

Chromocapillary Experiments with Photosensitive Surfactants and Superhydrophobic Surfaces

A dissertation submitted by

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in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in

Mechanical Engineering

Tufts University

February 2026

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Abstract

Inverse Method for Measuring the Adsorption and Desorption Coefficients of Multi-Isotherm Surfactants

The adsorption and desorption coefficients of a surfactant are key thermophysical properties for modeling the transient behavior of the interface between a vapor phase and a surfactant laden liquid phase. The two are commonly reported as a single value: a ratio between the two known as the equilibrium constant. Our work fills a needed gap in the literature as there are currently no reported methods to measure the two coefficients independently.

Lin et al. (1990) imply a potentially viable method based on their work measuring the binary diffusion coefficient, another surface transport related property, but their study was limited to single-species solutions. In a single-species solution, the surface tension of fresh menisci initially starts near that of the pure solvent, then relaxes in a single step process as surfactant experiences net adsorption to the interface. However, in a multi-species solution, this relaxation can have multiple steps as the species may absorb and desorb at different rates or even drive one another off the interface.

Our work uses a photosensitive azobenzene-type surfactant, i.e. a photosurfactant, which can act as both a single and multi-species system depending on the light conditions it is exposed to. Unless isolated from light for a prolonged amount of time to allow the solution to reach thermodynamic equilibrium, a solution of photosurfactant will be composed of a mixture of both energized *-cis* and relaxed *-trans* photoisomers. The two isomers function as two distinct species in the solution, each with different equilibrium constants and maximum packing densities. By using colored LEDs, we can take advantage of the differing absorption spectra of the two isomers to control the relative molar ratio between them. Alongside the Department of Chemistry at Tufts

University, we have developed an experimental procedure to characterize the molar ratio between the two isomer species under prescribed controlled lights conditions.

Given a set of thermophysical properties, our model simultaneously resolves the species equations for the two isomers on both the meniscus (interfacial concentration in moles per unit area) and in the bulk (bulk concentration in moles per unit volume) as a function of time to estimate the rate of relaxation of surface tension of a fresh liquid-vapor interface. By fitting experimental relaxation data taken under strictly controlled light conditions to this model, we can use an inverse method to extract the unknown input properties, the equilibrium constants of both species, and resolve them into separate adsorption and desorption coefficients.

We measure the transient surface tension of pendant air bubbles in a photosensitive surfactant laden solution under strictly controlled light conditions using a technique called axisymmetric drop shape analysis (ASDA). First, we take high quality, high contrast images of the pendant bubble under the specified light conditions and then measure the location of the liquid-vapor interface to a sub-pixel resolution. Then, we fit those points to an analytical drop shape model consisting of a system of first-order, non-linear, ordinary differential equations through an iterative, multi-parameter optimization algorithm. One of the parameters being optimized the desired surface tension measurement. We verified the accuracy of our surface tension measurements by comparing static measurements of distilled, deionized water and isopropyl alcohol, and transient measurements of surfactant laden solutions to literature values.

Internal Flow Microfluidic Channel with Reentrant Structures for Low-Surface Tension Liquids

The boundary condition between a liquid and a vapor phase is effectively shear-free since the shear forces exerted by the vapor on the liquid are negligible compared to those of the liquid on the vapor. This means, unlike the no-slip boundary condition seen between a liquid and a solid, the liquid and vapor can have a non-zero interfacial velocity. If the inside of a pipe could be given a partially shear-free perimeter instead of fully no-slip boundary condition, the speed of the internal flow would be faster even with the same inlet pressure. However, practically, suspending useful menisci in this state for an extended period is nontrivial.

The ratio of the liquid-vapor contact at the pipe wall needs to be kept as low as possible to maximize the lubrication affect, but the longer the vapor menisci are the more unstable and prone to wetting they become. If an outside force agitates the textured surface in a way that causes the menisci to collapse and wet into the vapor plastron cavities, the hydrodynamic slip is lost until the cavities are dried out. This assumes that it is possible to create suspended menisci to begin with. Low surface tension fluids, such as alcohol, can only form small menisci due to their low liquid-vapor contact angle.

Experiments to measure the apparent slip of liquid over mixed-boundary condition interfaces are most often done with liquids that have a higher surface tension than the azobenzene-laden solution, such as water, since their Cassie state is more easily formed and maintained due to larger advancing contact angles. A more robust Cassie state means the liquid can form larger menisci before wetting, reducing the overall solid-vapor fraction of a channel and increasing its apparent slip.

Slip experiments with low-surface tension liquids are not possible because their advancing contact angles are less than ninety degrees, meaning they will not be able to form suspended menisci and will instead wet fully into the hydrophobic structure, the so-called Wenzel state. However, you can increase the apparent contact angle of the liquid by adding reentrant features to the solid structures the menisci are meant to suspend between. Accordingly, we are developing a first of its kind, internal flow microfluidic device with reentrant structures for the purpose of suspending low-surface tension liquids over textured hydrophobic surfaces in the non-wetting Cassie state.

Our photolithography microfabrication process uses SU-8 negative photoresist as the main structural body of the proposed channel. Typically, negative photoresists are more commonly used for mold making in microfluidics. This process is designed to explore the use of additive microfabrication as a means of creating reentrant structures (as opposed to ones created through subtractive etching processes or surface treatment) at a micro as opposed to more common nano scale. The hope is that our new design will not only be able to suspend low-surface tension fluids in the Cassie state for extended periods of time but also be a more cost-effective and accessible option microfabrication option for prototyping by using more commonly available methods that rely on less advanced equipment.

Light-Driven Flow in a Textured Microfluidic Device Using Chromocapillary Marangoni Stress

Previous work by Peaudecerf et al. (2017) shows that even trace amounts of surfactants can create concentration gradients sufficient to immobilize menisci by inducing Marangoni stresses adverse to the flow, eliminating the lubrication effect of the mixed boundary condition. As the surfactants adsorbed to menisci are pushed downstream, they collect at solid triple-contact points. This creates a low-to-high surfactant concentration in the direction of the flow and accordingly a high-to-low surface tension gradient. In some cases, these Marangoni stresses can even reverse the direction of flow. Inspired by this phenomenon, Dr. Michael Mayer, one of our collaborators from Imperial College London, has developed a model for a potential method to enhance hydrodynamic slip over a mixed solid-vapor boundary by actively controlling the surface tension gradient along the liquid-vapor menisci in a transversely ridged internal flow channel. This chromocapillary effect is small but constitutes unexplored physics of flow.

Photosensitive azobenzene-type surfactants more favorably undergo *cis-trans* or *trans-cis* isomerization depending on the wavelength of light they are exposed to, both in the bulk and on a liquid-vapor interface. The two species have different maximum packing densities on the meniscus so they each induce a different relaxation in surface tension. Visible blue light encourages isomerization to the more densely packing *-trans* state while ultraviolet light favors the less densely packing *-cis* isomer. By targeting different sections of the menisci with specified wavelengths of light, optically tunable surfactants could be used to induce favorable rather than adverse surface tension gradients.

Acknowledgements

This work was supported in part by NSF grant number 2140033.

I am grateful to all my friends, colleagues, and family for their support through my time at Tufts University, but would like to extend special thanks to...

...Rob White, who (despite no initial official connection to this project) made time to spend a full week with me in the clean room to help develop my lithography process. The guidance and training I received from him were invaluable to my research, and getting to assist with his MEMS course was one of the most enjoyable teaching experiences I had at Tufts.

...the members of Guasto Lab at Tufts University: Jeffrey Guasto for the generous use of his lab's microscopy suite, and Richard Henshaw and Louison Thorens for their help imaging my devices and paying their thirds of the rent on time. Jeff was always a welcome source of advice and guidance both in and out of the classroom.

...James Vlahakis for training me on every piece of equipment I used in the Tufts Micro and Nano Fabrication Facility during my time at Tufts and for being a source of both scientific and professional advice.

...Georgios Karamanis for pushing me to be a better engineer by bluntly pointing out every single flaw in my experiments and telling me that I needed to be a freight train.

...Erica Kemmerling for trying to murder with questions while sitting on the panel for the oral component of my qualifying exams and then inviting me to assist with her courses. The standards you held me to motivated me to be a better academic. While the dedicated and thoughtful way you ran those courses, despite their difficulty, motivated me to be a better educator.

...The Tufts University Department of Mechanical Engineering's Bray Lab. The two years I worked there opened my eyes to how rewarding teaching engineering can be. I thank all the staff and students I worked with there but would like to give special attention to Nicole Batrouny for the compassion and dedication she brought to her teaching. The genuine, wholehearted care you had for our students inspired me to be a better teacher and source of support for them by living up to your example.

...Haotian Jia for being trusted colleague and collaborator who was always ready to go to Whole Foods. I will miss working alongside you both figuratively and literally. I hope the next person I share a desk with is at least half the friend you are.

...the coaches and athletes of the Men's Competitive Team at Community Rowing, Inc. With you I found friendship and community that kept me in reasonably good shape and mostly functioning sanity. You are a huge reason that I hope to stay in the Boston area after graduation.

...Aaron Arnold for picking up my slack as captain this past year, always expecting the very best from me, and being a dear and caring friend behind the threats of waterboarding.

...Nick Jordan, Hannah Lyons-Galante, and their daughters Eleanor and Adeline for opening their home to me while I finished writing my thesis and making me eat a vegetable for once. I hope I can one day repay the generosity you showed me.

...the assembled heroes and scoundrels of Hargrave House, the Scrum, the Players Agency, Thruster Buster, the Heartbreakers, the Murder Mavens, the investigators of Bright Falls, the Nebulous Knights, Xtra-Thiquenessé, and the No-Names. Thank you for the unforgettable (for better or worse) stories we told together.

...my mother Elisabeth Birosak and my grandmother Mary Louise Birosak for their unwavering (if progressively more worried) support of my decision to go to graduate school. Thank you for making me realize that I haven't just been in school these last seven years but have been building a life here in Boston.

...and, finally, my late grandfather, Michael Joseph Birosak (June 15, 1943 – August 29, 2011), to whom this thesis is dedicated. I dearly wish you could have been here to celebrate this with me. I apologize in advance for speaking too quickly at my defense.

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Nomenclature

Abbreviations

Abbreviation	Full Term
ADSA	Axisymmetric Drop Shape Analysis
ALFI-S	Axisymmetric Liquid-Fluid Interface Smoothing
PDMS	Polydimethylsiloxane

Dimensionless Numbers

Symbol	Description	Definition
β	Bond number	$\frac{\Delta\rho g R_0^2}{\gamma}$
S	Drop shape diameter ratio	d_s/d_e
H	Drop shape factor	$H(S) = -\beta \left(\frac{d_e}{R_0}\right)^2$

Greek Symbols

Symbol	Description	Units
Δ	Change in	-
α	Angle of rotation between reference frames	radians
ε	Molar absorptivity	$\text{L mol}^{-1} \text{cm}^{-1}$
γ	Surface tension	mN m^{-1}
θ	Contact angle	radians
λ	Wavelength	nm
ρ	Density	kg m^{-3}
ϕ	Agle of rotation	radians

Roman Symbols

Italic

Symbol	Description	Units
<i>A</i>	Surface area	m ²
<i>Abs</i>	Absorbance	-
<i>E</i>	Objective function to minimize	m ²
<i>M</i>	Number of sets of <i>N</i> points	-
<i>N</i>	Number of points in each of the <i>M</i> sets of points	-
<i>P</i>	Pressure	Pa
<i>R</i>	Radius of curvature	m or pixels
<i>S</i>	Scaling factor	m pixels ⁻¹
<i>V</i>	Volume	m ³
<i>X</i>	Horizontal coordinate location in experimental reference frame	pixels
<i>X_{tr}</i>, <i>X_{ci}</i>	Molar ratio of <i>-trans</i> or <i>-cis</i> photoisomer species	-
<i>Z</i>	Vertical coordinate location in experimental reference frame	pixels

Symbol	Description	Units
<i>b</i>	Radius of capillary tube	m
<i>c</i>	Concentration	mol
<i>d</i>	Pendant drop/bubble diameter	pixels

d_n	Minimum distance between two points	m
e	Least squares difference	m ²
g	Gravity	m s ⁻²
h	Height	m
l	Path length	cm
s	Path-length parametrized coordinate location in model reference frame	m
x	Horizontal coordinate location in model reference frame	m
y	Secondary vertical coordinate location in model reference frame	m
z	Vertical coordinate location in model reference frame	m

Non-Italic

Symbol	Description	Units
S	Path-length parametrized coordinate axis in model reference frame	m
X	Horizontal coordinate axis in model reference frame	m
Y	Secondary vertical coordinate axis in model reference frame	m
Z	Vertical coordinate axis in model reference frame	m
x	Horizontal coordinate axis in experimental reference frame	pixels
z	Vertical coordinate axis in experimental reference frame	pixels

Subscripts

Symbol	Description
0	Characteristic or initial value
1	In-plane
2	Out-of-plane
<i>ci</i>	Of the <i>-cis</i> photoisomer species
<i>e</i>	At the location of the maximum diameter of the pendant drop/bubble
<i>i</i>	Incremental count in a set of points
<i>l – v</i>	Liquid-vapor
<i>n</i>	Incremental count in a set of <i>N</i> points
<i>s</i>	At a distance d_e from the apex of the pendant drop/bubble
<i>s – l</i>	Solid-liquid
<i>s – v</i>	Solid-vapor
<i>tr</i>	Of the <i>-trans</i> photoisomer species
<i>x</i>	For the horizontal coordinate direction
<i>z</i>	For the vertical coordinate direction

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Chromocapillary Experiments with Photosensitive Surfactants and Superhydrophobic Surfaces

Michael A. Birosak

An Inverse Method for Measuring the Adsorption and Desorption Coefficients of Multi-Isotherm Surfactants

Background and Overview

Done in collaboration with the Department of Mathematics at Imperial College London and the Department of Chemistry at Tufts University, we are developing a novel method to measure adsorption and desorption coefficients of interfacial surfactants by using transient surface tension measurements of pendant air bubbles in a surfactant laden liquid. These two coefficients are commonly reported as a single value, the equilibrium constant, which is the ratio of adsorption to desorption coefficient. Our work fills a needed gap in literature as there are currently no directly reported methods to measure the two coefficients independently.

Lin et al. (1990) imply a potentially viable method but instead measure the binary diffusion coefficient and their study is limited to single-species solutions. In single-species surfactant solutions, the transient relaxation of surface tension is a single step process. The surface tension of fresh menisci initially starts near that of the pure solvent, then relaxes in a single step process as surfactant experiences net adsorption to the interface. However, in a multi-species solution, this relaxation can have multiple steps as the species may absorb and desorb at different rates or even drive one another off the interface.

Our work uses a photosensitive azobenzene-type surfactant, i.e. a photosurfactant, which can act as both a single and multi-species system. Unless isolated from light for a prolonged amount of time to allow the solution to reach thermodynamic equilibrium, a solution of photosurfactant will be composed of a mixture of both energized *-cis* and relaxed *-trans* photoisomers. Even though they are the same chemical compound, the two isomers function as

two distinct species in the solution, each with different equilibrium constants and maximum packing densities. (Cicciarelli et al. (2007)).

An easy demonstration of this phenomenon is tracking the contact angle of a sessile droplet of the surfactant laden liquid as the two species adsorb to the surface. Figure 1 shows a plot of contact angle over time for the drop and corresponding images to show the change in shape over time. Note the two distinct values the contact angle trends towards. The initial value around 53° is when the more rapidly adsorbing *-cis* isomer attaches to the surface. The following value around 38° is when the slower adsorbing *-trans* isomer squeezes those *-cis* isomers off the interface. This is where contact angle stabilizes as the interface becomes saturated with the *-trans* isomer.

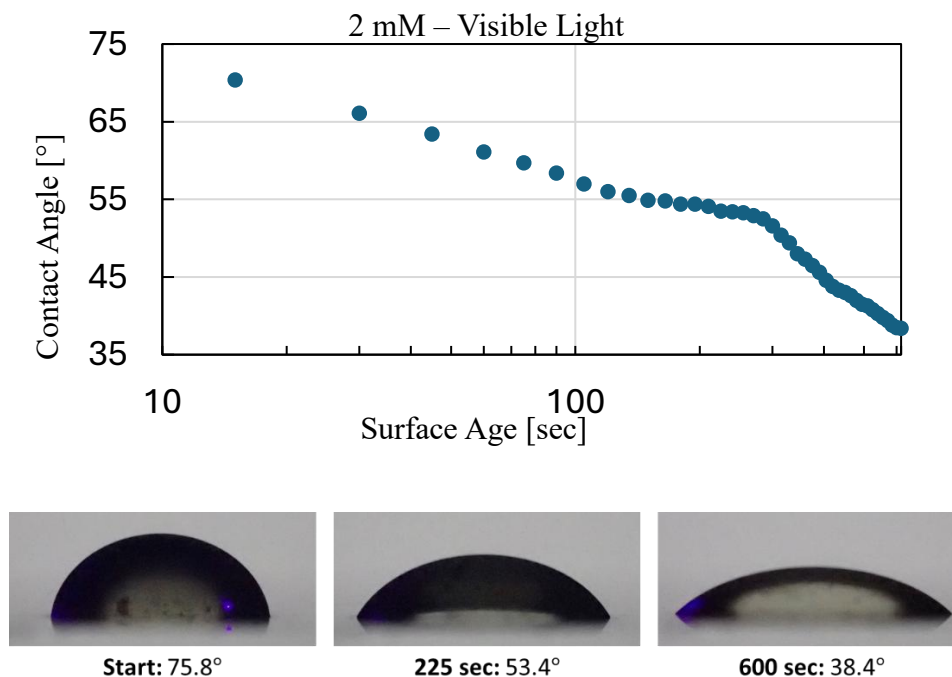


Figure 1: Transient contact angle of a sessile surfactant laden drop of water

Given a set of thermophysical properties, our model simultaneously resolves the species equations for the two isomers on the meniscus (interfacial concentration in moles per unit area) and in the bulk (bulk concentration in moles per unit volume) as a function of time to estimate the

rate of relaxation of surface tension of a fresh liquid-vapor interface. By matching the model to experimental relaxation data, we can use an inverse method to extract unknown input properties. If we prescribe the isomeric composition of a solution with controlled light exposure, our model will be able to extract the equilibrium constants of both species and resolve them into separate adsorption and desorption coefficients.

