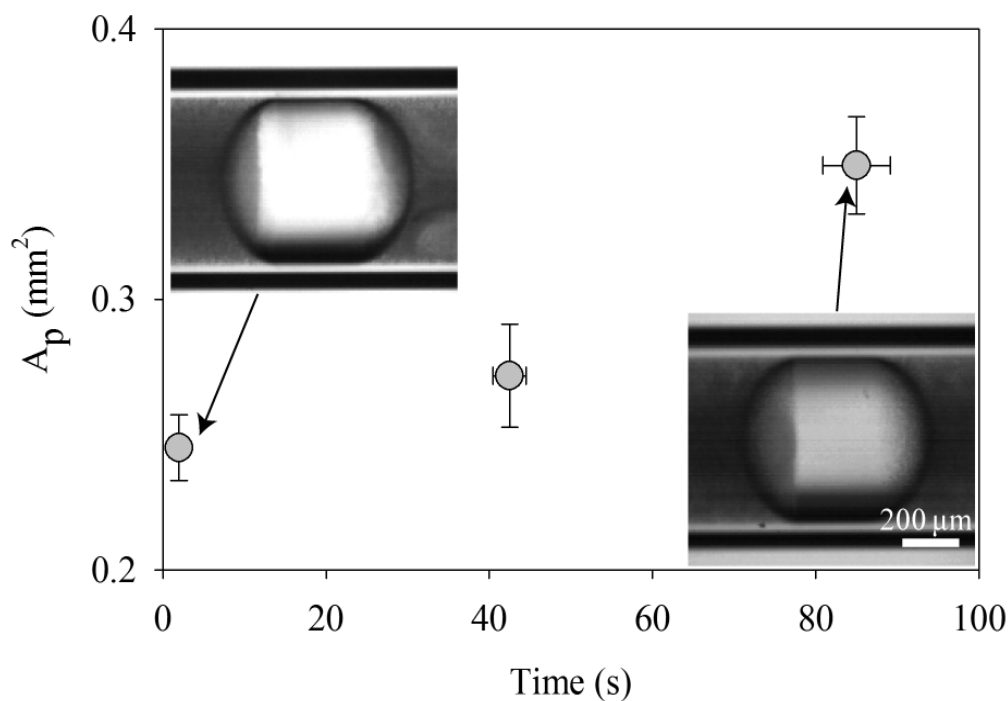


Figure 6.4. Particle-stabilized area A_p at the rear of the droplet versus time in the circular capillary. Inset images show representative droplets for the indicated times. Error bars result from propagated error based on the standard deviation of the bubble velocity. Error bars in the surface area are propagated based on the standard deviation of the length of the particle-covered region. Values and standard deviations are based on measurement of 5 drops.

Octanol droplets that emerge from the capillary rise to the air-water interface in the reservoir. The droplet interface is not completely stabilized by particles when the droplet emerges from the capillary, so when the droplet rises to the air-water interface it spontaneously forms an oil lens. Particles that had adsorbed to the interface during droplet translation in the capillary remain trapped at the interface of the lens, as shown in the inset images of Figure 6.5. By measuring the projected area of particles at the interface, a clear increase in the particle-covered area A_p is observed with increasing residence times. Due to refractive index differences between octanol and water, the value of A_p is

measured in the circular region approximately 200 μm inside the observed edge of the octanol lens. The residence time τ_{res} is equal to the length of the capillary L_c divided by the velocity U of the droplet. Residence times are varied in the data shown in Figure 6.5 under constant inner and outer flow rates by varying the capillary length. At low residence times, the surface coverage of particles approaches zero.

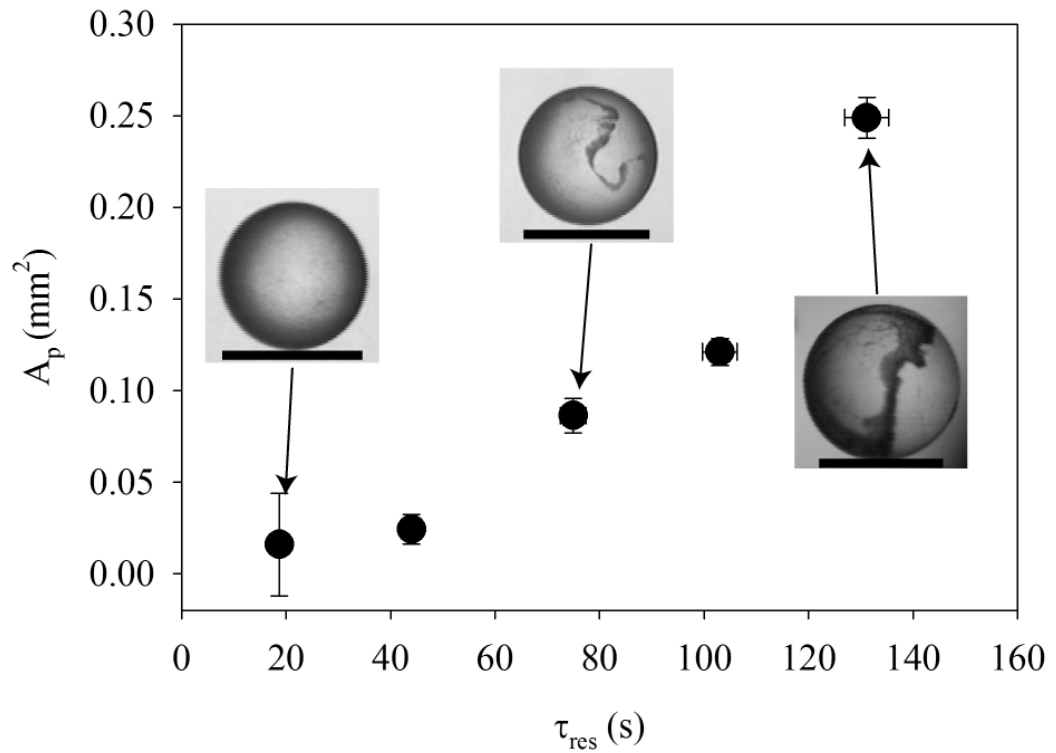


Figure 6.5. Particle-stabilized area A_p versus residence time for droplets generated in Case A. Vertical error bars represent the standard deviation of five measurements. Horizontal error bars are propagated based on the standard deviation of the bubble velocity based on five measurements. Inset images show the octanol lens at three different residence times. The scale bar in each image is 1 mm.

Although measurements of A_p based on the particle coverage on the octanol lens are only approximations due to the loss of particle resolution around the edge of the lens, the resulting observation still indicates an increase in total particle coverage as the total residence time in the channel increases. This indicates that particle coverage on dispersed droplet interfaces can be tuned by controlling the amount of time that the droplet is confined in the microchannel. The rate of particle adsorption must also play a role, and the competition between the adsorption timescale and the residence time of the droplet in the channel will dictate the surface coverage.

6.3.2. CONTROLLED GENERATION OF BUBBLES OF NONEQUILIBRIUM SHAPES

In our previous work, we showed that bubbles generated by a microfluidic T-junction in a surface active mixture of CTAB and silica exhibit nonspherical bubble shapes when outside the confinement of the microchannel.²⁰ Sequential images of a bubble exiting a circular capillary in Case D and expanding to a nonequilibrium shape are shown in Figure 6.6. As the bubble exits the capillary, the front of the bubble relaxes to a spherical cap shape that increases in size as the air bubble continues to exit the microchannel. As the bubble exits the channel, the interface shape outside the capillary deviates from a sphere. The rear of the bubble remains at a higher curvature than the bubble front, and this high-curvature region persists even after the bubble has completely exited the capillary.