We collect the needed data using a technique called axisymmetric drop shape analysis, ADSA, that compares experimentally determined meniscus shapes to ones predicted analytically by a generalized, experiment specific version of the Young-Laplace equation. The synthesis and initial chemical characterization of the surfactants and preparation of test solutions used in these experiments was done in collaboration with Dr. Nigel Kidder-Wolff at the Tufts University Department of Chemistry.

Photosurfactant Preparation and Initial Characterization

Synthesis and Solution Concentration

The Tufts University Department of Chemistry synthesized an azobenzene-type, nonionic, photosensitive surfactant for our experiments comprised of a butyl tail group, an ether oxygen middle polar group, an alkyl spacer with four methylene groups, and a headgroup of two ethylene oxide moieties. The particulars of the synthesis of this surfactant, $C_4AzoOC_4E_2$, is outside the scope of this thesis and is detailed in Shang et al. (2003).

The azobenzene group photoisomerizes the surfactant between its *-cis* and *-trans* states in response to different wavelengths of light. Light in the visible spectrum encourages more cis-trans isomerization (peak absorbance happening around 440 nm) and vice versa for light in the ultraviolet spectrum (peak absorbance happening around 330 nm). Both species show greatly

reduced absorbance at longer wavelengths. In absence of illumination, the surfactant will revert to its less energized *-trans* state as it returns to thermodynamic equilibrium. Work done by Ciccirelli et al. (2007) estimated the time constant for thermal reversion to be approximately thirty hours at 25°C.

Aqueous solutions of the azobenzene were prepared at various concentrations in a dilution series. Their concentrations were then confirmed by analysis with Beer's Law. They were kept completely isolated from light for at least seventy-two hours before an experiment to ensure the solution was entirely in an effectively all *-trans* isomer state.

Isomeric Composition

By isolating a solution in the dark for several days and allowing it to relax to thermal equilibrium, you can create a solution with a mole fraction of *-trans* isomer that is effectively $X_{tr} = 1$. However, there is no photostationary state with where the molar ratio of *-cis* isomer is $X_{ci} = 1$ because there will always be some photoconversion back to the *-trans* isomerization even under illumination. For a solution comprised of a mixture of *-cis* and *-trans* isomers, our model requires the molar ratio of the two species, so we have developed a method to determine that ratio by using UV/vis absorption spectra and nuclear magnet resonance (^1H NMR) measurements.

The UV/vis absorption spectrum, A_{total} , of an aqueous solution with two surfactant species is the molar ratio weighted sum of the individual response spectra, Abs_{tr} and Abs_{ci} , of the two species as shown below. Kang et al. (2000). At low concentrations, the molar absorption coefficients of the two isomers, ϵ_{tr} and ϵ_{ci} are set wavelength dependent material properties.

$$Abs_{total} = [\epsilon_{tr}(\lambda)X_{tr} + \epsilon_{ci}(\lambda)X_{ci}]lc_{total} \quad (1)$$

If l and c_{total} , the path length of the measurement and the total bulk concentration of the solution, are both known, determining the molar absorptivity of the *-trans* ϵ_{tr} can be determined with a single UV/vis measurement of a solution isolated from light for several days to ensure that $X_{tr} = 1$ and $X_{ci} = 0$.

Determining the molar absorptivity of the *-cis* species, ϵ_{ci} , from a mixed isomeric ratio solution requires nuclear magnet resonance measurements of both a photostationary 100%*-trans* solution and a photostationary mixed solution. The ^1H NMR measurement of the all *-trans* solution allows us to identify the hydrogen bonds associated with that specific isomer, since we know that there are effectively now *-cis* isomers present. So, when a measurement is taken of the mixed solution, any peaks on the reading that are from the *-trans* species can be isolated. Figure 2 shows one of our NMR readings with the peaks of the two species respective hydrogen bonds marked.

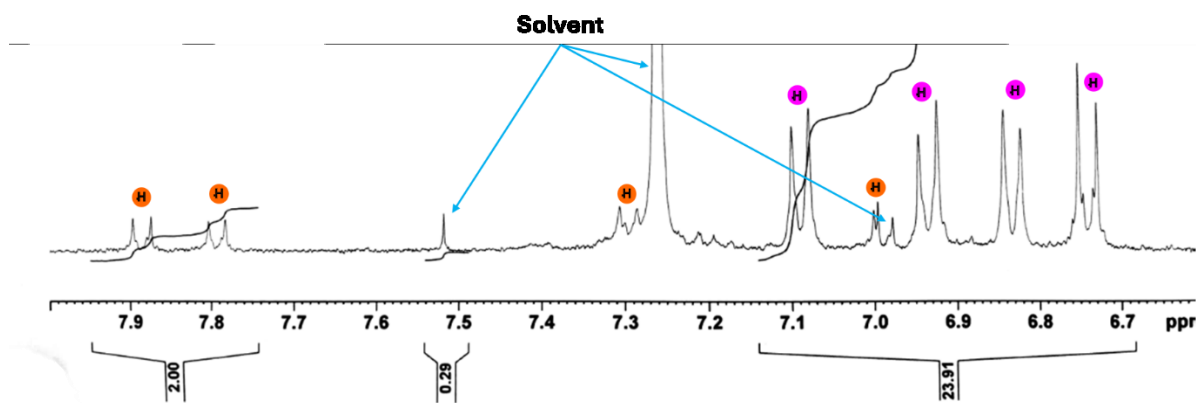


Figure 2: ^1H NMR measurement of photostationary azobenzene surfactant after exposure to visible blue light for one hour

By integrating the peaks and counting the number of contributions from the constituent isomers, we can determine the $X_{ci}:X_{tr}$ molar ratio of this specific photostationary state to be 15: 85. Now, the known molar ratios are used with a UV/vis measurement of a mixed solution at the same photostationary state to determine ϵ_{ci} . As with ϵ_{tr} , the molar absorption coefficient of

the *-cis* isomer species is a wavelength dependent material property. This means that at low concentrations, we can assume that ϵ_{tr} and ϵ_{ci} are known properties for any given photostationary state. So, ultimately, the only unknowns in Eqn. 1 for some Abs_{total} UV-vis measurement of a photostationary solution at a known concentration are X_{tr} and X_{ci} . The sum of the two molar ratios must equal one since there are no other species present which further reduces the number of unknown parameters to one. Numerical optimization in a program such as MATLAB can then be used to match experimental data to Eqn. 1 to extract the unknown ratios.

In theory, we could perform NMR measurements for each photostationary of interest, but that is more time consuming, expensive, and produces more complicated readings to process compared to this method of determining the isomeric composition of any photostationary state from a single faster and simpler UV/vis measurement. Figure 3 shows several measurements for the molar absorptivity of the two species as determined from this method.

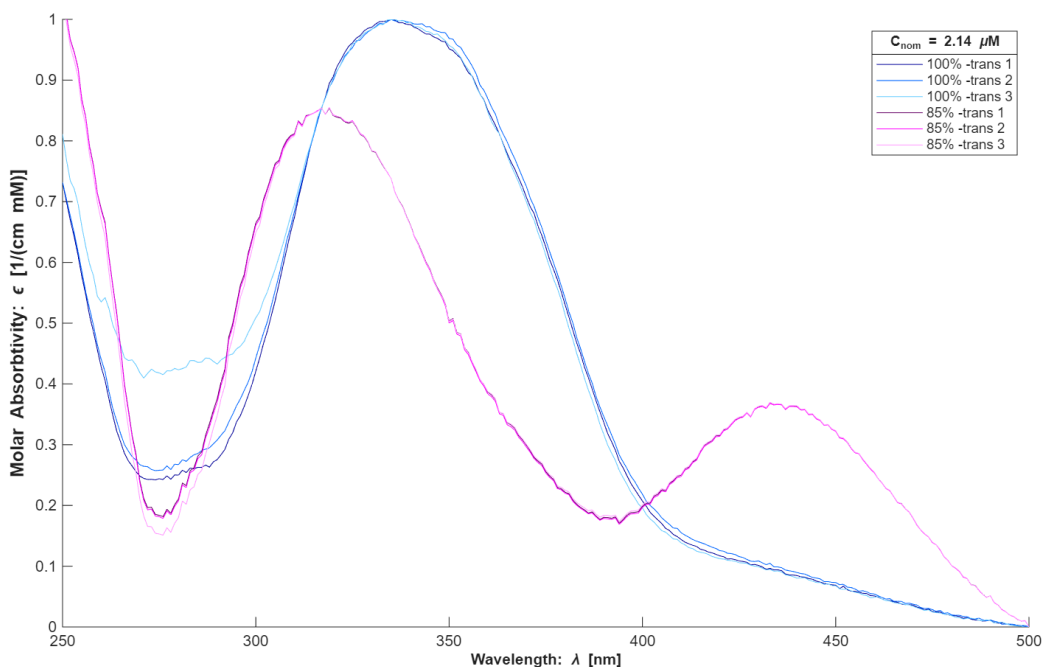


Figure 3: Molar absorptivity spectra of photostationary azobenzene solutions at 100%-trans and 85%-trans molar ratios

Additionally, we exposed a solution to visible light for an hour to allow it to reach some photostationary mixed *-cis/-trans* state and then allowed it to thermodynamically relax isolated from light in the UV/vis spectrometer where we took hourly spectra measurements. Figure 4 shows the UV-vis spectra and corresponding X_{tr} ratio of the solution solved for using the above method it undergoes thermodynamic relaxation over approximately sixty-six hours. The solution starts with a higher concentration of *-cis* and ends with a higher concentration of *-trans* isomers as expected.

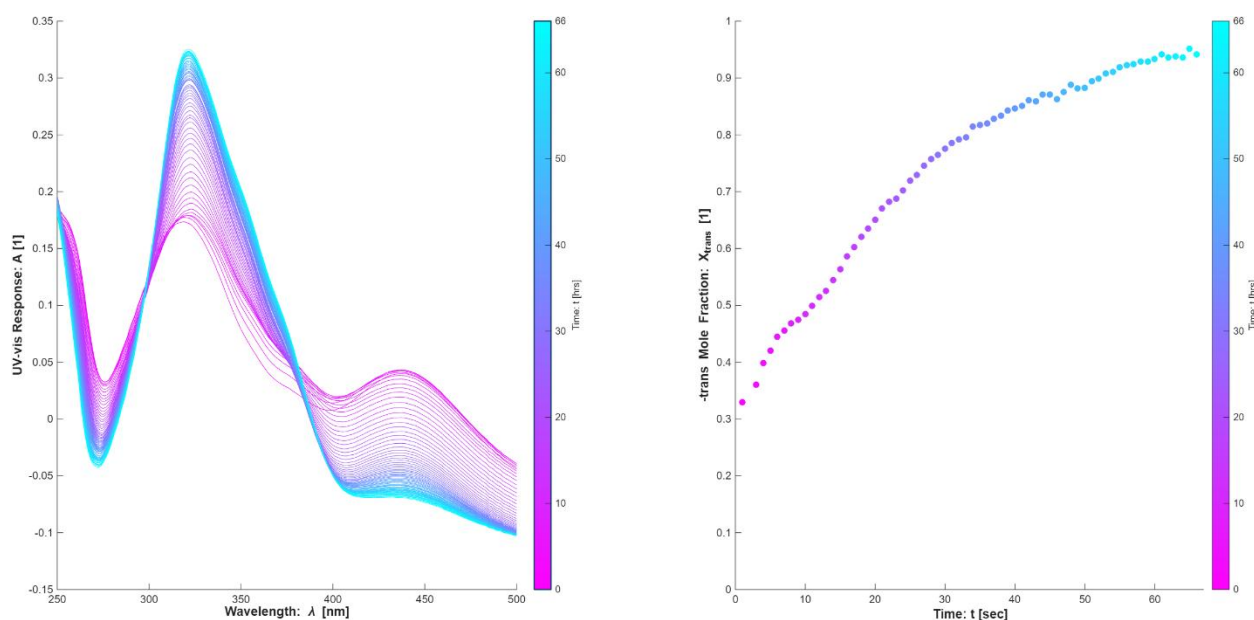


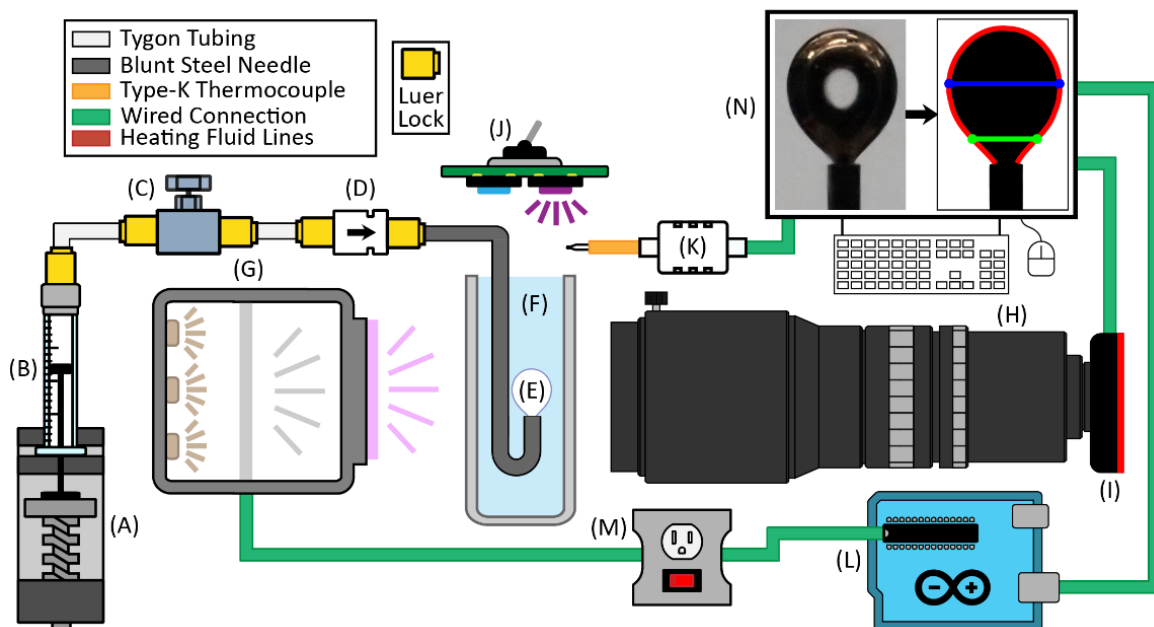
Figure 4: UV-vis spectra and corresponding X_{tr} ratio of a solution as it undergoes thermodynamic relaxation over sixty-six hours from a mixed isomeric composition towards an all *-trans* state

Image Acquisition

Physical Apparatus

Figure 5 shows a (not to scale) schematic of the physical apparatus used to collect high quality, high contrast images of pendant air bubbles in the surfactant laden solution under strictly controlled light conditions. The particulars of the axisymmetric drop shape analysis are explained

in a later section. This section focuses on the creation of pendant bubbles, experimental conditions, and image acquisition methods.



A	Motorized syringe pump	H	Zoom lens
B	100 μL glass syringe	I	Camera
C	Valve	J	Blue/ultraviolet LEDs
D	Check valve	K	Type-K Thermocouple
E	Pendant bubble	L	Microcontroller
F	Quartz cuvette	M	IOT controlled relay
G	Background light	N	Computer

Figure 5: Apparatus for image collection of pendant bubbles to be analyzed using axisymmetric drop shape analysis

Items A through F of Figure 5 shows the bubble generation system. A syringe pump is used to provide a controlled amount of air through a valved length of flexible tubing to a stainless steel 22-gauge needle. The needle bent back on itself in a hook-like shape and held vertically above an open quartz cuvette filled with the surfactant laden solution. Both the needle and the cuvette are rinsed with isopropanol and distilled water between experiments to ensure no cross-contamination

between different concentrations of the photosurfactant. This also serves to remove any smudges, water spots, or dust on the cuvette/needle that could compromise either the purity of solution or the quality of imaging. The verticality of the needle (and the pendant bubble that forms from it tip) is critical to the accuracy of the ASDA. If the needle is not vertical and the bubble is bent slightly the profile is no longer axisymmetric and the accuracy is impacted.

Figure 6 shows a digitized drop shape profile of a non-vertical bubble due to improper formation from the needle. The red circle on the image highlights where the bubble is stuck to the tip of needle instead of only making contact at the inner diameter of needle's opening, as it does on the left side of the image, ruining its axial symmetry. While the difference between the central axes of the bubble (the red lines marking formed by the intersection of perpendicular lines from the apex of the bubble and the points at its maximum diameter) and the vertical projections of the sides of the needle (the lines in blue) may seem small, this image is unsuitable for ASDA measurement. This profile is from a pendant air bubble in distilled, deionized water which should have a surface tension around ~ 72 mN/m, but the warped shape causes the ASDA routine to return an obviously incorrect measurement of ~ 60 mN/m.