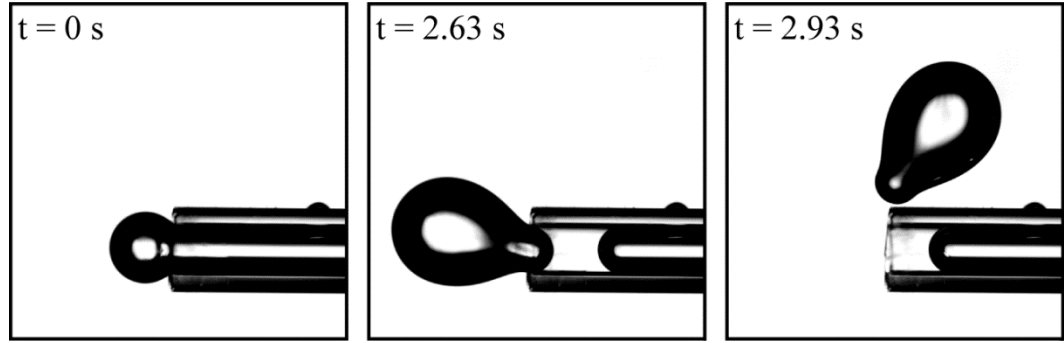


Figure 6.6. Sequential images of a bubble generated in a CTAB-silica mixture exhibiting a nonequilibrium shape outside of confinement. The time elapsed from the first image is shown in the upper left of each image. The outer diameter of the capillary is 1 mm. The second bubble observed in the second and third images was generated at the inner capillary and is not due to break-up within the capillary or pinch-off at the capillary end.

As the bubble exits the capillary, the shape transition of the bubble from a long slug to a more spherical shape leads to a decrease in the total surface area of the bubble. As the surface area decreases, the concentration of silica on the bubble surface increases. At a high enough surface coverage, prior research indicates that particle-covered interfaces act like a solid material capable of supporting a nonspherical shape.²¹⁻²³ A similar effect is observed here when the particle surface concentration increases to a large enough coverage to form a jammed network at the interface.

The mechanism of particle jamming at the elongated slug bubble interface can be used to generate a variety of nonequilibrium bubble shapes, as shown in Figure 6.7. The shape of the bubble is quantified using the relative volume v , where

$$v = \frac{V}{\left(\frac{4\pi}{3}\right)\left(\frac{A}{4\pi}\right)^{3/2}}. \quad (6.2)$$

To calculate the reduced volume, the bubble is assumed to be axisymmetric, then the surface area A is calculated based on the first theorem of Pappus²⁴ and the volume V of the bubble is calculated using the disk method for the thresholded image. The reduced volume is commonly used to describe the shape of vesicles formed with a lipid bilayer at the interface.²⁵ The generated bubbles range from an approximately cylindrical shape at reduced volumes near 0.5 to a spherical shape as the reduced volume approaches unity. For values between $0.5 < v < 1$, the particle-stabilized bubble exhibits a section of higher curvature protruding from a more spherical region.

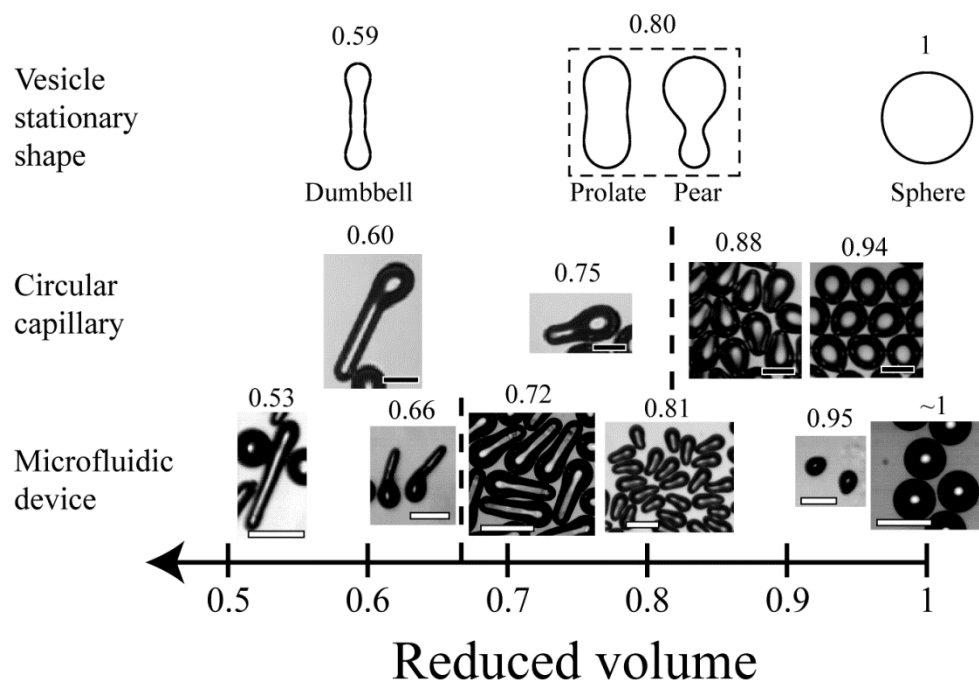


Figure 6.7. Range of nonequilibrium shapes produced in microchannels and in circular capillaries organized by reduced volume. The numbers above each image indicate reduced volume for the bubbles in the image. Bubbles in the bottom row of images are generated in microfluidic devices, and bubbles in the middle row are generated in a circular capillary. The images in the top row correspond to axisymmetric shapes generated from a minimization of free energy in the vesicle shape. The bubbles produced to the right of vertical dashed line in each row are monodisperse. Bubbles to the left of the dashed line are produced as part of a mixture of bubble shapes. The scale bar for the images of bubbles generated in the circular capillary is 1 mm. The scale bar for the bubbles generated using microfluidics is 200 μm .

The generated bubble shapes can be either monodisperse or a mixture of bubble shapes, depending on the way the bubbles are generated. These limits are indicated by dashed lines in Figure 6.7. For the bubbles generated in microfluidic devices, polydisperse drop shapes are generated due to the bubble breaking up in the microchannel. This was observed in Chapter 5 when the neck connecting the two lobes of the bubble during the shape transition became unstable. Break-up of

the bubble can also occur for long bubbles at the outlet due to neck formation and thinning at the orifice. Polydisperse bubbles are formed from the circular capillary when the bubble generation method changes from a continuous production of bubbles with uniform spacing in the channel to periodic production of short trains of bubbles. The bubbles generated to the right of the dashed lines are monodisperse with a standard deviation in the reduced volume of the order of 3 - 8%. For all bubble shapes generated, the majority of bubbles are stable at the air-solution interface for over 12 hours.