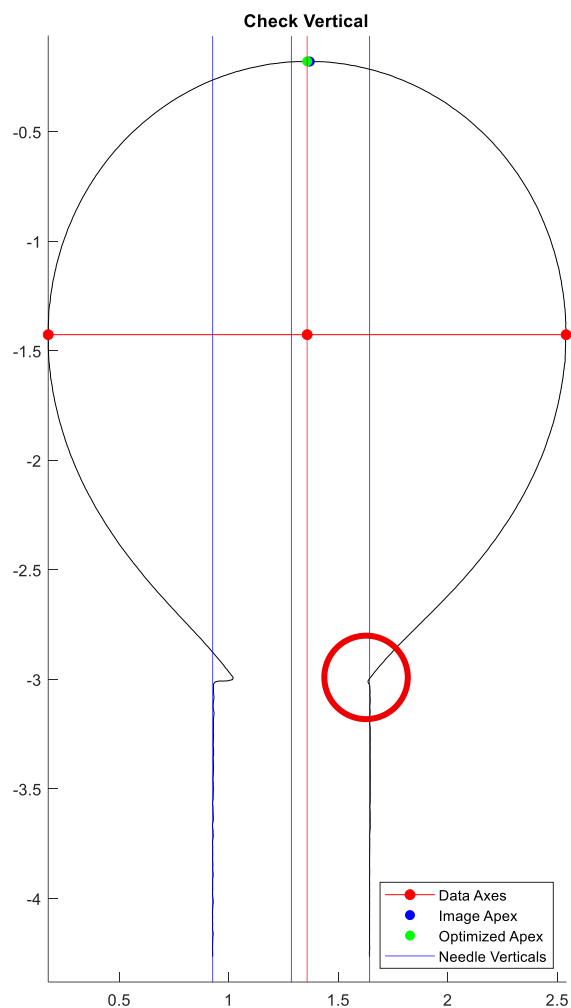


Figure 6: A poorly aligned pendant air bubble where the verticals of the bubble and the needle are misaligned due to the bubble improperly adhering to the needle

Figure 7 shows a pendant bubble's initial more spherical shape when its surface tension is near that of pure water (left, 72.30 ± 0.43 mN/m) compared the shape it deforms to as buoyant forces grow stronger relative to surface tension as the surfactant adsorbs to the surface (right, 31.24 ± 0.03). Note how uncertainty of the second measurement is much smaller than the first. This is because ASDS is more accurate for well-deformed drop shapes, for reasons explain in the later section covering the technique in detail.

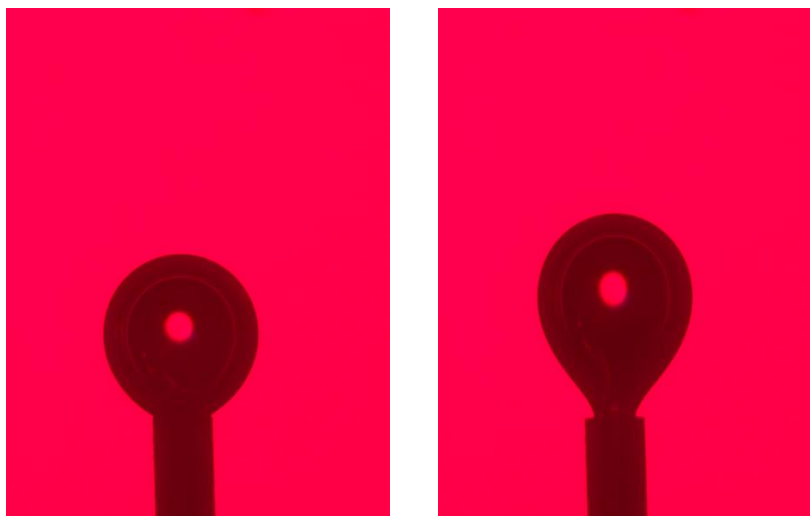


Figure 7: Two images of the same pendant bubble taken approximately one hour apart with surface tensions 72.30 ± 0.43 mN/m (**left**) and 31.24 ± 0.03 (**right**)

Items G and H on Figure 5, the background light and the camera's zoom lens allow us to take high-quality, high-contrast images as in Figure 5. The sharper the difference between the background of the image and the dark silhouette of the bubble, the more accurately the profile can be located. The backlight provides a uniform back illumination of diffuse light. Additionally, the imaging apparatus is fully enclosed in a light-proof box during data collection. This prevents outside light from reflecting on the bubble, compromising the quality of the image. Figure 8 shows the difference between a more and less suitable bubble image. The left bubble is poorly focused, and the image is noisy from ambient reflections while the right bubble has a sharp contrast between the foreground and background with minimal reflections. The central bright spot on the bubble is the background light itself seen through the drop. However, while the right bubble in Fig. 5 is more clearly focused and has fewer reflections, the angled needle indicates that results might still be skewed since axial symmetry could be compromised, like the improperly measured bubble from Fig. 6.

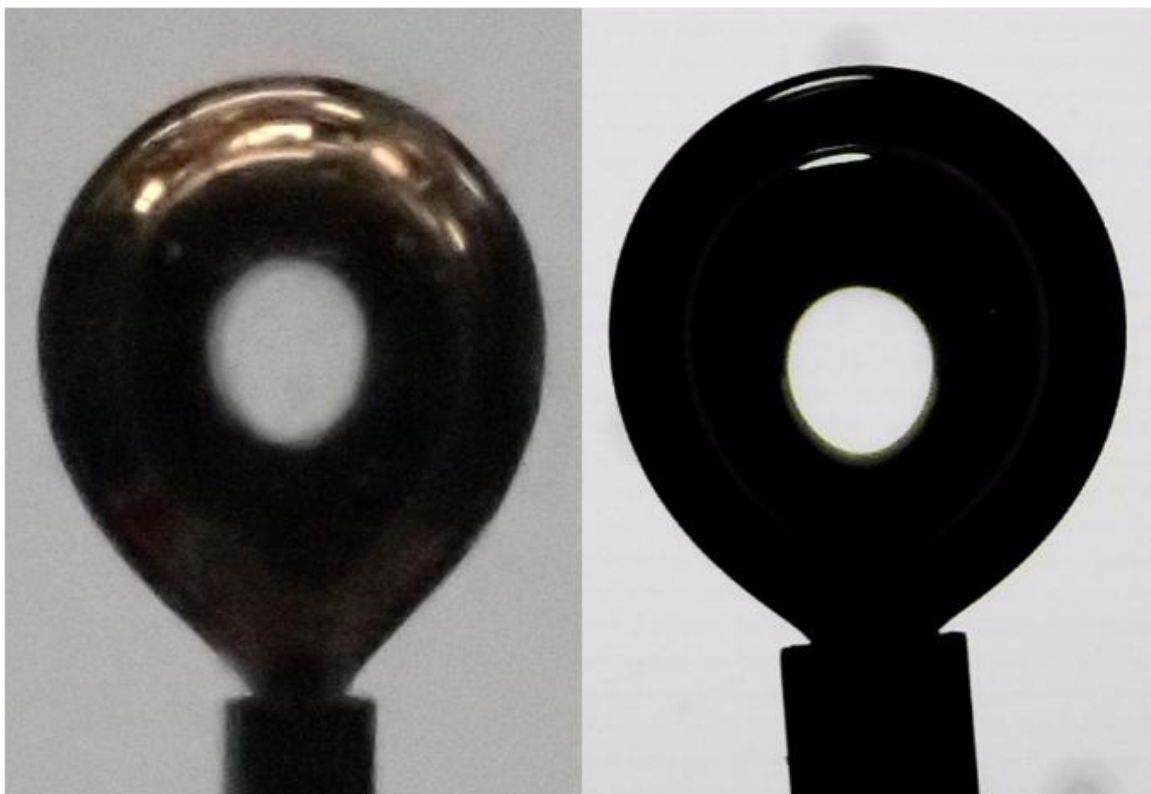


Figure 8: A poorly focused image of pendant bubble with image noise from reflections from ambient light on the top of the bubble (**left**) and a well-focused image of a pendant bubble with a crisp outline and minimal extra reflections (**right**)

Typically, images taken for ADSA are done with a more neutral white or light-colored background (as in Figure 8) but our experiments are performed with a red background light (as in Figure 7). The photosurfactant used in our experiments has negligible absorption at long wavelengths, so the red background light (from a 750 nm long pass filter) is unlikely to cause any unwanted photoconversion during our experiments. Additionally, the background light is controlled by a microcontroller synched to the image acquisition computer to only turn on during image acquisition, like a camera flash, further reducing the likelihood of the background light causing unwanted photoconversion. These controls are an improvement on similar work done with photosurfactants by Cicciarelli et al. whose lighting conditions were less precise than ours. They did not use as long of wavelength of light and left their backlight on the entire time.

Data Collection

A test solution of some known concentration has its initial photostationary state set prior to data collection. *-trans* adapted solutions are isolated from light for at least 72 hours prior to an experiment. Solutions with a mixed isomeric composition are exposed to illumination for at least one full hour prior to an experiment to ensure they reach the expected photostationary state found through the measurement method described in the previous section.

At the start of an experiment a preliminary bubble is inflated to focus the camera and set the bounds of the image analysis (most of each frame is empty background) for the set of images. Once data collection begins, the syringe pump is engaged to rapidly purge air through the bubble holding needle. The rapid detachment of several bubbles in quick succession ensures the imaged meniscus is free of any surfactant that might have adsorbed before it was inflated from within the holder. Once a fresh bubble is stable on the needle the backlight is turned off and from here on the experiments are performed in darkness except for the moment of image acquisition.

Again, as discussed above, even though a larger (and more deformed) bubble is preferred for ADSA, we need to limit the chances of buoyant forces on the bubble overcoming the slowly reducing surface tensions forces securing it to the holder. We found that bubbles with volumes of 4-6 μL were most suitable for our experiments.

Preliminary measurements for surface tension of the bubble are taken during the experiment using a simpler (and so faster to calculate) shape factor based tensiometry outlined in the following section to ensure full relaxation is reached. Bubble volume is estimated graphically by approximating the total volume as a stack of conical frustums one pixel high. A type-K thermocouple measures the ambient temperature whenever an image is taken as well. Assuming

the solution to be the same temperature as its local surroundings, this measurement was used to provide an accurate value for the density of water (according to tabular thermophysical property data).

Again, it is critical that these experiments are performed under strictly controlled illumination conditions by setting the photostationary composition of the two species before data collection and preventing any uncontrolled photoisomerization for the duration of the experiment.

Image Analysis

Image Preparation

The raw image of the pendant bubble requires some pre-processing before it is fully suitable for profile extraction. Figure 9 shows an unprocessed image of a pendant bubble (left), a step of the iterative noise removal routine (center), and a processed image ready for edge detection (right).

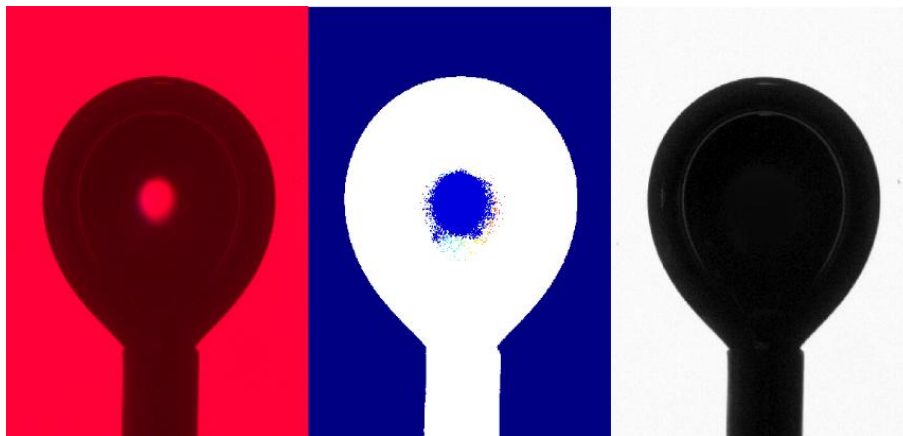


Figure 9: An unprocessed image of a pendant bubble (**left**), a step of the iterative noise removal routine (**center**), and a processed image ready for edge detection (**right**)

Our edge detection method only requires that the image be in grayscale (a trivial conversion from a color image) but the sensitivity of our method means that it can find artificial edges in an

image, such as in the unavoidable reflections of the backlight through the bubble itself, external objects floating in the solution, or smudges on the cuvette or camera lens. It is possible to adjust the sensitivity threshold to ignore the ‘weak’ edges produced by variations in the image but that risks compromising the accuracy of locating the ‘strong’ edges of the bubbles profile. To remove this unwanted noise, we perform the following steps:

1. Crop the image into the relevant range of pixels determined at the beginning of the experiment
2. Convert the image to grayscale by extracting each pixel’s intensity from the image file
3. Determine a pixel intensity threshold using Otsu’s method and binarize the image
4. Identify connected regions of pixels and find the two largest (the bubble and the background) through connected component labeling. This is the center image of Figure 9.
5. Average the intensity values of smaller connected sections of pixels inwards from their bordering regions. This is the right image of Figure 9.
6. Repeat steps (3-5) until the binarization only detects two regions with strong edges

Otsu’s method for image binarization consists of determining a pixel intensity threshold (above which a pixel is bright/white/1, below which it is dark/black/0) such that the variance of pixel intensity among those two separate groups is minimized. Sometimes Otsu’s method is used for edge detection, but we use a more technique that measures edge location on the sub-pixel scale while Otsu’s method is limited to the size of the pixels.

Regions of pixels with the same intensity (now all either 1 or 0 after image binarization) are identified and sorted by size in a process known as component labeling. The two largest connected sections should be the lighter background (intensity equals 1) and the darker main bubble silhouette (intensity equals 0). Any smaller sections such as reflections on the drop

(intensity equals 1) or floating debris (intensity equals 0) are flagged as noise. Those variations in the image are smoothed by averaging those pixel's intensities inwards from their surrounding neighbors. These two steps are then performed iteratively until Otsu's method only detects two connected pixel regions, the background and the silhouette.

This image is now suitable for sub-pixel edge detection and should be free of any isolated noise (shapes that do not overlap with the profile of the bubble), but adhering noise (any shapes that do overlap with the profile of the bubble) needs to be removed at a later step in the analysis process. Figure 10, reproduced from Zuo et al. (2006), shows isolated noise from (a) the backlight and (b) suspended particles as well as adhering noise from (c) satellite bubbles and (d) stuck particles.

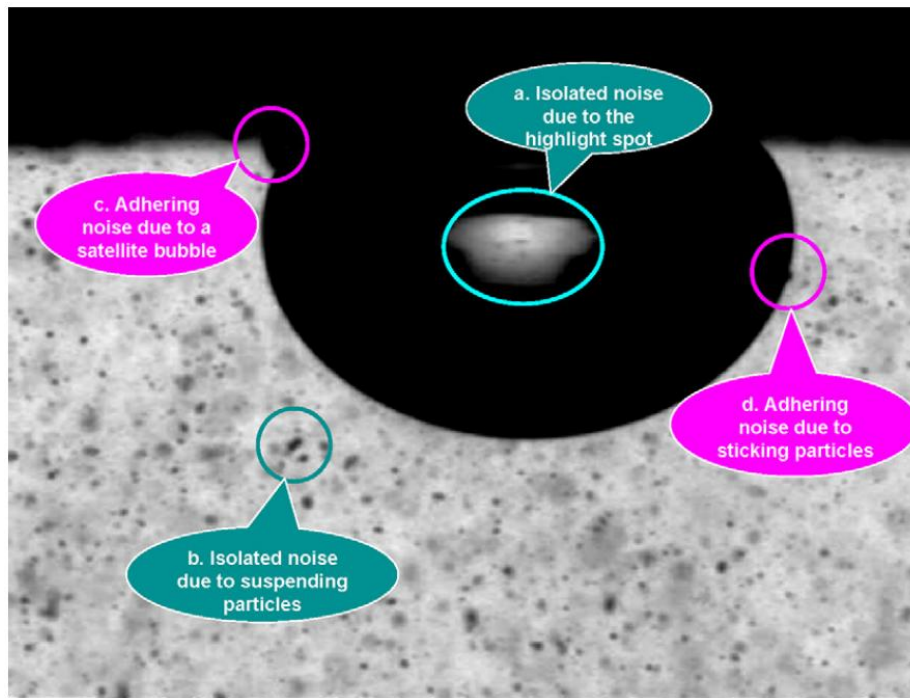


Figure 10: Reproduced from Zuo et al. (2006), this shows isolated noise from (a) the backlight and (b) suspended particles as well as adhering noise from (c) satellite bubbles and (d) stuck particles

Edge Detection

The final step before performing the actual ADSA routine is extracting the cartesian coordinate locations of the bubble's profile. Before modern computing, drop shape profile points were tediously selected by hand, but now software can automate the process. All of our image analysis and ADSA optimization were performed in the MATLAB, but we decided that MATLAB's preexisting edge detection methods were insufficient for our work. These methods are all limited by the scale of the pixels in that they assign each pixel as either an edge or not an edge. This can cause unintended errors since the profile of the bubble is smooth and the resolution of the image may not be fine enough to capture slight variations in curvature.