These generated bubble shapes are in contrast to the prolate, pear, and dumbbell shapes observed for lipid bilayer membranes at a minimized free energy shown in Figure 6.7. These shapes are generated from a solution of the parametric equations for the vesicle shape²⁵ performed in MATLAB. The shape is described in axisymmetric r and z coordinates by an arclength s measured from the north pole of the shape and the angle ψ between the tangent of the arc contour and the r -axis. The relationship between the axisymmetric coordinates and the arc length and tangent angle is

$$\frac{dr}{ds} = \cos \psi \quad (6.3a)$$

and

$$\frac{dz}{ds} = -\sin \psi . \quad (6.3b)$$

The equations used to generate the vesicle shapes are equation (6.3a) and

$$\frac{d\psi}{ds} = u , \quad (6.4a)$$

$$\frac{du}{ds} = -\frac{u}{r} \cos \psi + \frac{\cos \psi \sin \psi}{r^2} + \frac{\gamma}{r} \sin \psi + \frac{\bar{P}r}{2} \cos \psi, \text{ and} \quad (6.4b)$$

$$\frac{d\gamma}{ds} = \frac{(u - C_0)^2}{2} - \frac{\sin^2 \psi}{2r^2} + \bar{P}r \sin \psi + \bar{\Sigma}. \quad (6.4c)$$

The shape equations include the Lagrange multipliers $\bar{P} = P/\kappa$ and $\bar{\Sigma} = \Sigma/\kappa$ which are normalized by the bending modulus κ and the spontaneous curvature C_0 . All length scales are normalized by a characteristic length scale. The boundary conditions are $\psi(0) = 0$, $\gamma(0) = 0$, and $r(0) = 0$. For given $\bar{P}$, $\bar{\Sigma}$, and C_0 , different values of $u(0)$ are chosen until the interface reaches a stable shape at the total arclength S of $\psi(S) = \pi$, $\gamma(S) = 0$, and $r(S) = 0$. The parameters used to generate the vesicle shapes shown in Figure 6.7 are given in Table 6.2.

v	$\bar{P}$	$\bar{\Sigma}$	C_0	$u(0)$
0.60 (dumbbell)	1.0	-0.300	1.500	1.207
0.80 (prolate)	3.0	-0.476	1.890	1.980
0.80 (pear)	-1.5	1.009	1.454	1.417
1	-1.0	1.000	1.270	1.050

Table 6.2. Parameter values used to generate the stationary vesicle shapes shown in Figure 6.7.

The nonequilibrium bubbles shown in Figure 6.7 are generated in Cases C through G, which includes a variety of flow conditions in different cross-sectional geometries. The bubble shapes generated in the microfluidic and capillary devices are not equivalent to vesicle shapes except in the spherical limit. This is because the bubble shapes are generated under the dynamic conditions of particle adsorption during slug flow in a confining channel. In order to control the nonequilibrium bubble shape of particle-stabilized bubbles, it is necessary to understand the relevant timescales for the production of these materials.

From Chapter 5, we know that particles adsorb to the interface over a timescale comparable to the residence time of the bubble in the microchannel, τ_{res} . The residence time for a bubble translating at a velocity U through a channel of length L_c between the bubble generation orifice and the outlet is L_c/U . The primary particle adsorption timescale assumes that particles adsorb only to the end cap region of the bubble. This adsorption timescale is given by

$$\tau_{ads} = \frac{4\pi^2}{\sqrt{3}} \frac{\mu\rho_p}{kT\rho_f} \frac{r_p^4}{(r_p + \varepsilon)^2} \left(\frac{4}{3\text{Pe}} \right)^{1/3} \frac{1}{x_p} \frac{P_b}{2\pi R_h} L_b \quad (6.5)$$

which was developed by modeling the convective mass transfer of particles to the end cap of the bubble interface. The model assumes that particles of radius r_p and density ρ_p adsorb to a spherical end cap of radius R_h and form a hexagonally-packed layer around the perimeter P_b of the bubble that propagates forward to eventually cover the entire length L_b of the bubble. A mass fraction x_p of particles is initially suspended in a fluid of density ρ_f . The particles must diffuse across a mass-transfer boundary layer that scales inversely with the Peclet number Pe to the 1/3 power. The Peclet number for the bubble moving at velocity U through a channel with the outer phase fluid moving at a superficial velocity U_s is

$$\text{Pe} = \frac{|U_s - U| R_h}{D} \quad (6.6)$$

where we take the absolute value of the difference between the bubble velocity and the superficial velocity to account for the fact that a bubble can travel faster or slower than the superficial velocity depending on the device geometry. We assume that the diffusivity D of the particles is based on the Stokes-Einstein equation²⁶ $D = kT / 6\pi\mu r_p$, where k is the Boltzmann constant, T is the

temperature, and μ is the outer phase fluid viscosity. The particles are assumed to have an effective packing radius of $(r_p + \varepsilon)$ to account for deviations from a hexagonally close-packed structure at the interface.

The adsorption timescale takes into account the geometry of the channel as well as the shape of the slug bubble. When the capillary number Ca defined as

$$Ca = \frac{\mu U}{\sigma} \quad (6.7)$$

is small, $Ca \ll 1$, the effects of the viscous stress on the interface are small compared with the surface tension σ . The interface shape at low Ca can be modeled using the equilibrium shape of a bubble confined in a capillary. For experiments performed in Cases C and D, the approximate range of capillary numbers probed is $4 \times 10^{-5} < Ca < 6 \times 10^{-5}$, and the range of capillary numbers probed in Cases E through G is $1 \times 10^{-4} < Ca < 7 \times 10^{-4}$, meaning that in all experiments we assume that the interface is well described by the surface tension-dominated shape. The end cap radius R_h of the bubble is equivalent to the hydrodynamic radius of the channel. For the circular capillary R_h is equal to R , the capillary radius. For a rectangular channel of height H and width W , the hydraulic radius is given by

$$R_h = \frac{HW}{H + W}. \quad (6.8)$$

The perimeter of the bubble is also affected by the channel cross-section geometry. In the circular capillary we estimate that the bubble perimeter is approximately equal to the perimeter of the capillary, $P_b \approx 2\pi R$. In the rectangular channel, the equilibrium cross-section of a bubble is approximately

that of a rounded rectangle with radius of curvature R_c near the corners of the channel.²⁷ The perimeter of the bubble is given by

$$P_b \approx 2(H + W + (\pi - 4)R_c) \quad (6.9)$$

where the radius of curvature is determined by the channel geometry,

$$R_c = \frac{H + W - \sqrt{H^2 + (\pi - 2)HW + W^2}}{4 - \pi}. \quad (6.10)$$

The adsorption timescale given in equation (6.5) assumes that particle adsorption does not occur along the length of the bubble in the channel. Due to the finite volume of fluid around the bubble in the thin film or corner regions of the bubble in the channel, the local concentration of particles suspended in the fluid will decrease as particles adsorb to the interface. This depletion effect can significantly reduce the flux of particles to the interface in those confined regions. The effect of depletion is estimated by using the depletion number S_d , which is the ratio of the volume of particle suspension in the mass transfer boundary layer of thickness δ_b across the available bubble surface area A_D to the finite volume region V_D .²⁸

$$S_d = \frac{A_D \delta_b}{V_D} \quad (6.11)$$

When $S_d \ll 1$, the available volume of particle suspension in V_D acts like an infinite reservoir; however, as S_d approaches unity or greater, the depletion effect will be significant.

The thickness of the mass transfer boundary layer depends on the region where it is located. The mass transfer boundary layer in the thin film region depends on the thin film thickness δ calculated by Bretherton,²⁹ given by

$$\delta = 0.643(3Ca)^{2/3} \tilde{R} \quad (6.12)$$

for a bubble with a no-slip interface, where $\tilde{R} = R$ for the circular capillary and $\tilde{R} = R_c$ for the rectangular microchannel as shown by Wong *et al.*¹⁸ The mass transfer boundary layer thickness in the thin film region for circular or rectangular capillaries is approximated from

$$\delta_b \approx \frac{\delta^{2/3}}{Pe^{1/3}} L^{1/3} \quad (6.13)$$

which is the characteristic boundary layer thickness between two plates³⁰ that have a length equal to the length L of the bubble. To approximate the mass transfer boundary layer thickness in the corner regions of a rectangular channel, the thin film thickness in equation (6.13) is replaced by the characteristic length scale for fluid flow of $0.414R_c$ in the corner region. For the conditions in Cases C – G used to generate the bubbles shown in Figure 6.7, $S_d > 3$ in both the thin film regions of the circular and rectangular channels as well as the corner regions of the rectangular channels. In the end cap region of the bubble, $S_d \ll 1$; this is due to the large reservoir of fluid in front of and behind the bubble relative to the product of the mass transfer boundary layer thickness and the spherical cap surface area. This indicates that equation (6.5) is the characteristic timescale for particle adsorption in Cases C – G.