Figure 11 shows the difference between edges located by the commonly used, but pixel resolution limited, Canny edge detection method compared to a sub-pixel edge detection method. The Canny method is unable to accurately capture the shape of the curved profile as well as the sub-pixel method. This is especially apparent in the right image of Figure 11 with a more vertical section of the profile. Multiple locations on the profile would have the same radius (from the centerline of the bubble), which we know is impossible for a curved bubble. To get a smooth profile from a method like Canny detection, we would need to artificially smooth the coordinate locations somehow.

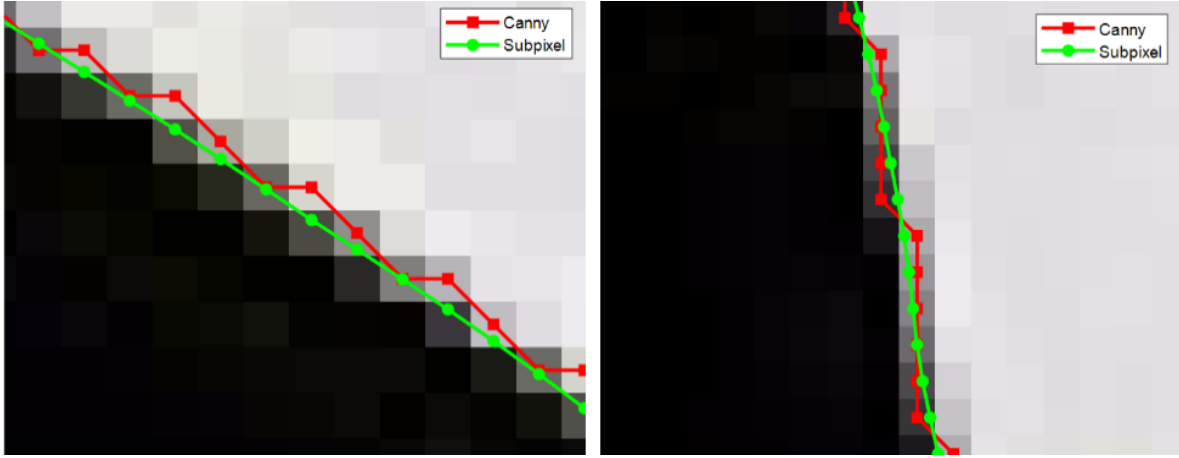


Figure 11: Comparison of pixel resolution limited Canny edge detection (red squares) and sub-pixel edge detection (green circles) on a pendant bubble

Instead, we implement a sub-pixel edge detection method developed by Trujillo-Pino et al. (2011) that estimates profile coordinate locations using a method they call the partial area effect. Each pixel in a grayscale image has some intensity. Low intensity pixels are darker and high intensity pixels are brighter. At the edge between a dark foreground and light background, the pixels there will show some gradient between two intensities. Trujillo-Pino et al.'s method assumes that an edge pixel is split between a dark and a light section by the edge line. The intensity shown in the image is the area weighted average of the intensities of these two sections. Figure 12, reproduced from their paper, gives an example of how this breaks down an image.

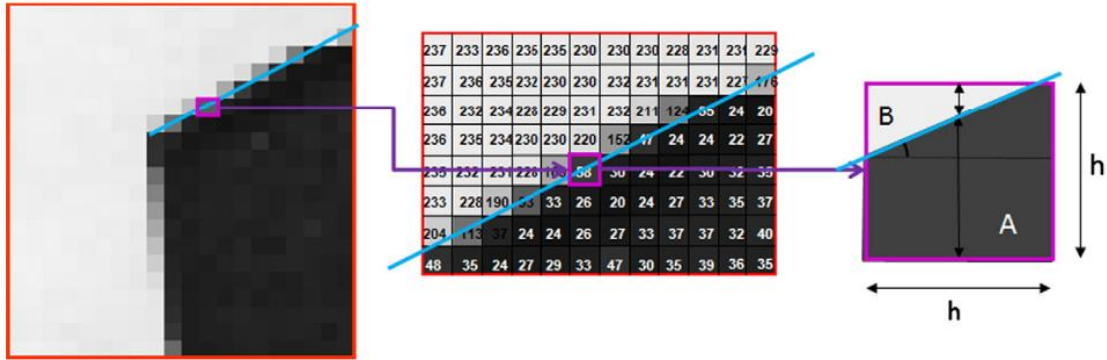


Figure 12: Reproduced from Trujillo-Pino et al. (2011). Shows their method of sub-pixel edge detection using the partial area effect

Using an iterative method comparing a moving cluster of pixels, the ratio the two areas is assumed from the pixel intensity, and a system of equations is solved for that packet of pixels for a line whose slope means that all the pixels within the moving region of interest have the correct intensities. The sensitivity of this method requires the previously described image preparation to prevent false edges. Finally, the points are sorted into clockwise order from the bottom left of the bubble to the bottom right to make importing the profile into the optimization algorithm easier since the drop-shape model explained in the following section produces a similarly oriented profile.

Drop Shape Modeling

The following section derives a model for a pendant drop deformed by buoyant forces starting from a background on surface tensions forces and meniscus shape, early drop shape models that formed the fundamentals of ASDA, and final differential model for drop shape that can be processed with modern computing power.

Hydrostatic Pressure Driven Meniscus Curvature

Consider the vertical capillary rise h of a liquid with surface tension γ in a smooth-walled circular tube of radius of radius R as shown in Figure 13 below.

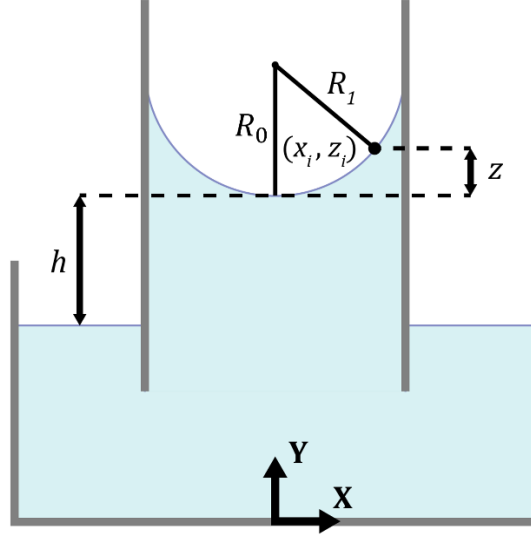


Figure 13: Vertical capillary rise h of a liquid with surface tension γ in a smooth-walled circular tube of radius R_0 , the radius of curvature at the apex of the meniscus

We can derive a simple expression for the vertical rise, h , of the fluid by starting from the Young-Laplace equation for the pressure difference, ΔP , over an interface with surface tension γ whose curved shape has the with principal radii of curvature R_1 and R_2 .

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2)$$

Since the tube is circular, the principal in-plane and out-of-plane radii of curvature, R_1 and R_2 , are equal to the radius of the tube, R_0 .

$$R_0 = R_1 = R_2 \rightarrow \Delta P = \frac{2\gamma}{R_0} \quad (3)$$

The pressure difference across the interface is equal to the hydrostatic pressure of the column of liquid at the apex of the meniscus, ΔP_0 , which is defined by the difference in density between the liquid and vapor phases, $\Delta\rho$, and local gravity, g .

$$\Delta P_0 = \Delta\rho gh = \frac{2\gamma}{R_0} \quad (4)$$

This can be algebraically manipulated into a simple expression for the height of the liquid column.

$$h = \frac{2\gamma}{R_0 \Delta\rho g} \quad (5)$$

Through a similar derivation, you can account for the liquid-vapor contact angle, θ , by performing a force balance in the vertical direction between upwards component of the surface tension force (found by integrating around the perimeter of the tube) and gravity.

$$h = \frac{2\gamma \cos \theta}{R_0 \Delta\rho g} \quad (6)$$

While slightly more accurate, both expressions inherently assume a flat meniscus by defining the pressure difference only at the apex and a circular tube. This neglects the small difference in hydrostatic pressure across the change in height y from the apex of the meniscus to the contact point at the wall of the tube in addition to any effects from a non-hemispherical meniscus shape. It would be more accurate to say that the pressure at some arbitrary point on the interface (x_i, z_i) is defined as the hydrostatic pressure at the apex of the meniscus plus the additional change in pressure from the height $z = y - h$.

$$\Delta P_i = \frac{2\gamma}{R_0} + \Delta\rho g z = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (7)$$

You can generalize this expression further by defining the principal radii of curvature in terms of the first and second derivatives of the shape of the interface using analytical geometry.

$$\frac{1}{R_1} = \frac{y''}{(1+y'^2)^{3/2}} \quad (8a)$$

$$\frac{1}{R_2} = \frac{y'}{x(1+y'^2)^{1/2}} \quad (8b)$$

For a figure of revolution (in this case one that is not necessarily perfectly hemispherical), the in-plane and out-of-plane radii of curvature are still equal where the two planes intersect at the central axis at the apex of the meniscus, i.e. $R_1 = R_2 = R_0$. Using this common radius, you can non-dimensionalize this expression and extract a useful non-dimensional parameter known as the Bond number, β .

$$2 + \frac{R_0 \Delta \rho g z}{\gamma} = \frac{R_0}{R_1} + \frac{R_0}{R_1} \quad (9)$$

$$2 + \beta \frac{z}{R_0} = \frac{R_0}{R_1} + \frac{R_0}{R_1} \quad (10)$$

$$\beta = \frac{\Delta \rho g R_0^2}{\gamma} \quad (11)$$

The Bond number is a ratio of body forces (in this case gravity) to surface tension forces and can be used to understand how the shape of bubbles and droplets are determined by the relative strengths of the two. For example, in either of the simple expressions we derived for capillary rise increasing the magnitude of the surface tensions will result in a taller column of liquid. This would be a situation with a lower Bond number, as defined in Equation 11, where the surface tensions forces in the denominator overpower the gravitational body forces in the numerator.

Another example would be the shape a sessile drop of liquid since the contact angle of a sessile droplet is dependent on balance of forces between the solid-liquid (γ_{s-l}), liquid-vapor (γ_{l-v}), solid-vapor (γ_{s-v}) surface tensions and gravity as shown in Figure 11 below. A droplet with a higher Bond number will have a smaller contact angle, since the buoyant body forces are stronger than surface tension, as shown in left image of Figure 14. Whereas a droplet with the lower Bond number will have a larger contact angle since the surface tension forces trying to minimize the surface area of the drop are relatively stronger than gravity, as shown in right image of Figure 14.

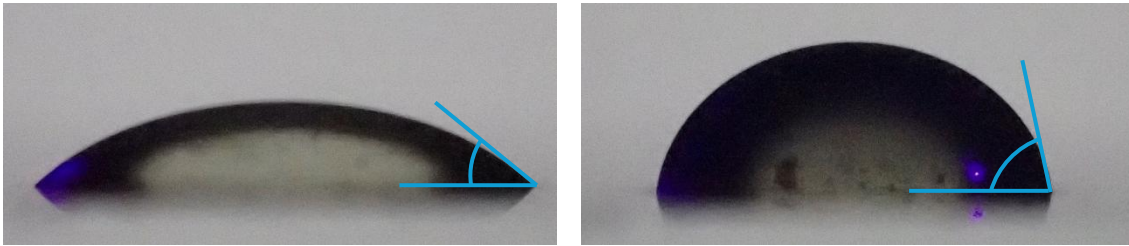


Figure 14: Comparison of a sessile droplet of liquid with a relatively lower Bond number where gravity is stronger than surface tension resulting in a smaller contact angle (**left**) and a droplet with a relatively higher Bond number where surface tension is stronger than gravity resulting in a larger contact angle (**right**)

Similarly, for pendant droplets or bubbles, the amount of vertical elongation and deformation of the drop (or bubble, the two are mathematically identical) from a spherical shape is determined the Bond number. A higher Bond number means a more deformed shape (for example, the right image of Figure 7) as gravity pulls against surface tensions and a lower Bond number means a more spherical shape (for example, the right image of Figure 7).

In the late nineteenth century, Bashforth and Addams numerically integrated Equation 10 by hand to create tabular values of non-dimensional coordinate locations of the profiles of pendant droplets for a range of Bond numbers in terms of ϕ , the angle of rotation from the central axis. This work formed the basis of axisymmetric drop shape analysis (ASDA), the method of

determining the surface tension of a curved meniscus by graphically measuring the coordinates of an interface and profile matching them to a drop shape model that we use in this study.

Shape Factors

Using Bashforth and Adams tabular values, the Bond number of a drop or bubble could be determined through profile matching, but to determine the actual surface tension, γ , you also needed some geometric reference to convert from their non-dimensional values to physical units. Originally, the physical reference value used for conversion was the apex radius of curvature R_0 but that is difficult to measure graphically. So, later work defined the more easily determined shape factor $S = d_s/d_e$, where d_e is the maximum diameter of the bubble (or droplet) and the d_s is the diameter measured d_e from the apex of the shape, as shown in Figure15 on a pendant air bubble in liquid water. These diameters are much easier to measure directly from an image than the radius of curvature.

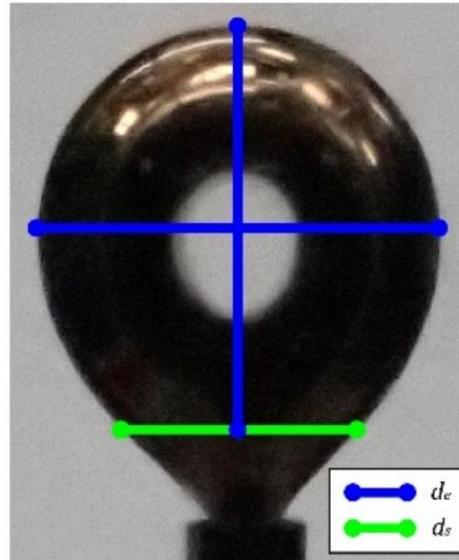


Figure 15: The diameters d_e and d_s used to calculate the shape factor $S = d_s/d_e$ of a pendant droplet or bubble

By defining the quantity $H = -\beta \left(\frac{d_e}{R_0}\right)^2$, we can use the Bond number to alternatively express surface tension as

$$\gamma = \frac{-\Delta\rho g d_e^2}{H} \quad (12)$$

where H is a function of the shape factor S . The relationship between H and S was first determined empirically, but later work determined an analytical relationship between the two. Assuming that the density difference between the two phases and local gravity is known, you can accurately determine the surface tension of the interface between them using only these two diameters (and the tabular values for S and H). One drawback of this method is that the uncertainty of your surface tension measurement is very dependent on the shape of the drop. The uncertainty in measuring d_e and the location of the drop apex are only dependent on the accuracy of the experimental equipment used for imaging, but this is not so for d_s . As Bond number decreases (and drops become more spherical) the uncertainty of d_s increases exponentially.

For example, say the experimental uncertainty of the location the edge of a droplet is ± 1 unit (typically pixels for digital images). Given the measurement at each end, the total uncertainty of d_e would be ± 2 units since each end can vary by ± 1 . With similar uncertainty in the location of the apex, there is a ± 3 unit vertical range (combining those two uncertainties when measuring from the apex of the drop) for the location at which to measure d_s . At lower Bond numbers, when the drop is more spherical, the smaller slope of the droplet's edge's tangent line in the region of d_s means there is a larger horizontal range for the edge's location. This can cause a significant difference in the diameter of the drop over that ± 3 unit vertical range, in addition to the ± 2 units uncertainty in whichever diameter over that range is selected. In contrast, when Bond number is higher and the droplet is elongated the steeper slope means the horizontal range for location is

smaller. Figure 16 shows an illustrative, not to scale example of how these uncertainties stack and are worsened by the local slope of the drop shape.

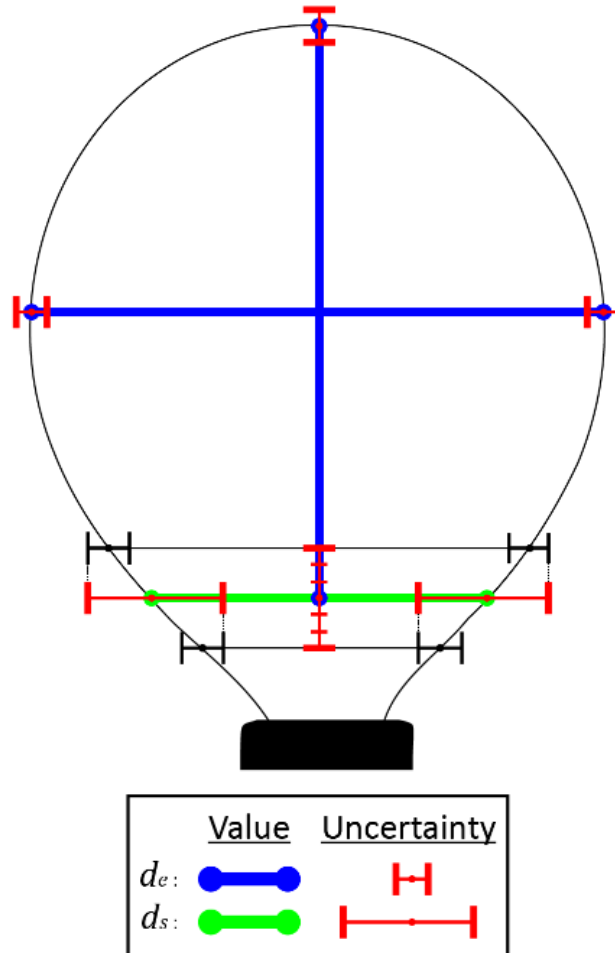


Figure 16: Illustrative example of how the uncertainties of coordinate location of a drop shape profile are worsened by the local tangent slope of the profile

Conveniently, the overall accuracy of this technique can be improved as much as you can improve the accuracy and precision of the measurements of d_e and d_s . However, since this method essentially only uses two measurements, it is very sensitive experimental noise. Noise could be anything that disrupts the quality of the image (like poor lighting or lack of focus) or anything that compromises the axial symmetry of the bubble (vibrations, misalignment of the droplet/bubble

holder, optical distortion of the camera, etc.). As modern computing power has developed, more accurate automated methods of fitting the coordinates of the entire drop shape profile to more advanced drop shape models have been developed, but these models are also more accurate for well-deformed drop profiles. While more advanced, modern models are still similar to Bashforth and Addams centuries old technique in that they both, essentially, determine interfacial properties by measuring aberration of a profile from a perfectly spherical shape.

Path Length Parametrized Drop Shape

Figure 17 shows a path length parametrized coordinate system used to define the shape of a pendant bubble formed by the interaction of buoyant forces from the density difference between the bubble and surrounding liquid, the varying hydrostatic pressure of the liquid, and the surface tension of the interface between the two. The X - and Z -axes are orthogonal to each other and intersect at $(x = 0, z = 0)$. S is the path length along some drop profile from the common origin for all three coordinates at $(x = 0, z = 0, s = 0)$. ϕ is the tangent angle at some point on the profile (x_i, z_i) . Note that the angle formed between the Z -axis and a line perpendicular to the tangent line at that point is also equal to ϕ .

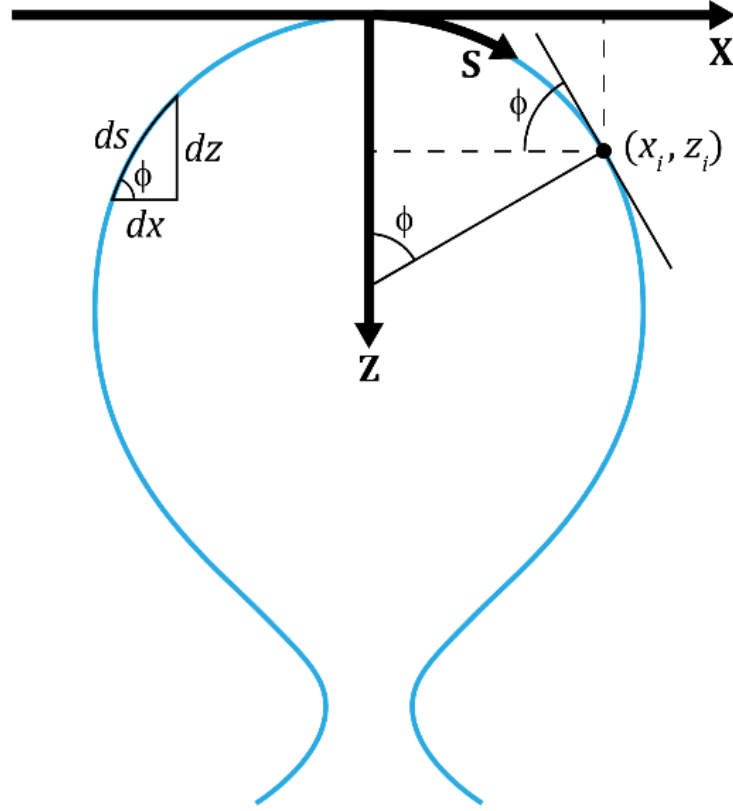


Figure 17: Path length parametrized model for an axisymmetric pendant drop in terms of X (horizontal Cartesian location), Z (vertical Cartesian location), S (path length along drop shape from the common origin at $(x = 0, z = 0, s = 0)$, and ϕ (angle of rotation from Z axis)

The goal of the following derivation is, similarly to the above treatment of capillary rise in a circular tube, to find a more general expression for the shape of a curved interface starting from Laplace's equation. The result will be a system of coupled, non-linear, ordinary, first-order differential equations for the x and z coordinate locations and the corresponding ϕ values of the points that form a drop shape profile as functions of s , path length from the apex of the shape at the drop. This model is also valid for pendant bubbles since they are mathematically equivalent to pendant droplets, differing only by a negative sign on the density phase difference that reflects the graph along the X -axis.

We start by defining the differential change in path length ds in two different ways. First, using the trigonometric relations of the right triangle formed by ds , dz , and dx and the angle of the tangent line

$$ds = dx \cos \phi \quad (13)$$

$$ds = dz \sin \phi \quad (14)$$

and with the arc length traced by the in-plane radius of curvature over the angle $d\phi$.

$$ds = R_1 d\phi \quad (15)$$

Equations 13 through 15 can be rearranged into differential equations for x , z , and ϕ .

$$\frac{dx}{ds} = \cos \phi \quad (16)$$

$$\frac{dz}{ds} = \sin \phi \quad (17)$$

$$\frac{d\phi}{ds} = \frac{1}{R_1} \quad (18)$$

For figures of revolution, the radius of curvature along the plane perpendicular to the page can be found using spherical coordinates.

$$\frac{1}{R_2} = \frac{\sin \phi}{x} \quad (19)$$

Equations 18 and 19 can be substituted into Equation 7, our still valid version of the Young-Laplace equation with the expanded pressure term that accounts for the difference in hydrostatic pressure.

$$\Delta P_i = \frac{2\gamma}{R_0} + \Delta \rho g z = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \gamma \left(\frac{d\phi}{ds} + \frac{\sin \phi}{x} \right) \quad (20)$$

Equation 20 can be algebraically manipulated into a differential equation for ϕ as function of s .

$$\frac{d\phi}{ds} = \frac{2}{R_0} + \frac{\Delta\rho g}{\gamma} z - \frac{\sin\phi}{x} \quad (21a)$$

Equation 21 has a singularity at $(x = 0)$ so we locally define the derivative for ϕ using the arc length at the apex of the shape as expressed in Equation 15.

$$\left. \frac{d\phi}{ds} \right|_{s=0} = \frac{1}{R_0} \quad (21b)$$

Equations 16, 17, and 21a-b form a set of coupled, non-linear, ordinary, first-order differential equations for the horizontal and vertical coordinates x and z , and tangent angle ϕ of the profile's shape in term of the path length from the apex s given the initial conditions $x(s = 0) = z(s = 0) = \phi(s = 0) = 0$. Note, this model only returns one half of the profile, but since the drop is axisymmetric it can be mirrored across the vertical Z -axis to plot the entire shape. We solve this system using a 4-th Order Runge-Kutta method.

Optionally, this model can be extended with differential equations for the surface area A and volume V of the droplet above some coordinate (x, z, s) as functions of s by approximating the axisymmetric shape as a stack of differentially thin conical frustums. Note, this is surface area and volume of a full, axisymmetric drop shape not a half profile like Equations 16, 17, and 21a-b. Similarly to the earlier differential equations, the initial conditions Equations 22 and 23 are $A(s = 0) = V(s = 0) = 0$. These equations are not used in the optimization routine to determine the unknown physical parameters but are trivial to add to the computation when plotting the final, optimized model for visual comparison to a drop profile.

$$\frac{dA}{ds} = 2\pi x \quad (22)$$

$$\frac{dV}{ds} = \pi x^2 \sin \phi \quad (23)$$

As opposed to the previous method using shape factors which only uses two measurements, you can use an entire set of drop shape profile coordinates for profile matching, reducing the individual error introduced by any single incorrectly located coordinate location. The full system of equations used in the model is summarized for convenient reference in Table I below.

Table I: Summary of path length parameterized model for an axisymmetric pendant droplet formed by the interaction of buoyant, hydrostatic, and surface forces

Drop Profile Components		Differential Equation and Initial Condition(s)	Equation Number
x	Horizontal location on X -axes	$\frac{dx}{ds} = \cos \phi$ $x(s = 0) = 0$	Eqn. 15
z	Vertical location Z -axes	$\frac{dz}{ds} = \sin \phi$ $z(s = 0) = 0$	Eqn. 16
ϕ	Slope of tangent line	$\frac{d\phi}{ds} = \frac{2}{R_0} + \frac{\Delta\rho g}{\gamma} z - \frac{\sin \phi}{x}$ $\left. \frac{d\phi}{ds} \right _{s=0} = \frac{1}{R_0}$ $\phi(s = 0) = 0$	Eqn. 21a-b
A	Surface area of full drop shape up to point of interest	$\frac{dA}{ds} = 2\pi x$ $A(s = 0) = 0$	Eqn. 22
V	Volume of full drop shape up to point of interest	$\frac{dV}{ds} = \pi x^2 \sin \phi$ $V(s = 0) = 0$	Eqn. 23

Tensiometry Through Profile Matching

Optimization Parameters

For a given pair of values for surface tension γ and apex radius of curvature R_0 , the system of equation derived in the previous section can produce a drop shape profile for a pendant drop. Those two unknown parameters could be iteratively optimized to find an analytical model composed of profile coordinates (x_i, z_i) that closely matches an experimentally measured set of profile coordinates (X_i, Z_i) . While more computationally intensive to implement, this method is more robust than determining surface tension from $S = d_e/d_s$ and tabular shape factor values since it is not limited to a surface tension measurement per image. d_e and d_s can only be measured once per image, but by selecting different sets of points from the drop profile each time we can perform multiple optimization routines on the same image.

However, the experimental profile and model profile are neither aligned on the same coordinate axes nor at the same scale. Aside from the linear scaling transformation from pixels to meters in both horizontal and vertical directions, the two coordinate frames can also be linearly and rotationally offset, as shown in Figure 18. This means that not only do we have to optimize parameters for γ and R_0 but we also need additional parameters to align and scale the two frames together properly.

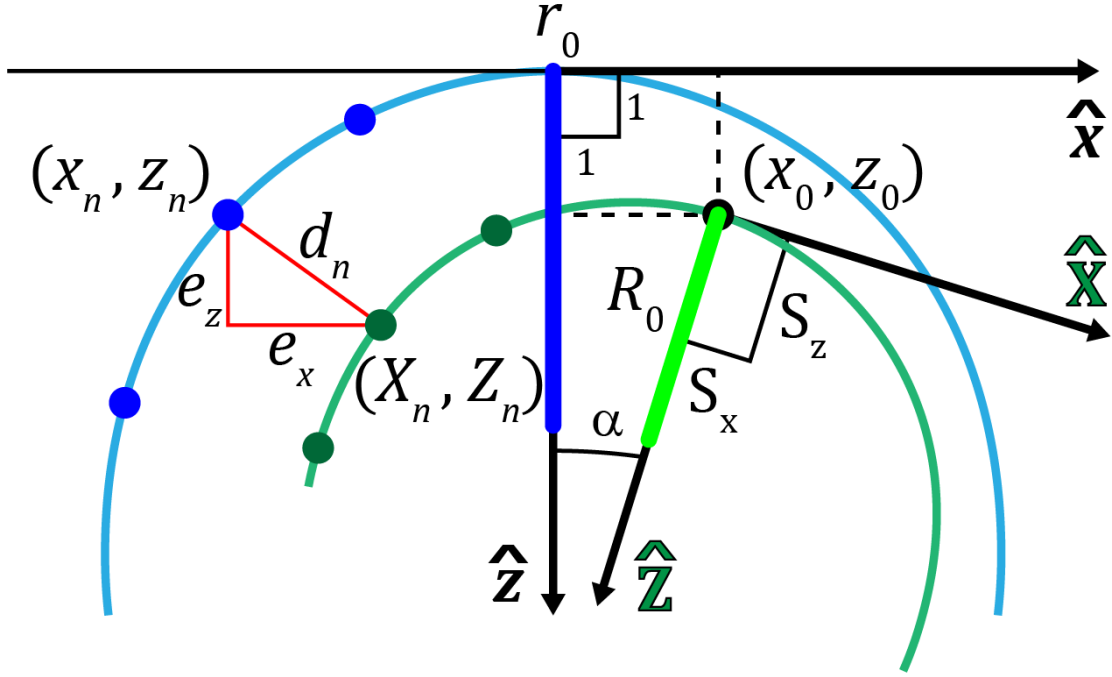


Figure 18: Comparison between the coordinate axes used by the experimentally measured drop shape profile (X, Z) and model generated drop shape profile (x, z)

The following transformation matrix is used to convert points from the frame of the experimental data to that of the analytical model and vice versa. This matrix accounts for

1. horizontal and vertical translation between the origin of the two frames at the apex of the drop shapes: x_0 and z_0
2. linear scaling between the units of length (pixels and meters) used on the horizontal and vertical axes of the two frames: S_x and S_z
3. and angular rotation between the two frames: α

$$\begin{bmatrix} X \\ Z \\ 1 \end{bmatrix} = \begin{bmatrix} S_x \cos \alpha & -S_z \sin \alpha & x_0 \\ S_x \sin \alpha & S_z \cos \alpha & z_0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} x \\ z \\ 1 \end{bmatrix} \quad (24)$$

Assuming that we know the density difference between the two phases and gravity, this results in four additional optimization parameters to account for besides surface tension γ and apex radius of curvature R_0 to match the two profiles: x_0 and z_0 (the location of the data's origin on the model axes), α (the angle of rotation between the two frames), and S_z (vertical scaling between the two frames). S_x is not part of the optimization routine because to return a unique solution one cannot simultaneously optimize both scaling terms (S_x and S_z) alongside R_0 . We determine S_x by measuring the diameter of the needle holding the pendant bubble both graphically (in number of pixels counted from the image after edge detection) and physically (using a vernier micrometer) and calculating the ratio between the two. Conveniently, scaling and rotation components of transformation matrix are determined by the physical rotational misalignment between bubble and the camera's lens and the lens's geometry, respectively. This means that once they are determined for the first image in a set from a single experiment by optimization, the same values can be reused for any other images from that experiment, reducing the number of optimization parameters down to four (x_0 , z_0 , R_0 , and γ).

It is helpful to have reasonable estimates for all the parameters when performing the optimization routine. Estimates for x_0 , z_0 , and R_0 are found by fitting the top 100 points of the drop shape to a plot of a circle (as shown on the left of Figure 19) and determining the values from the circle's radius and the coordinates of its center. The sub-pixel located edge profile can be used to approximate the measurements needed to determine surface tension from the shape factor $S = d_e/d_s$ (as shown on the right of Figure 19).

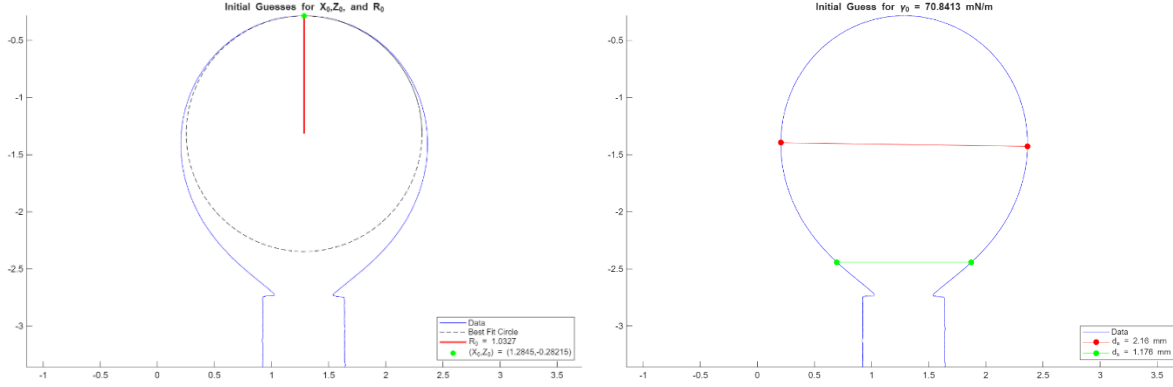


Figure 19: Method of determining reasonable initial guesses for x_0 , z_0 , and R_0 by curve fitting a circle to the apex of the drop profile (left) and for a reasonable guess for γ by estimating the shape factor $S = d_e/d_s$ (right)

Optimization Model

As previously stated, this method of graphical tensiometry improves on the previous methods using shape factors by being able to perform multiple surface tension measurements from the same image by using different smaller subsets of profile coordinates selected from the full profile. Consider the n -th profile coordinate in a set of N profile coordinates. The linear distance between the location of this coordinate in the model's reference frame (x_n, z_n) and its corresponding location on the experimental reference frame (X_n, Z_n) is d_n . The least squares between these two points, e_n , can be expressed in terms of its constituent vertical and horizontal components

$$e_n = \frac{1}{2}d_n^2 = \frac{1}{2}(e_x^2 + e_z^2) = ((x_n - X_n)^2 + (z_n - Z_n)^2) \quad (25)$$

which can be separated using the transformation matrix from Equation 24.

$$e_x = x - x_0 - S_x X \cos \alpha + S_z Z \sin \alpha \quad (26a)$$

$$e_z = z - z_0 - S_x X \sin \alpha - S_z Z \cos \alpha \quad (26b)$$

So, ultimately, the objective function to minimize using numerical optimization for a set of N points selected from a drop shape profile is

$$E = \sum_{n=1}^N e_n \quad (27)$$

To further reduce the influence of the error of any random point, M different sets of N points are selected from the drop profile extracted from an image for optimization. The final reported value for surface tension is the average result of the M optimizations. We perform these M optimizations with a smaller number of points than one single optimization with the entire profile for measurement redundancy, computational efficiency, and to reduce the impact of random uncertainty of any single profile point. When using $N > 50$ for a pendant drop with a defined neck (i.e. elongated from a spherical shape), the ADSA technique is highly accurate. Being able to use a smaller set of fewer points was a larger concern when computing power was limited by the technology of the time, but with modern processors that is less of a concern. We found that a routine of $M = 10$ larger sets of $N = 500$ coordinates provided a satisfying balance of computation time and measurement stability for our experiments. Additionally, it is important to select these points in such a way that it is representative of the entire profile. Selecting points from only the area of the apex returns of nearly circular profile which is less accurate for ADSA as discussed above. The points in the region of the neck of the bubble are the most important to be included, analysis of this technique has shown a breakdown in the method correlating to smaller vertical ranges (from the apex of the drop) of point selection.