In Chapter 5, we showed that the adsorption timescale is related to the length of the bubble that is stabilized by particles a through a simple relationship:

$$\frac{a}{L_b} = \frac{t}{\tau_{ads}}. \quad (6.14)$$

This model was verified by equating the particle-stabilized bubble length with the growth of the rear lobe during the unique shape transition of the bubble in the microchannel. From Figure 6.6, the bubbles are observed to emerge from the capillary with the rear of the bubbles retaining a nonequilibrium shape of higher curvature along some length L_p . Assuming that the particles that pack along the rear of the bubble during translation in the channel do not redisperse along the bubble interface or desorb from the interface when the bubble exits the channel, the length of the particle-stabilized region outside the microchannel can be estimated from

$$\frac{L_p}{L_b} = \frac{\tau_{res}}{\tau_{ads}}. \quad (6.15)$$

This estimate assumes that a single bubble is present in the microchannel during translation through the surface-active particle mixture, implying that the bubble has a large fluid reservoir to flow through before exiting the channel. Bubbles can also be generated in finite bubble trains and continuous bubble trains. In finite bubble train production, a small number of bubbles are produced periodically at the orifice and travel along the channel as a group with an approximately uniform spacing between bubbles in the train. A large fluid reservoir is present ahead of and behind the bubble train. Continuous bubble production is common in microfluidic devices,³¹ and produces a continuous segmented gas-liquid flow through the channel. All three production methods have been used here to generate bubbles in nonequilibrium shapes.

Figure 6.8 shows how the length scale ratio of equation (6.15) varies with the timescale ratio τ_{res}/τ_{ads} for bubbles generated in Cases C – G. These results

encompass bubble sizes from 3 to 8 times the channel width and various bubble velocities, which are both taken into account in equation (6.5). Comparing the particle adsorption model with direct observation of the bubble shape in Chapter 5 (Figure 5.12c), the adsorption time used to scale the experimental results is four times larger than the value calculated in equation (6.5). When bubbles are produced in finite bubble trains, only the first bubble of each train is analyzed. At low values of the dimensionless timescale, L_p/L_b approaches zero, indicating that very few particles have adsorbed to the bubble interface. As τ_{res}/τ_{ads} increases, the length scale ratio also increases, although there is a deviation in the measured values for bubbles generated in a circular capillary and bubbles generated using rectangular microfluidic channels. Bubbles generated in microfluidic channels or the circular capillary do not match the model predicted by equation (6.15). There is a linear scaling $L_p/L_b \sim \tau_{res}/\tau_{ads}$ in the microfluidic data between $0 < \tau_{res}/\tau_{ads} < 5$, and a similar linear relationship is observed for data in the circular capillary in the range of $0 < \tau_{res}/\tau_{ads} < 10$. This is most likely due to the fact that the particle adsorption timescale in equation (6.5) is based on a close-packed monolayer of particles, however multilayers of particles at the interface are often observed on particle-stabilized bubbles and drops. Multilayer formation of the CTAB-silica mixture at the air-water interface would have a linear scaling due to the rate of particle adsorption, but the timescale ratio would be multiplied by some front factor β less than 1: $L_p/L_b = \beta (\tau_{res}/\tau_{ads})$.

This increase in the length scale ratio L_p/L_b implies that more particles have packed at the interface during translation in the channel to form a jammed network when the bubble is removed from confinement. The bubbles generated in rectangular microchannels exhibit a sharp increase in the length scale ratio at

dimensionless times below 5. Above this timescale, the bubbles plateau at a length scale of approximately 0.4. This means that it takes approximately 5 times the characteristic timescale for the shape transition characterized in Chapter 5 to occur before the bubble has enough particles adsorbed to the interface to stabilize a large relative length of the bubble outside the microchannel.

Below a dimensionless timescale of 10, the length scale ratio for bubbles produced in the circular capillary are in agreement for all three cases studied. For $\tau_{res}/\tau_{ads} > 10$, the initial bubbles generated in bubble trains have a significantly higher surface coverage than bubbles generated continuously. Bubbles generated continuously in the circular capillary reach a plateau in the length ratio of approximately 0.25 at a dimensionless timescale of 10. The bubbles generated in a circular capillary require larger dimensionless times to completely stabilize the interface; however, bubbles generated in circular capillaries do not exhibit the two-lobed shape transition described in Chapter 5.

The two-lobed shape transition, which is observed in Cases E – G, is not accounted for in the particle adsorption model. The neck region in between the two lobes is exposed to a larger volume of the particle-surfactant mixture compared with the volume in the thin film and corner regions. This will increase the available mass of particles to adsorb to the interface in this region, which reduces the depletion effect and allows for a greater mass flux of particles to the interface.