Axisymmetric Liquid-Fluid Interface Smoothing

The larger number of points also allowed us leeway to reject some of the points while still retaining a larger set for optimization when we applied our noise removal method for adhering

noise. Unlike the method for removing isolated noise as explained in an earlier section which can be done prior to edge detection, the technique we use to remove adhering noise (axisymmetric liquid-fluid interface smoothing, ALFI-S) can only be done as part of the optimization process on a set of located edge coordinates.

ALFI-S was developed by Zou et al. (2004) and consists of using repeated optimization routines that an experimental and analytical drop shape profile to remove any distortion to the profile's shape due to any adhering noise. Examples of such noise are shown in Figure 10. Once an optimized profile is determined, we find the average and standard deviation of the set minimum distances it found for each profile coordinate, d_n from Figure 18. Assuming these values form a normal distribution, any coordinate whose distance is more than three standard deviations different than the average distance can be safely excluded as erroneous with 99.7% confidence according to the empirical rule. The optimization routine is then repeated without these coordinates.

This process is repeated until no points are rejected. Part of the reason we selected a larger number of points N for our M optimizations for each image is to have a set that can be reduced in number without compromising its accuracy for curve fitting. Even though it adds considerable computation time, the benefit of this approach is that it can remove aberrations in the bubble image that previous noise removal steps missed. Our earlier methods can remove isolated noise (outlining suspended particles in the solution and the internal highlight from the backlight) but are unable to remove adhering noise (things that stick to the profile itself). Figure 20 shows how suspended particles identified as part of the profile by edge detection at two different locations on the bubble are removed by ALFI-S.

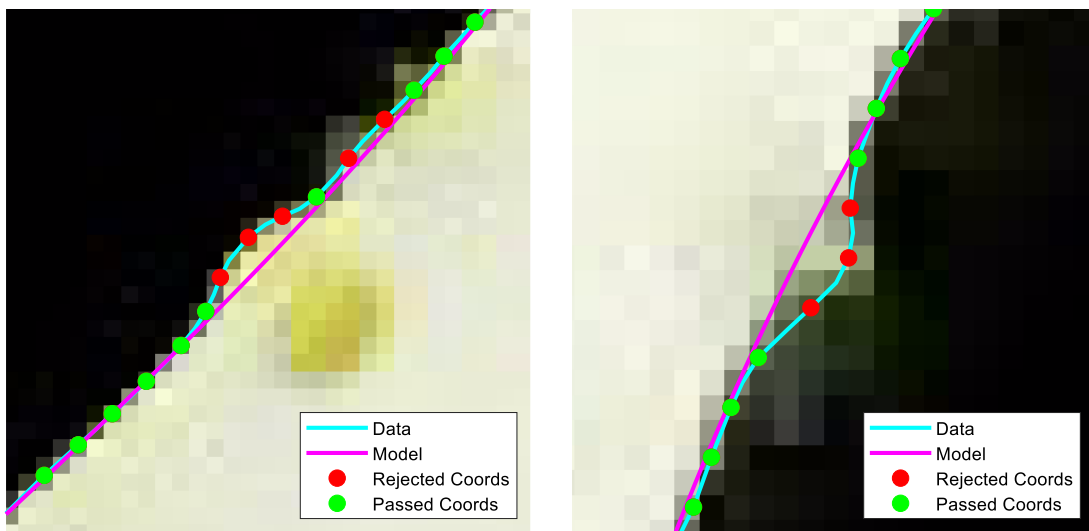


Figure 20: ALFI-S is used to exclude adhering noise from the set of profile coordinates used in the optimization routine to measure surface tension

Surfactant Tension Measurement

Validation of Measurement Procedure

We validated our measurement apparatus and procedure against literature values for the surface tension of pure water and isopropanol. For both liquids we took sixty images over five minutes at a steady 20°C ambient temperature under the same lighting conditions required to prevent uncontrolled photoconversion of surfactant laden solutions. Each image was analyzed $M = 10$ times using $N = 500$ randomly selected points from the profile, and subject to ALFI-S noise removal. We measured the surface tension of distilled, deionized water to be 72.45 ± 0.02 mN/m (compared to a NIST reported value of 72.74 mN/m for liquid water at the same temperature) and that of isopropanol to be 21.23 ± 0.32 mN/m (compared to a NIST reported value of 22 mN/m). The larger uncertainty in our measurement of isopropanol's surface tension is likely due to the much smaller bubble volume isopropanol can form before being detached from the holder by

buoyant forces. Though slightly underestimating literature values (which could be due to trace contaminants in our test fluids), our method shows good accuracy and repeatability.

Transient Surface Tension Measurement

Figure 21 shows a selection of transient surface tension relaxation curves of aqueous solutions of photosensitive azobenzene-type surfactants at various concentrations and initial photostationary states. Each of the experiments start with surface tensions near that of pure water and relax towards values that match existing literature values for the surface tensions of interfaces saturated with *-cis* or *-trans* photoisomers. Our results also show qualitatively similar results to those of Ciccirelli et al. (2007), who performed similar measurements of transient surface tension of a pendant bubble in a surfactant-laden solution using axisymmetric drop shape analysis.

Blue light adapted trials of solutions with concentrations of 1 mM (purple circles) and 20 μ M (dark blue circles) show a two-step relaxation behavior as expected due to the differing rates of adsorption of the two species. *-cis* isomers adsorb more rapidly but are squeezed off the interface by the slower adsorbing but more densely packing *-trans* isomers. Both curves trend initially towards surface tension values near the 39.6 mN/m value reported by Shang et al. for a *-cis* saturated interface and then towards values like Shang's 28.9 mN/m for the *-trans* saturated. These two trials also illustrate the impact that solution concentration has on the timescale of relaxation. While both solutions are above the critical micelle concentration for both isomers and trend towards the same values of surface tension, the lower concentration solution takes much longer to do so.

Our trial with a 20 μ M sample kept in the dark (light blue triangles) to ensure an all *-trans* isomeric composition only trended towards the lower surface tension value since there were no -

cis isomers present as expected. It also shows a comparable time scale for relaxation compared to the other 20 μM solution.

Finally, our trial using an all *-trans* solution with a concentration of 1 μM (green triangles), which is below the critical micelle concentration of the surfactant, shows single step relaxation to a higher saturated interface value. This also likely matches the results from Shang et al. (if their graph is interpolated) that show below the critical micelle concentration the saturated interface surface tension decreases with concentration.

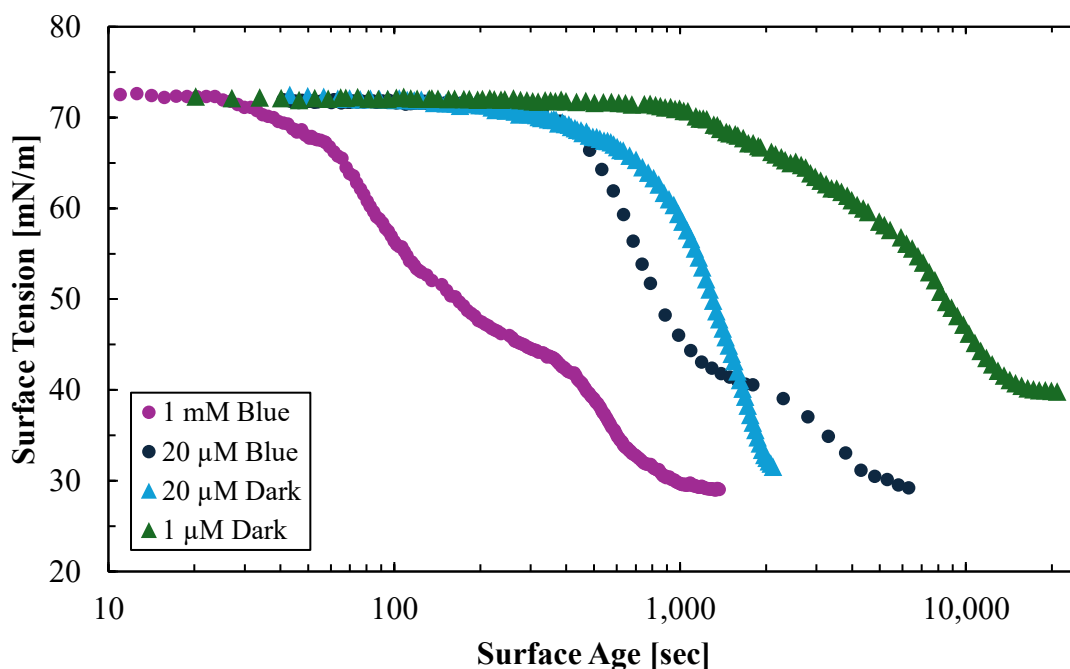


Figure 21: Transient surface tension relaxation curves of aqueous solutions of photosensitive azobenzene-type surfactants at various concentrations and initial photostationary states

An ASCII formatted tabular record of the data shown in Fig. 21 is included in the Appendix. Archived (not explicitly included for the sake of brevity) data from additional, redundant, or less comprehensive experiments, and data from experiments using pure water or isopropanol to validate our methods are available upon request from Professor Marc Hodes of Tufts University.

The pendant bubble images themselves and the MATLAB code used to analyze them are also available upon request as well.

My work was limited to the development of our surfactant characterization and surface tension measurement methods, and the collection of the transient surface tension data. The extraction of the unknown adsorption and desorption coefficients from this data is the responsibility of our collaborators at Imperial College London. That work is still ongoing and will be published in full in a forthcoming paper not included in this thesis.

Figure 22 (reproduced with the permission of its author, Dr. Michael Mayer) illustrates some preliminary results from that work. Our collaborator's developing transient surface tension model already shows promising ability to match my experimental data and report realistic values for the desired thermophysical properties of interest.

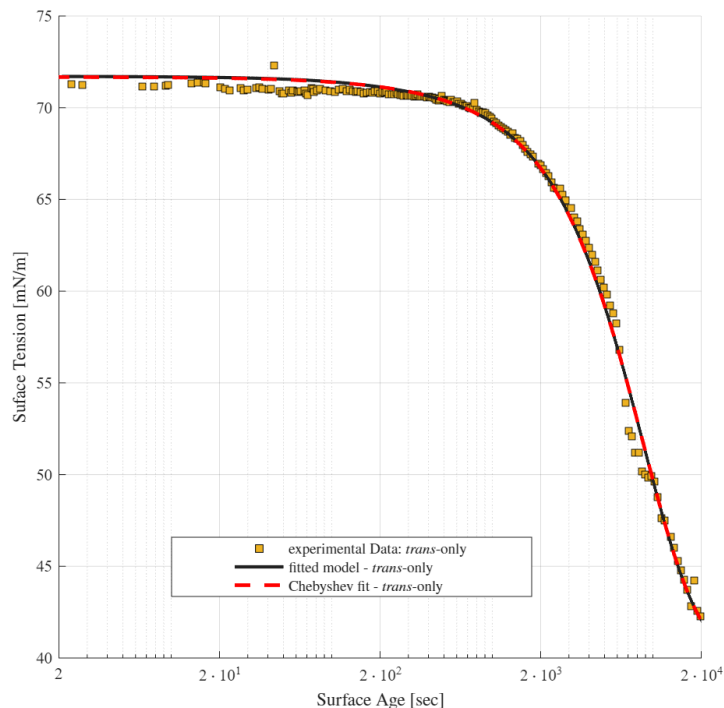


Figure 22: Preliminary results from matching my experimental measurement of transient surface tension to an equivalent model developed by our collaborators at Imperial College London (reproduced with permission from Dr. Michael Mayer)

Internal Flow Microchannels with Reentrant Structures for Low-Surface Tension Liquids

Background and Overview

We are developing a first of its kind internal flow microfluidic device with reentrant structures for the purpose of suspending low surface tension liquids over textured hydrophobic surfaces in the non-wetting Cassie state. The project was developed as part of our experiments with

Figure 23 shows the difference between the fully developed streamwise velocity profiles between two parallel plates for a situation where the walls have a no-slip boundary condition (A, on the left) and one with apparent slip along the wall (B, on the right).

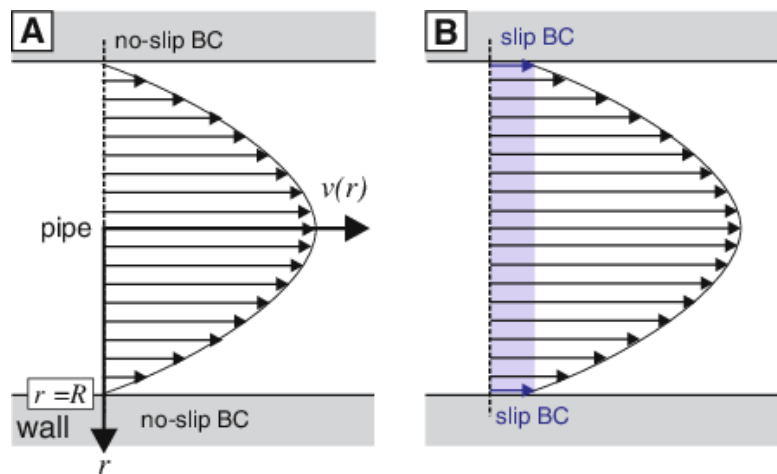


Figure 23: Streamwise velocity profiles for no-slip (A, left) and apparent slip (B, right) boundary conditions. Figure reproduced from Luo et al. (2021)

Couette flow between two solid parallel plates has a velocity profile like the one shown in Figure 23(A) due to the viscous forces at the wall inducing a liquid-solid no-slip boundary condition between the two phases. The profile shown in Fig. 7(B) could be from liquid flow suspended by ‘plates’ of vapor. The boundary condition between a liquid and a vapor is nearly

shear-free since the shear forces exerted by the vapor on the liquid are negligible compared to those of the liquid on the vapor. This means the two can phases can flow together with a non-zero velocity along the ‘wall’. While suspending a liquid phase in a vapor phase is not feasible for most applications, a textured wall with a mixed solid-vapor boundary condition can still produce some hydrodynamic slip since the average velocity along the wall (over both the no-slip solid and shear-free vapor phases) would be non-zero.

The left image of Figure 24 shows an isometric view of a schematic for an internal flow microchannel with a mixed boundary condition of transverse ridge on the walls of the channel. As liquid fills the channel, the surface tension of the liquid causes menisci to form between the ridges, the so-called non-wetting Cassie-Baxter state. As the ratio of the solid contact area to vapor contact area for the fluid becomes smaller (i.e. more of the perimeter of the channel is vapor rather than solid) the channel would theoretically produce progressively more apparent slip.

The right image of Figure 24 shows a top-down view of a similar microfluidic channel made of polydimethylsiloxane (PDMS, a silicone-based polymer commonly used when making microfluidic devices) molded from a negative mold made using photolithography being filled with water seeded with fluorescent microparticles to visualize the flow. You can see how as the bolus of water fills the channel from left to right menisci are formed between the ridges suspending the fluid over trapped plastrons of air. The liquid has a no-slip boundary condition where it contacts the solid ridges (zero velocity) and a nearly shear-free one where it flows over a suspended meniscus (non-zero velocity). Because of this mixed boundary condition, the mean streamwise velocity of the flow over the effective wall at the tips is non-zero.

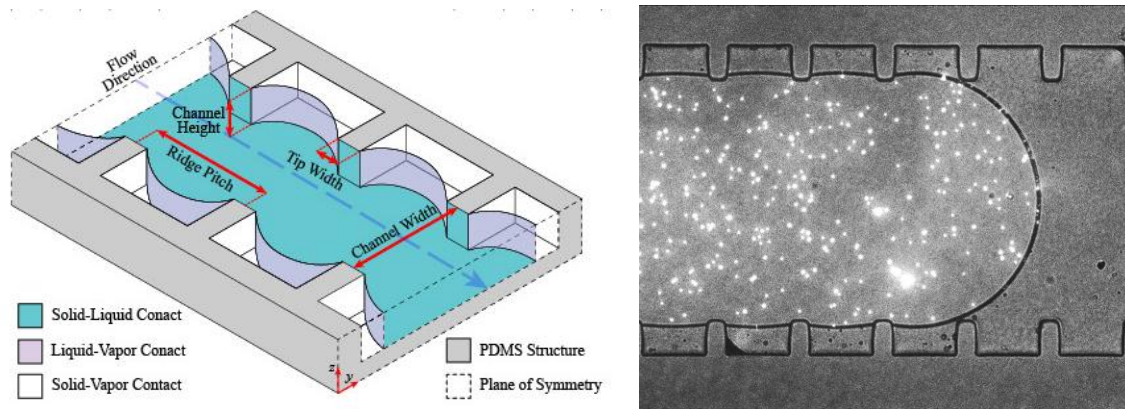


Figure 24: A drawing of transversely ridged hydrophobic microchannel marked with relevant geometric properties **(left)** and a PDMS microfluid device being filled with water **(right)**

Experiments to measure the apparent slip of a liquid flowing over mixed-boundary condition interfaces are most often done with liquids that have a higher surface tension than the azobenzene-laden solution or an alcohol, such as water, since their Cassie state is more easily formed and maintained due to larger advancing contact angles. A more robust Cassie state means the liquid can form larger menisci before wetting, reducing the overall solid-vapor fraction of a channel and increasing its apparent slip. Slip experiments with low-surface tension liquids are not possible because their advancing contact angles are less than ninety degrees, meaning they will not be able to form suspended menisci large enough to cause meaningful slip and will instead wet fully into the hydrophobic structure, the so-called Wenzel state.