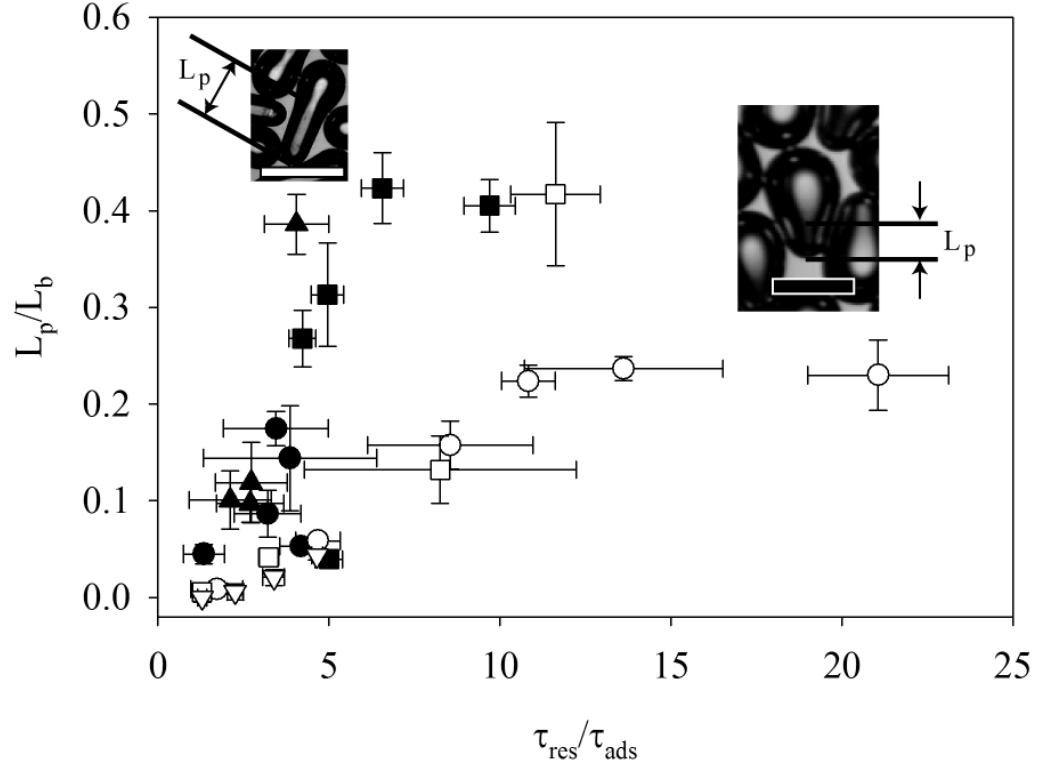


Figure 6.8. Ratio of the particle-stabilized length L_p relative to the length of the bubble inside the channel L_b versus the residence time τ_{res} relative to the adsorption timescale τ_{ads} . The different symbols represent the different cases from Table 6.1: (∇) Case C – bubble trains, ($\square$) Case D – bubble trains, ($\circ$) Case D – continuous slug flow, ($\bullet$) Case E – single bubbles, ($\blacktriangle$) Case F – single bubbles, ($\blacksquare$) Case G – single bubbles. The inset images show the distance L_p measured on bubbles with different reduced volumes. The scale bar for the left inset image is 200 μm . The scale bar for the right inset image is 1 mm. Error bars represent a standard deviation in measured parameters for 5 bubbles.

The distinct difference in the data generated in the circular capillary at large dimensionless timescales indicates that the bubble generation method affects the total particle loading at the interface. Figure 6.9 shows the length scale ratio and the reduced volume of trains of 6 and 8 bubbles for Case D at $\tau_{res}/\tau_{ads} = 11.6 \pm 1.4$. The first bubble in the train obtains the lowest reduced volume and the highest length scale ratio compared to the bubbles following.

There is a sequential increase in the reduced volume and decrease in L_p/L_b for the second and third bubbles in the train. The length scale ratio reaches a minimum value of approximately 0.10 from the fourth bubble until the second-to-last bubble, and the resulting bubble shape is close to spherical. Although the bubbles in the middle of the train have lower particle coverage, the final bubble obtains a higher particle coverage than the middle of the train.

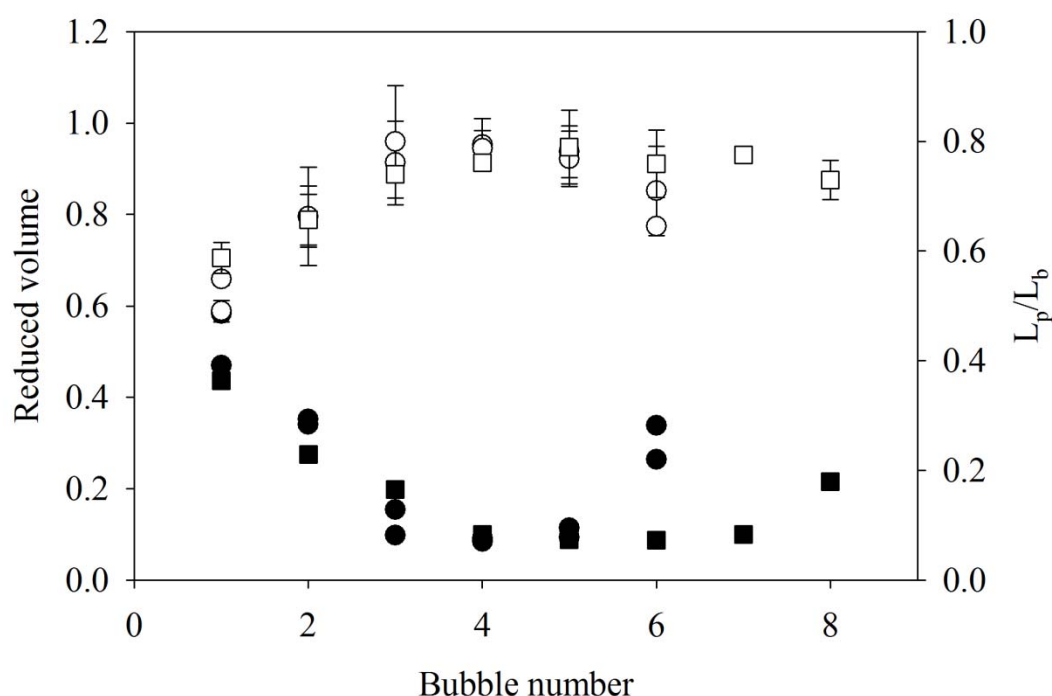


Figure 6.9. Reduced volume of the bubble shape and length scale ratio versus placement in a bubble train of ($\circ$, $\bullet$) 6 and ($\square$, $\blacksquare$) 8 bubbles. The open symbols indicate the reduced volume, and the filled symbols indicate L_p/L_b . Two bubble trains of 6 bubbles are plotted to indicate reproducibility. Error bars in the reduced volume are a standard deviation based on calculating the volume and surface area of both halves of the 2D projection of the bubble shape.

The fact that bubbles in the middle of the train exhibit a lower coverage than bubbles at the front or rear indicates that bubbles with compartmentalized fluid volumes in between bubbles will achieve lower surface coverage. At low

capillary numbers, the fluid slug separating translating bubbles exhibits a circulation pattern with closed streamlines.³² When closed streamlines are present, the streamlines closest to the bubble interface will be depleted of particles due to adsorption to the interface. The only way for the particle concentration to be replenished near the interface is by particle diffusion across streamlines, which slows down the convection-dominated adsorption process. This indicates that continuous bubble trains should achieve a plateau in the length ratio when the streamlines in the fluid slug are depleted of particles. After this point, the timescale for adsorption will increase dramatically.

Long bubbles that are partially stabilized by particles along some length in the channel can exhibit break-up at the outlet. In Cases E – G, bubbles with a bubble length greater than 10 times the channel width form a neck at the orifice as the front part of the bubble emerges from the channel. The first bubble generated in the sequence reaches a spherical shape while the bubble formed from the rear of the slug remains in a nonequilibrium shape outside the microchannel. This leads to a bidisperse distribution of shapes, as shown in Figure 6.10 for bubbles generated in Case F.

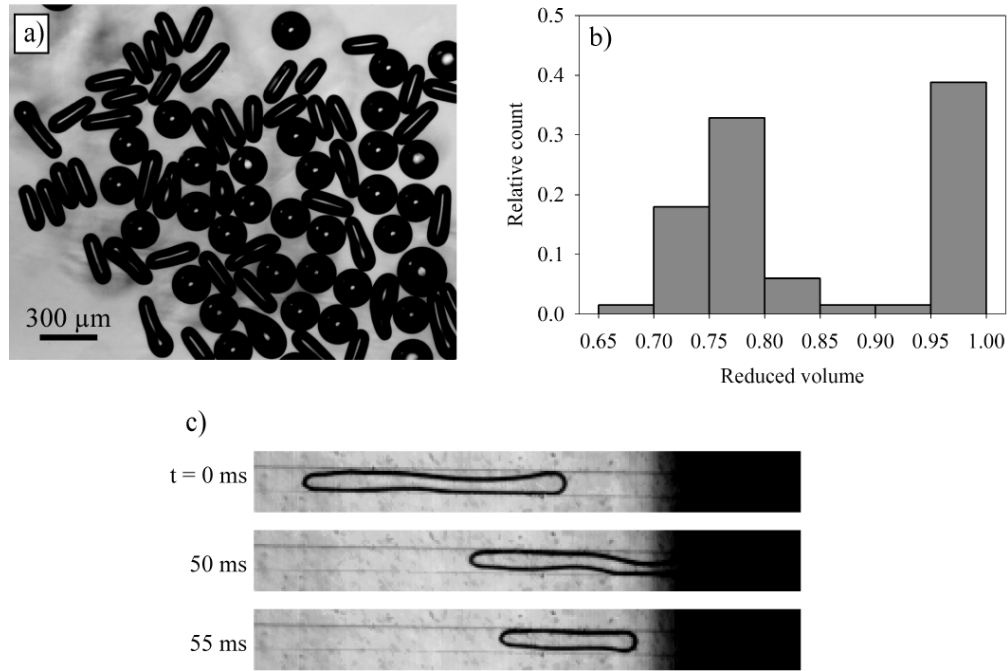


Figure 6.10. (a) Image of bidisperse bubble shapes due to break-up of bubbles at the outlet and (b) histogram of the reduced volume for the bubbles shown in (a). (c) Images of the bubble break-up at the outlet of the microchannel, showing a nonuniform bubble shape prior to break-up. The outlet at the right of each image is dark due to light scattering from the edge of the microfluidic device. The channel width for the images in (c) is 96 μm.

Before break-up, the flow conditions for the images in Figure 6.10 generated bubbles at a dimensionless timescale τ_{res}/τ_{ads} of approximately 1.5. By measuring the bubble length prior to break-up at the outlet and comparing that with the lengths of the elongated bubbles formed outside the microfluidic device, we calculate a length scale ratio $L_p/L_b = 0.41 \pm 0.06$ from an average of ten bubbles. This is much higher than expected based on the data in Figure 6.8. The large length scale ratio indicates that there is a larger flux of particles to the interface than expected for adsorption to a spherical cap. The images in Figure 6.10c show that the bubble exhibits a nonuniform shape inside the microchannel

prior to break-up at the outlet. This shape allows for a larger volume of particles to flow along the length of the bubble, meaning that the particle flux should be larger than expected in the adsorption model presented here. As shown in Chapter 5, particle adsorption along the length of the bubble leads to a much faster rate of particle loading to the interface due to the large surface area available along the bubble length.

6.4 DISCUSSION

The latex particle adsorption experiments show that particle adsorption to fluid interfaces occurs when a dispersed slug phase flows through a surface-active particle suspension. A direct observation of the particle packing at the octanol droplet interface shows that the rear of the droplet has a high surface coverage in both circular and square capillaries. This agrees with the model for particle adsorption presented in Chapter 5. Although a packed end-cap region is expected for droplets traveling faster than the velocity of the outer phase fluid, a packed end cap region is also observed for the droplet in the square capillary, which is moving slower than the average outer fluid velocity.

Measurements of the velocity profile inside a viscous droplet in a square channel indicate forward flow in the corners of the channel around the droplet, but a reverse flow toward the droplet rear around the thin film regions where the droplet is confined by the channel walls.³³ This observation indicates that particles would be forced to the end cap region in square or rectangular capillaries due to flow in the thin film regions, which covers a higher fraction of the droplet perimeter compared to the forward flow in the corner regions.

No two-lobed shape transition is observed for octanol droplets in square channels with particles packed at the rear as is observed during the generation of CTAB-silica stabilized bubbles in rectangular channels. We argued in the previous Chapter that a two-lobed bubble shape occurs in the microchannel due to excess drag at the bubble rear from the packed particle region. The inviscid gas bubbles generated in Cases E – G have a negligible shear stress at the front of the bubble. Octanol has a viscosity that is 7.5 times larger than that of water, which means that the clean droplet interface would experience significant drag due to shear stress at the interface. The difference in shear stress between the viscous front of the droplet and the particle-stabilized rear of the droplet prevents the formation of the two-lobed structure in Case B.

Measurements of the particle covered area outside of the circular capillary result in lower values than measurements of the particle-covered areas inside the capillary. From the inset images in Figures 6.4 and 6.5, the rear of the droplets in the capillary have a higher local packing fraction compared to the particles trapped on the octanol lens outside the capillary. Also, differences in the light intensity of the images due to index of refraction differences between octanol and water mean that any particles in the darker regions are neglected. Although these measurements are not in agreement for the total surface coverage of particles, they both individually show an increase in the particle surface coverage as the residence time increases.

The bubbles generated in the CTAB-silica suspension exhibit nonspherical bubble shapes due to convection-dominated particle adsorption to the bubble

interface. Based on the observed bubble shapes outside the microchannel and the particle adsorption model, the rear of the bubble has a higher concentration of particles compared to the front. This indicates that the surface mechanical properties of the interface will also vary between the front and rear of the bubble. This symmetry-breaking can be useful in using the particles as catalytic motors at the interface to drive capsule motion to a targeted area.³⁴ Nonspherical shapes have a more efficient packing than spheres,³⁵ allowing for more efficient capsule storage.

The results from plotting the length scale ratio L_p/L_b versus the timescale ratio τ_{res}/τ_{ads} shows that the model developed in Chapter 5 for particle adsorption to the translating bubble interface can be used to control the generation of nonequilibrium bubbles. Bubbles generated in the microfluidic device reach a plateau around $L_p/L_b = 0.4$; however, the model predicts that eventually the bubbles should be completely stabilized by particles. In our measurement, we assume that the packed length of bubbles outside the device is equivalent to the packed length along the bubble inside the microchannel. The bubbles generated in this method have all partially relaxed to a spherical shape while exiting the capillary tube, which necessarily means that the surface area of the bubble has decreased. This decrease in surface area would occur until the particle layers resisted further surface area loss, in which case the measured length outside the channel would be smaller than the particle stabilized length inside the channel. The interfacial mechanical properties of nanoparticle layers at a highly curved interface are not well understood; however, our model still shows that increasing

τ_{res}/τ_{ads} leads to longer packed bubble lengths outside channel, which indicates a higher surface coverage overall with the increasing timescale ratio.

This model is not used to calculate the adsorption timescale for latex particles adsorbing to the octanol droplet interface due to the relatively large size of the particles. Assuming an outer phase velocity of 1 mm/s and octanol-water interfacial tension of 8.5 mN/m,³⁶ the capillary number for an octanol droplet in water is 1.1×10^{-4} . Using the capillary number and the circular capillary radius in equation (6.12) yields a thin film thickness of 0.93 μm , which is smaller than the latex particles used in these experiments. Large particle effects for adsorption to bubble interfaces should also be included, which is common in flotation literature.³⁷

The nonequilibrium shape of the bubble in the microchannel shown in Figure 6.10c is most likely due to uneven drag along the bubble as well as roughness within the microchannel. Once the bubble is stabilized with particles in the microchannel, small deviations away from an equilibrium bubble shape are observed, as shown in Figure 5.3. Since the bubble has already receded from the side walls, bubble break-up due to a necking instability is more favorable at the channel outlet.

The measurements performed on bubble trains show that particle adsorption is hindered when bubbles are spaced closely together. Based on the higher particle adsorption on bubbles in the front and rear of the train, we conclude that this effect is due to slow transport across closed streamlines in the fluid slugs between bubbles. This observation suggests a possible explanation for

the difficulty in generating particle-stabilized emulsions and foams in microfluidic devices³⁸ as opposed to high-shear emulsification methods. The common continuous bubble or droplet production method significantly decreases the particle adsorption rate to the interface.

6.5 SUMMARY

The experiments performed in this chapter show that nonequilibrium bubble shapes can be controlled by varying the residence time relative to the particle adsorption timescale for confined bubbles moving through straight channels. Two different geometries were used to generate bubbles and drops with adsorbed particles at the interface. A direct observation of particles adsorbing to the octanol droplet interface shows that surface-active particles will adsorb to confined slug shaped droplets translating in a circular or square channel. For both cross-section geometries, the particles pack at the rear of the droplet even when the droplet velocity is slower than the outer phase fluid velocity. The amount of particles adsorbed to the interface is shown to increase as the residence time increases.