However, you can increase the apparent contact angle of the liquid by adding reentrant features to the hydrophobic structures. Figure 25 shows reentrant “nanonails” fabricated by Ahuja et al. (2007). See how even with an acute contact angle, the liquid is unable to wet around the structure’s overhanging head due to the surface tension forces.

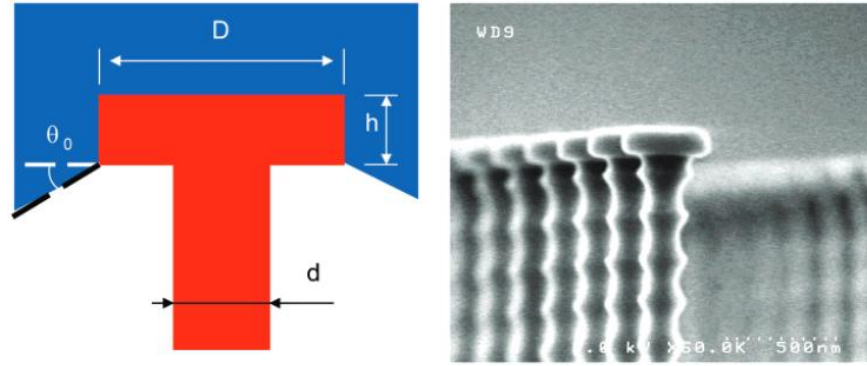


Figure 25: Superhydrophobic reentrant “nanonails.” Figure reproduced from Ahuja et al. (2007)

Reentrant structures have been used to suspend drops or sheets of low surface tension liquid in the Cassie state over flat surfaces, but they have not yet been used in internal flow applications. Integrating these structures into existing slip channel design could increase the range of liquids that are viable for internal flow slip-length experiments.

Reentrant Channel Design

Structural Unsuitability of PDMS

Many microfluidic devices are cast from PDMS on molds made using SU-8 soft lithography then permanently covalently bonded to a glass viewing slide to seal the open face of the channel. Using a design like the one used by Byun et al. (2008), we were able to produce transversely ridged channels capable of very limited formation of the Cassie state when filled with water but were unable to suspend menisci using a lower surface tension fluid like our azobenzene photosurfactant. Even when the hydrophilic glass slide used to seal the channel was replaced with a flat sheet of hydrophobic PDMS, it was still common to see menisci collapse into the trenches between the ridges by wetting along the smooth floor and ceiling of the channel. It was at this point that we realized we needed to incorporate reentrant features into our design if we wanted to be able to suspend aqueous solutions of our photosurfactant (which can demonstrate surface tension

as low as ~ 30 mN/m) in the Cassie state. These features would also not only need to be along the transverse ridges on the wall but also along the ceiling and floor of the channel as well.

Even if the vertical ridged structure of the PDMS could be changed from flat ridge tips to a reentrant style “nail head”, this channel still would not be able to flow a low-surface tension liquid in the Cassie state because the standard PDMS mold making techniques would not be able to create reentrant edges along the floor and ceiling due to. PDMS devices are made by pouring liquid PDMS over a mold and then releasing the PDMS from the mold once it has cured into a solid by peeling it off the mold substrate. Even if a mold for a reentrant channel could be made, the PDMS would likely either be unable to flow into the small features of the mold required for proper reentrance or be unable to be removed from the negative shape of the mold surrounding them without being torn off.

Chemical Unsuitability of PDMS

The polymer nature of PDMS means that any uncured monomers in the solid sometimes diffuse into the internal liquid flow of the channel (Hourlier-Fargette et al. 2018). Biological research is often concerned about how this may taint sensitive samples (Regehr et al. 2009), but here we are concerned that these trace amounts may alter the interfacial properties of the vapor-liquid meniscus. The bulk flow of the liquid pushes any surfactants adsorbed to menisci downstream to collect at solid triple-contact points. This creates a low-to-high surfactant concentration and accordingly a high-to-low surface tension gradient. Gradients in surface tension can induce Marangoni stresses on the surface of the liquid strong enough to affect the bulk flow of the channel. Previous work by Peaudecerf et al. (2017) has shown that even trace amounts of surfactants can create enough of a concentration gradient to immobilize menisci by inducing Marangoni stresses adverse to the flow.

Methods using thermal aging or solvent baths are sometimes used to purify the PDMS of these monomers, but these methods can impact the hydrophobicity of the material. PDMS is often exposed to oxygen plasma to temporarily render it hydrophilic and promote covalent bonding between it and another active surface as a means of sealing the open channels made by photoresist molds. The surface typically regains its hydrophobicity within an hour of exposure to oxygen plasma as the low molecular weight species in the PDMS (non-crosslinked monomers) diffuse back to the purified surface, but if these monomers are driven from the PDMS it might not fully recover the hydrophobicity necessary for a superhydrophobic surface. Eddington et al. 2005.

SU-8 Photoresist for Channel Construction

Byun et al. (2008) made textured microchannels with their periodic ridge pattern transverse to the flow along the vertical sidewalls of the channel. We originally intended to mimic their design since it allowed them to directly image the flow using particle image velocimetry (PIV) image analysis without the use of a confocal microscope. After we decided that PDMS would not be suitable for our channel, we started to develop a microfabrication procedure to add reentrant features around the perimeter of the vertical trenches by using SU-8 negative tone photoresist as the main structural component of the channel instead of just as the mold of the channel (as it is more commonly used).

Ceyssens and Puers (2005) and Mata et al. (2005) were able to successfully use successive layers of SU-8 photoresist to create freestanding microstructures by using a series of photomasks and selective exposure parameters (as shown in Figure 26, reproduced from Ceyssens and Puers (2005)).

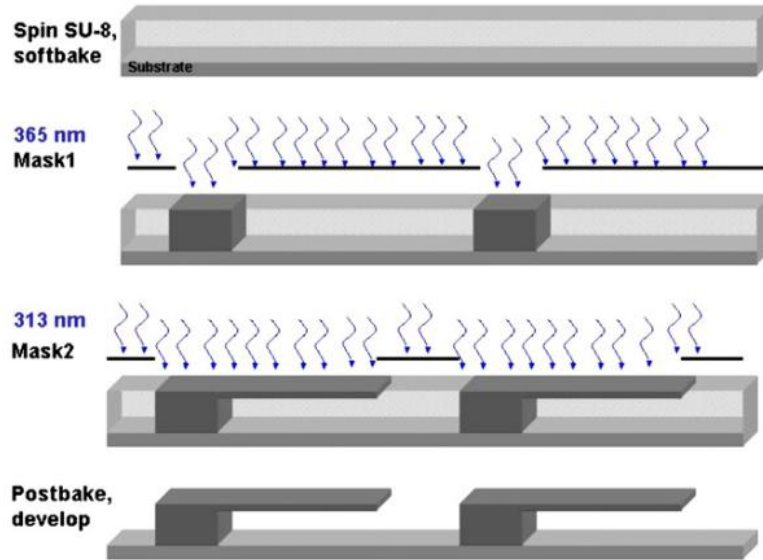


Figure 26: Example of multi-layer SU-8 device fabrication reproduced from Ceyssens and Puers (2005)

Ceyssens and Puers differed from Mata et al. in how they approached the formation of the separate layers. Ceyssens and Puers used a single formulation of photoresist for their entire devices and created the separate layers explored using variable wavelengths of UV in their exposure step and buried masking between the layers using metal deposition. We decided not to pursue this method due to the additional equipment and added complexity of metal deposition. Mata et al. used two different formulations of SU-8 (2100 and 2010) and found that overhanging structures were more reliably created when spinning SU-8 2010 onto 2100 instead of the opposite. They attributed this to the lower viscosity formulation of the SU-8 requiring a much shorter exposure dose than the higher viscosity lower layer. When SU-8 2010 was used as the top layer, despite the optical clarity of the photoresist, the shorter exposure was sufficient to crosslink the top layer but not long enough to provide enough activation energy to the lower layer of SU-8 2100. When they attempted to use SU-8 2100 as the top layer, the higher exposure dose would also fully crosslink the buried layer of SU-8 2010.

Figure 27 shows a top-down view of our initial design for three successive layers of SU-8 photoresists to construct vertical trenches on the sidewall with reentrant features around the full perimeter of the trench. The middle layer (blue) is essentially the channel design of Byun et al., with the rectangular ridges given flanges. The first and third layers (red and green) are both a part of the vertical, flanged ridges and provide barriers along the ceiling and floor of the channel.

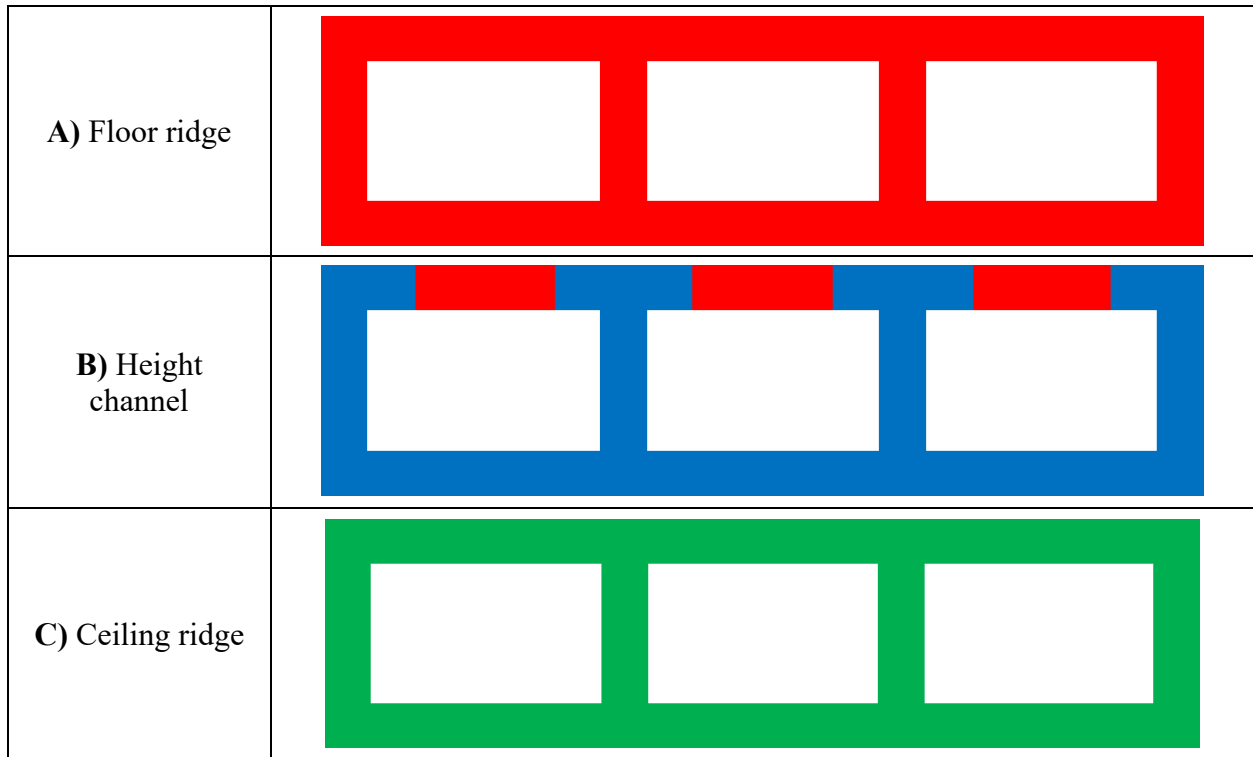


Figure 27: Successive layers SU-8 films selectively exposed to create vertical reentrant ridges

Unsuitability of Vertical Transverse Ridges

The two advantages the vertical trench design has over the horizontal design are the fewer number of spin-on and exposure alignment steps and the ease of imaging. Byun et al. was able to use their design to directly image the velocity profile of a channel using a single optical microscopy measurement instead of a series of confocal images across the height of the channel seen in other papers doing similar work. However, early prototyping in the clean room did not show promising

results when attempting to use multi-layer structures to form the side walls. Sharp corners were difficult to realize at this small scale with our equipment and the multiple layers proved challenging to reliably align, among other issues.

Additionally, further modeling done by our colleagues at Imperial College London showed that our wall ridges were likely not capable of providing a low enough solid-vapor contact ratio around the perimeter to show appreciative slip. While this might not be an issue for a channel simply being used to demonstrate the feasibility of using SU-8 to create internal reentrant structures we had hoped to use the channel as the foundation of the project explained the following chapter where we intended to use patterned light exposure on the microchannel to induce chromocapillary driven flow. Shorter menisci would lead to reduced chromocapillary (as well as reduced hydrodynamic slip) as well as complicate the micropatterning of masking to selectively expose the menisci to two colors of light.

Final Channel Structure

This led us to alter our design to create a channel with streamwise ridges along the floor of the channel instead of the walls. This would allow for much larger menisci by using an array of micrometer wide trenches (suitable for sustain menisci in the Cassie state) that are millimeters long.

The device will consist of a straight rectangular channel with an array of side-by-side trenches with reentrant edges on its floor. We are using a row of thinner trenches as opposed to one single wide trench in hopes that it will be easier to maintain the Cassie state. The rounded shape of the ends of the trenches should provide a more gradual transition to and from the full open with of the trench. This also removes the need to add mouse bites to the outer corners of the wall ridges to realize sharper features (a common issue in photolithography. The trenches will be much longer

than wide (centimeters as opposed to micrometers) in the streamwise direction) to provide a much lower solid-vapor contact ratio than the wall ridges channel.

Figure 28 shows a streamwise and top-down view of the channel (not to scale) with some key geometric design parameters. The beginning and end edges of the trenches transverse to the flow are half circles as opposed to flat in hope that it helps the advancing front of liquid cover the trench gradually as the channel fills not wet into them.

Figure 29 shows a more detailed view of a segment of the streamwise view of the channel. In this view, the channel would consist of two wall sections with a variable number of repeating sections to add as many trenches as desired to a channel design. Relevant geometric parameters and the approximate scales that they were designed for are explained in Table II.

Table II: Relevant geometric parameters of reentrant channel design and approximate dimensions

Label	Parameter	Dimension [μm]
<i>b</i>	Nail base width	25
<i>g</i>	Gap to wall	50
<i>H</i>	Main channel sidewall height	50
<i>l</i>	Entrance/exit length for fully developed flow	~10 mm
<i>L</i>	Length of vapor plastron trench	~65 mm
<i>N</i>	Neil base height	30
<i>n</i>	Nail head thickness	5
<i>r</i>	Reentrant overhang / undercut	5
<i>t</i>	Neil head width / vapor plastron spacing	35
<i>T</i>	Width of vapor plastron trench	35

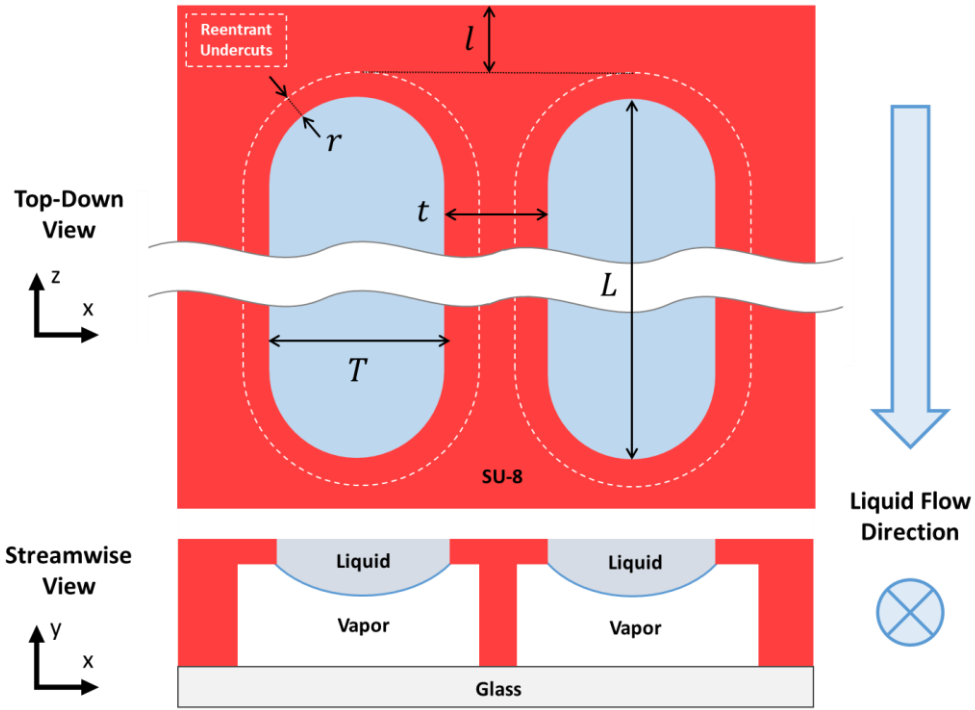


Figure 28: Top-down and streamwise view of reentrant channel showing the direction of flow and the location the reentrant undercuts. Dimensions and parameters explained in Table I.