Using the model developed in Chapter 5, we used the residence time to tune the particle coverage for bubbles generated in a nanoparticle-surfactant mixture of colloidal silica and CTAB. The ratio of the bubble residence time in the microchannel to the timescale for particle adsorption to the end cap of the bubble is a critical dimensionless timescale that determines the length of the interface that is jammed with particles to form a nonequilibrium shape. Finite bubble trains and continuous bubble production slow the rate of particle coverage

due to closed streamlines in the fluid slugs between bubbles. The steady production of monodisperse bubbles with a uniform nonequilibrium shape is possible when single bubbles travel in the microchannel.

1. Binks, B. P., Particles as surfactants—similarities and differences. *Current Opinion in Colloid & Interface Science* **2002**, 7, (1), 21-41.
2. Benjamins, J.; Vingerhoeds, M. H.; Zoet, F. D.; De Hoog, E. H.; Van Aken, G. A., Partial coalescence as a tool to control sensory perception of emulsions. *Food Hydrocolloids* **2009**, 23, (1), 102-115.
3. Chow, A. H.; Tong, H. H.; Chattopadhyay, P.; Shekunov, B. Y., Particle engineering for pulmonary drug delivery. *Pharmaceutical research* **2007**, 24, (3), 411-437.
4. Kim, S.-H.; Heo, C.-J.; Lee, S. Y.; Yi, G.-R.; Yang, S.-M., Polymeric particles with structural complexity from stable immobilized emulsions. *Chemistry of Materials* **2007**, 19, (19), 4751-4760.
5. Schmitt, M.; Limage, S.; Grigoriev, D. O.; Krägel, J.; Dutschk, V.; Vincent-bonnieu, S.; Miller, R.; Antoni, M., Transition from spherical to irregular dispersed phase in water/oil emulsions. *Langmuir* **2014**.
6. Datta, S. S.; Shum, H. C.; Weitz, D. A., Controlled buckling and crumpling of nanoparticle-coated droplets. *Langmuir* **2010**, 26, (24), 18612-18616.
7. Bon, S. A.; Mookhoek, S. D.; Colver, P. J.; Fischer, H. R.; van der Zwaag, S., Route to stable non-spherical emulsion droplets. *European Polymer Journal* **2007**, 43, (11), 4839-4842.
8. Studart, A. R.; Shum, H. C.; Weitz, D. A., Arrested Coalescence of Particle-coated Droplets into Nonspherical Supracolloidal Structures†. *The Journal of Physical Chemistry B* **2009**, 113, (12), 3914-3919.
9. Subramaniam, A. B.; Abkarian, M.; Stone, H. A., Controlled assembly of jammed colloidal shells on fluid droplets. *Nature materials* **2005**, 4, (7), 553-556.
10. Lee, D.; Weitz, D. A., Nonspherical colloidosomes with multiple compartments from double emulsions. *Small* **2009**, 5, (17), 1932-1935.
11. Shum, H. C.; Abate, A. R.; Lee, D.; Studart, A. R.; Wang, B.; Chen, C. H.; Thiele, J.; Shah, R. K.; Krummel, A.; Weitz, D. A., Droplet Microfluidics for Fabrication of Non-Spherical Particles. *Macromolecular rapid communications* **2010**, 31, (2), 108-118.
12. Cui, M.; Emrick, T.; Russell, T. P., Stabilizing Liquid Drops in Nonequilibrium Shapes by the Interfacial Jamming of Nanoparticles. *Science* **2013**, 342, (6157), 460-463.

13. Cheng, H.-L.; Velankar, S. S., Controlled jamming of particle-laden interfaces using a spinning drop tensiometer. *Langmuir* **2009**, 25, (8), 4412-4420.
14. Velev, O.; Furusawa, K.; Nagayama, K., Assembly of latex particles by using emulsion droplets as templates. 1. Microstructured hollow spheres. *Langmuir* **1996**, 12, (10), 2374-2384.
15. Xia, Y.; Whitesides, G. M., Soft lithography. *Annual review of materials science* **1998**, 28, (1), 153-184.
16. Ho, B.; Leal, L., The creeping motion of liquid drops through a circular tube of comparable diameter. *Journal of Fluid Mechanics* **1975**, 71, (02), 361-383.
17. Martinez, M.; Udell, K., Axisymmetric creeping motion of drops through circular tubes. *Journal of Fluid Mechanics* **1990**, 210, 565-591.
18. Wong, H.; Radke, C.; Morris, S., The motion of long bubbles in polygonal capillaries. Part 1. Thin films. *Journal of Fluid Mechanics* **1995**, 292, 71-94.
19. Jakiela, S.; Makulska, S.; Korezyk, P. M.; Garstecki, P., Speed of flow of individual droplets in microfluidic channels as a function of the capillary number, volume of droplets and contrast of viscosities. *Lab on a Chip* **2011**, 11, (21), 3603-3608.
20. Kotula, A. P.; Anna, S. L., Probing timescales for colloidal particle adsorption using slug bubbles in rectangular microchannels. *Soft Matter* **2012**, 8, (41), 10759-10772.
21. Xu, H.; Melle, S.; Golemanov, K.; Fuller, G., Shape and buckling transitions in solid-stabilized drops. *Langmuir* **2005**, 21, (22), 10016-10020.
22. Asekomhe, S. O.; Chiang, R.; Masliyah, J. H.; Elliott, J. A., Some observations on the contraction behavior of a water-in-oil drop with attached solids. *Industrial & engineering chemistry research* **2005**, 44, (5), 1241-1249.
23. Subramaniam, A. B.; Abkarian, M.; Mahadevan, L.; Stone, H. A., Colloid science: Non-spherical bubbles. *Nature* **2005**, 438, (7070), 930-930.
24. Kern, W. F.; Bland, J. R., *Solid Mensuration: With Proofs*. J. Wiley & Sons, Incorporated: 1938.

25. Seifert, U.; Berndl, K.; Lipowsky, R., Shape transformations of vesicles: Phase diagram for spontaneous-curvature and bilayer-coupling models. *Physical Review A* **1991**, 44, (2), 1182.
26. Einstein, A., Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen. *Annalen der physik* **1905**, 322, (8), 549-560.
27. Mason, G.; Morrow, N. R., Meniscus curvatures in capillaries of uniform cross-section. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* **1984**, 80, (9), 2375-2393.
28. Alvarez, N. J.; Walker, L. M.; Anna, S. L., A criterion to assess the impact of confined volumes on surfactant transport to liquid–fluid interfaces. *Soft Matter* **2012**, 8, (34), 8917-8925.
29. Bretherton, F., The motion of long bubbles in tubes. *Journal of Fluid Mechanics* **1961**, 10, (02), 166-188.
30. Probstein, R. F., Physicochemical hydrodynamics: an introduction. **2005**.
31. Squires, T. M.; Quake, S. R., Microfluidics: Fluid physics at the nanoliter scale. *Reviews of Modern Physics* **2005**, 77, (3), 977.
32. Thulasidas, T.; Abraham, M.; Cerro, R., Flow patterns in liquid slugs during bubble-train flow inside capillaries. *Chemical engineering science* **1997**, 52, (17), 2947-2962.
33. Jakiela, S.; Korczyk, P. M.; Makulska, S.; Cybulski, O.; Garstecki, P., Discontinuous Transition in a Laminar Fluid Flow: A Change of Flow Topology inside a Droplet Moving in a Micron-Size Channel. *Physical Review Letters* **2012**, 108, (13), 134501.
34. Baraban, L.; Makarov, D.; Streubel, R.; Mönch, I.; Grimm, D.; Sanchez, S.; Schmidt, O. G., Catalytic Janus motors on microfluidic chip: Deterministic motion for targeted cargo delivery. *ACS nano* **2012**, 6, (4), 3383-3389.
35. Donev, A.; Cisse, I.; Sachs, D.; Variano, E. A.; Stillinger, F. H.; Connelly, R.; Torquato, S.; Chaikin, P. M., Improving the density of jammed disordered packings using ellipsoids. *Science* **2004**, 303, (5660), 990-993.
36. Demond, A. H.; Lindner, A. S., Estimation of interfacial tension between organic liquids and water. *Environmental science & technology* **1993**, 27, (12), 2318-2331.

37. Nguyen, A. V.; George, P.; Jameson, G. J., Demonstration of a minimum in the recovery of nanoparticles by flotation: Theory and experiment. *Chemical engineering science* **2006**, 61, (8), 2494-2509.
38. Stocco, A.; Rio, E.; Binks, B. P.; Langevin, D., Aqueous foams stabilized solely by particles. *Soft Matter* **2011**, 7, (4), 1260-1267.

CHAPTER 7**CONCLUSIONS**

A better understanding of the properties of complex fluid interfaces is crucial to describing the material properties of emulsions and foams. This work provides a substantial contribution toward this understanding through two key components: i) a proper methodology for measuring the dilatational properties of complex interfaces, and, ii) a controllable method for generating foams with controlled particle loading at the interface.

Chapter 3 describes a small-amplitude analysis of dilatational rheology in capillary pressure tensiometers. We developed the framework necessary to analyze the response of an arbitrary interface. The framework developed provides both the dilatational modulus and a stability criterion for the start-up of pressure oscillations. Capillary pressure tensiometers are neither stress- nor strain-controlled apparatuses, and the modulus measured in these systems can contain effects from both intrinsic material properties and surface tension. In order to separate these contributions, we developed a methodology for probing the dilatational properties of the interface as a function of frequency and spherical cap radius. It is important that these devices be operated at small pressure amplitude so that higher harmonic oscillations do not distort the desired signal, and we discussed the conditions upon which higher harmonics in the surface area or surface stress will be evident. Lastly, we analyzed the capability of common capillary pressure tensiometers to measure interfacial stresses without also measuring bulk effects due to gravity or fluid flow. This work shows the

microtensiometer developed by Alvarez *et al.* (2010) performs measurements of dilatational properties with negligible contributions from the bulk fluids.

The framework developed in Chapter 3 was applied to experimental measurements of insoluble layers at an air-water interface in the microtensiometer. Using a novel fluid exchange method, we generated interfaces composed of surface-active materials that are not soluble in the aqueous phase. By controlling the hydrostatic pressure, we measured both the surface pressure as a function of surface area and the dilatational modulus as a function of frequency for palmitic acid, DPPC, and DMPC. We observed excellent agreement between the surface pressure-area relationships that we measured and measurements performed on Langmuir troughs reported in the literature by using a simple shift factor.

It is somewhat surprising that the small, highly curved interface of the microtensiometer agrees well with the large, planar interface of the Langmuir trough, since the total size of the interface in the microtensiometer is of the order of domain sizes observed for these types of materials at planar interfaces. Measurements of the dilatational modulus have also been compared successfully with the literature. A comparison of the dilatational modulus with the Gibbs modulus for these materials allowed us to observe deformation rate dependence of the modulus of DPPC. We applied the same measurement techniques to the insoluble component present in the nonionic surfactant Tween 80 and showed that the interface is stabilized by something more than single fatty acids at the interface.

The results presented in Chapters 3 and 4 develop the capabilities of the microtensiometer in both analyzing complex interfaces and in generating novel interfaces. Because the microtensiometer measures purely dilatational stresses, analyzing the relationship between surface stress and dilatation is straightforward. Insoluble monolayers were previously not accessible to capillary pressure tensiometers due to the difficulty in depositing layers at the interface. The methods developed in Chapter 4 for generating insoluble interfaces at air-water interfaces significantly expand the capabilities of the microtensiometer as a tool for measuring surface mechanical properties.

As this work was also motivated by the controlled formation of complex interfaces, we generated particle-stabilized bubbles and drops in microchannels to better control particle surface coverage. In Chapter 5 we showed that confined bubbles translating through a nanoparticle suspension in a microchannel exhibit unique shape transitions only when the particle suspension is surface active. The effects of colloidal silica modified with CTAB on bubble shape and velocity show that particle adsorption and packing at the bubble rear occurs over the timescale of flow in a microchannel. The adsorption of a large enough surface concentration of particles solidified the interface, dramatically changing the surface properties and causing the formation of a two-lobed bubble shape that indicated the amount of particle coverage at the interface. We developed a model to predict the rate of particle loading to the interface under convection-dominated mass transfer and showed that the particle flux to the end cap region of the bubble interface is the driving mechanism for particle adsorption. The depletion of particles from

suspension in the thin film and corner regions explains why the flux is predominantly to the bubble end cap.

The observations of particle loading at the bubble interface in the microchannel and the resulting stability of the particle-stabilized interfaces motivated us to use the particle adsorption timescale as a metric for creating monodisperse bubbles with a uniform nonspherical shape. In Chapter 6 we showed that a wide range of nonequilibrium bubble shapes could be generated, and that the key parameter in generating these bubbles is the particle adsorption timescale developed in Chapter 5.

Based on a direct observation of latex particles adsorbing on an octanol droplet, we showed that the rear of the dispersed droplet phase in the channel becomes packed with particles first due to particle adsorption, independent of whether the droplet is traveling faster or slower than the surrounding fluid. When the colloidal silica-CTAB mixture was used to stabilize bubbles, the bubbles emerged with the rear jammed in a nonequilibrium shape. We also showed that the particle-stabilized region of these bubbles that cause the nonequilibrium shape is directly proportional to the residence time of the bubble in the channel normalized by the particle adsorption timescale. Bubbles in rectangular channels become particle-stabilized faster than bubbles flowing in circular channels due to the unique bubble shape transitions that occur in the microchannel, which were first described in Chapter 5. We also showed that trains of bubbles flowing through the channel exhibit significantly less coverage in the middle of the bubble train due to closed streamline flow patterns between the bubbles. Continuous

bubble generation methods with multiple bubbles in the channel are therefore unsuitable for generating particle-stabilized bubbles that are monodisperse in shape and size using the model for particle adsorption developed in this thesis.

Overall, this work provides significant contributions to the measurement of single interfaces and the controlled generation of multiple interfaces. This thesis provides multiple tools, both analytical and experimental, for probing the dilatational properties of complex fluid interfaces and generating bubbles and drops with a controlled interfacial composition. These techniques are not limited to the materials used in this thesis but can be applied to a variety of different systems. On a broader scale, this thesis provides contributions to multiphase fluid rheology and provides the necessary tools to generate emulsions and foams with controlled surface coverage and known interfacial dilatational properties based on measurements of single interfaces of the same surface composition. This thesis also broadens the capabilities of microfluidics to generate emulsions and foams of monodisperse size and uniform nonspherical shape for controlled studies on the effects of droplet shape, size, and surface coverage on the stability and shear rheology of emulsions. The tools developed in this thesis will be crucial in better understanding the role of interfacial mechanics in complex fluids.