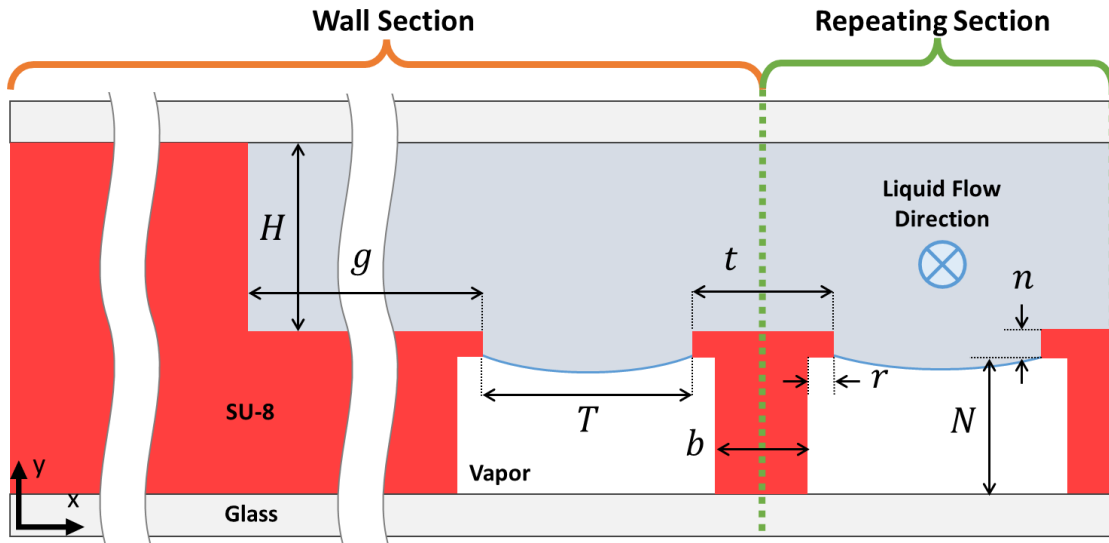


Figure 29: Detailed streamwise view of reentrant channel showing the direction of flow and relevant design parameters. Dimensions and parameters explained in Table II.

Microfabrication Plan and Potential Implications

The low surface tension of the photosurfactant-containing aqueous solution we plan to use in our experiments means that it would wet into the sort of ridged channels commonly found in literature for hydrodynamic slip experiments. We have designed the fabrication process for a microchannel design with reentrant ridges that will be able to flow low-surface tension liquid in the unwetted Cassie state. This would be a novel application of reentrant structures, which have up until now largely been used for external flow experiments. The structures of the trenches, nail heads, and side walls are built from the ground up using successive spin-coats and ultraviolet light exposures of stacked layers of SU-8 negative photoresist on a cleaned, transparent glass substrate that doubles as a viewing slide.

Figure 30 shows a sideview of the steps of the proposed process. The first layer of SU-8 (steps A-B) forms the periodic ridges. The second layer of SU-8 (steps C-D) forms the reentrant nail heads on the top of the ridges. The final layer of SU-8 (steps E-F) forms the side walls of the channel itself. A second viewing slide with trenches is made by repeating steps A-D and then skipping steps E-F directly to development. The two slides are thermally bonded together by applying pressure and heat. Step H shows a streamwise view of a completed, sealed channel. The summary of the process is as follows:

- (A)** Spin $30\text{ }\mu\text{m}$ layer of SU-8 2025 negative photoresist onto a glass microscope slide.
- (B)** Selectively cross the photoresist via patterned UV light exposure to create the internal walls of the ridges using first photomask.
- (C)** Selectively crosslink the photoresist via patterned UV light exposure to create the ridges' reentrant "nail heads" using second photomask.
- (D)** Spin on $50\text{ }\mu\text{m}$ layer of SU-8 2050 negative photoresist.

- (E) Selectively crosslink the photoresist via patterned UV light exposure to create the channel walls using third photomask.
- (F) Clear the non-crosslinked SU-8 with SU-8 developer (PM Acetate) to create the internal channel features
- (G) Seal the channel by bonding a second glass microscope slide to the open cavity

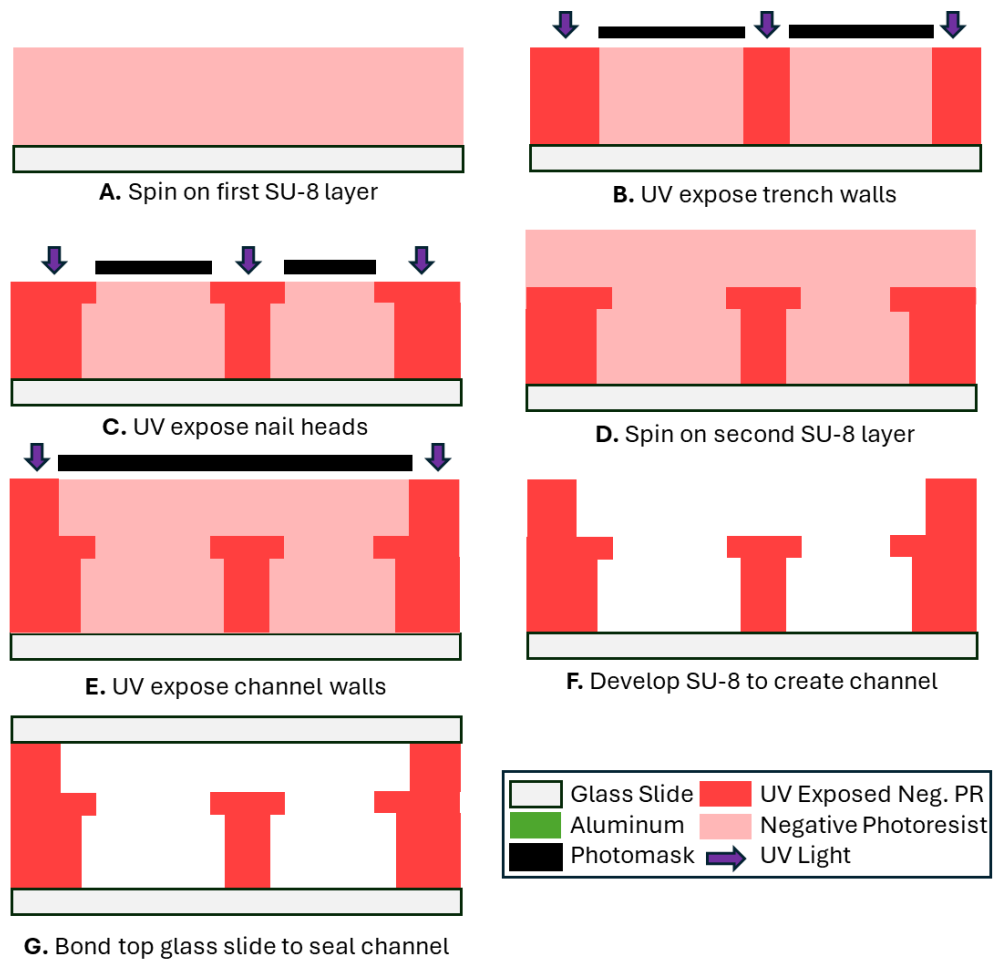


Figure 30: Proposed microfabrication plan for SU-8 reentrant channel

This additive fabrication method using SU-8 photolithography would also be a new method of creating reentrant features. Etching processes are often used to create these overhangs since that process naturally forms undercuts under the etching mask. We believe that photolithography would prove to be a more repeatable, faster, and safer process since etching times are highly condition

dependent (temperature, mixing, etchant concentration, etc.), often slow depending on the substrate being etched, and frequently use hazardous chemicals such as strong acids.

We still developed an alternative plan using wet-etching instead of our additive process in case our multi-layer method was unsuccessful, or we wanted to pursue an all-glass channel. An all-glass channel would be difficult to make hydrophobic (glass is hydrophilic) but we would have much greater surety that nothing from the channel's structure would be leaching into the flow. This proposed method is explained in the Appendix.

Our SU-8 structures would also be an increase in the size of typical reentrant features from the nanoscale to the microscale. If we can create reentrance at the microscale still capable of suspending menisci, it would open new design possibilities at a more accessible work scale. In microfabrication, the smaller the structures being created the more expensive and difficult to make they typically are. For example, being able to use mylar printed with emulsion photomasks instead of chrome on glass photomasks for lithography can mean a hundreds of dollars price difference. This would potentially open options for more rapid prototyping of a new class of microfluidic devices at a lower cost.

Fabrication Issues and Current State of Processing

Originally, we intended to take advantage of the different activation energies required by the two formulas during the UV exposure step to create the overhangs as Mata et al. did. The lower viscosity SU-8 was intended to crosslink in an exposure window short enough not to crosslink any of the higher viscosity SU-8 on the layer below. Unfortunately, we frequently observed delamination between the stacked layers of the different formulations of SU-8, as shown in Figure 31(A). We were able to prevent delamination with higher exposure doses, but this often resulted in both layers being fully merged and the loss of the reentrant features, as shown in Figure 31(B)

Our latest channels have shown much better reentrant features due to more gradual heating and cooling during the soft and post-exposure bakes (to manage thermal stresses) and sequential UV exposures on fewer, thicker layers of SU-8. Figure 30(C) shows one of our recent more successful lithography attempts where the difference between the two layers is more apparent. Figure 4(D) is an electron microscope scan of a diced channel that more clearly shows the overhang between the trench walls and nail heads. However, the dicing process is too destructive for us to get imageable cross-sections of every iteration, but between the scans we have been able to take and the progressively more distinct features we can see using optical microscopy, we are confident that each lithography attempt has more defined overhangs.

We are currently preparing these channels for optical microscope imaging using particle image velocimetry (PIV) to assess both the reentrant structure's ability to suspend low-surface tension liquids in the non-wetting Cassie state and any transient flows induced by the chromocapillary effect in photosurfactant-laden water. We plan to perform the PIV using long wavelength light since red hued light is less likely to cause photoconversion increasing our confidence that any flow is from a Marangoni stress we induce by shining ultraviolet light on the channel.

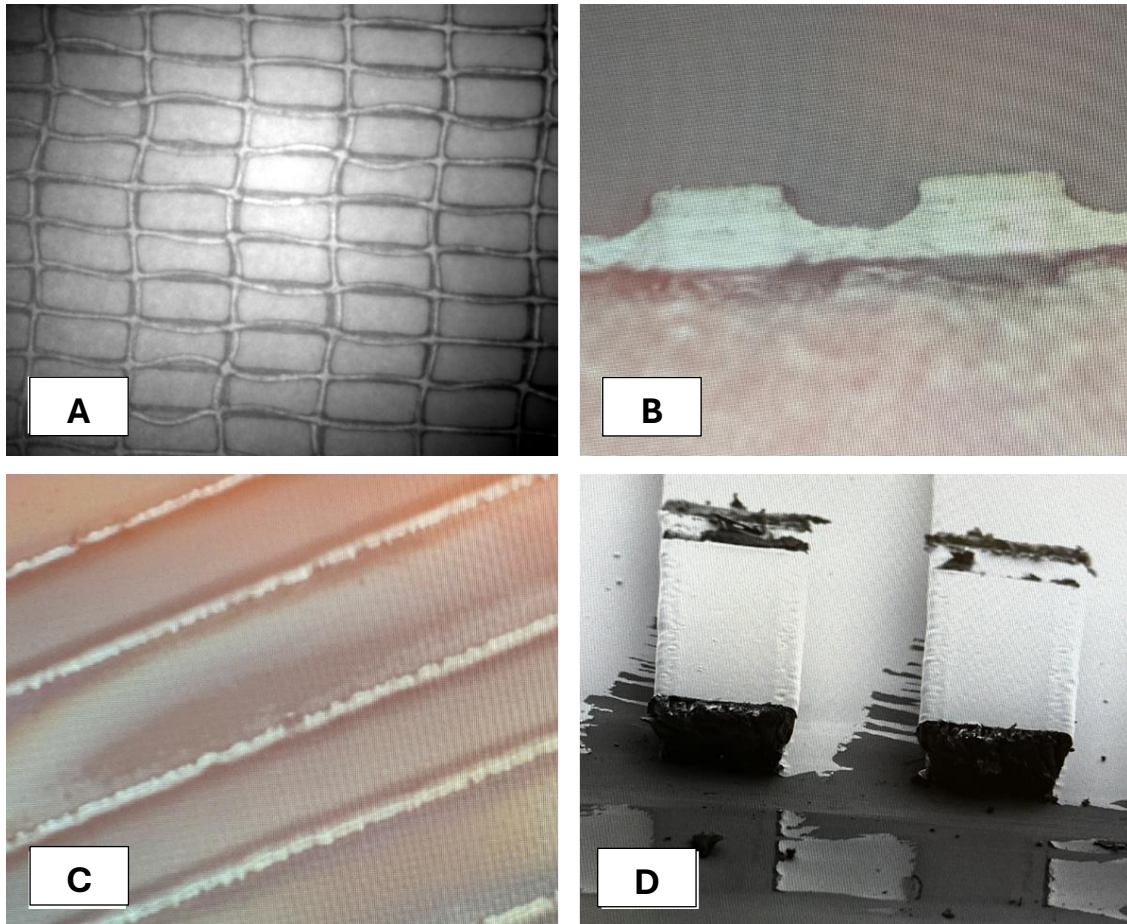


Figure 31: Challenges encountered during microfabrication (A-B) and recent advancements in creating reentrant structures (C-D)

Due to the unexpected closure of the Tufts University Micro and Nano Fabrication Facility in the final year of research, we had to contract outside clean room services at the University of Louisville. Our process has shown promising development at their facility, but work on this project has been suspended for the time being.

Light Driven Flow Using Chromocapillary Marangoni Stress

Background and Overview

The bulk flow of liquid carries surfactants adsorbed to menisci downstream to collect at solid triple-contact points. This creates a low-to-high surfactant concentration in the direction of the flow and accordingly a high-to-low surface tension gradient, as shown in Figure 32. Previous work by Peaudecerf et al. (2017) has shown that even trace amounts of surfactants can create enough of a concentration gradient to immobilize menisci by inducing Marangoni stresses adverse to the flow, eliminating the lubrication effect of the mixed boundary condition.

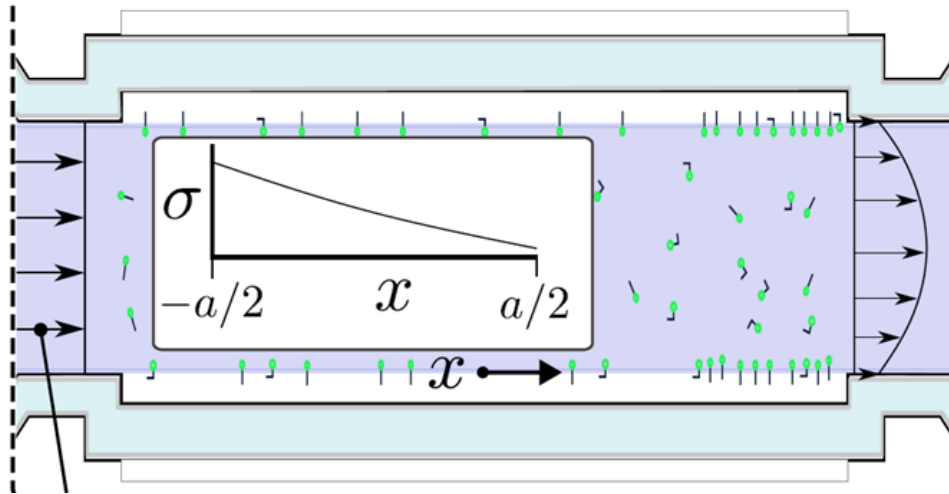


Figure 32: Adverse surface tension gradient induced by trace surfactants pushed to downstream triple contact points

The impact of this effect can be lessened (and hydrodynamic slip increased) by increasing the vapor-solid ratio at a mixed boundary condition, but larger menisci are more likely to undergo wetting from the Cassie state to the Wenzel state, eliminating the lubricating effect. The stability of the Cassie state of smaller menisci is more robust but are more susceptible to immobilization. In some cases, these Marangoni stresses can even reverse the direction of flow. Inspired by this

phenomenon, our collaborators at Imperial College London have developed a model for a potential method to enhance hydrodynamic slip over a mixed solid-vapor boundary by actively controlling the surface tension gradient along the liquid-vapor menisci in a transversely ridged internal flow channel. This is a small effect but constitutes unexplored physics of flow.

Photosensitive azobenzene-type surfactants more favorably undergo *cis-trans* or *trans-cis* isomerization depending on the wavelength of light they are exposed to, both in the bulk and on the interface. The two photo isomer states have different maximum packing densities on a liquid-vapor interface so they each induce a different relaxation in interfacial surface tension. Using targeted light exposure at specific wavelengths, optically tunable surfactants could be used to induce favorable rather than adverse surface tension gradients, as shown in Figure 33. Visible blue light on the upstream half of menisci will favor the more densely packing *-trans* isomer. Likewise, ultraviolet light on the downstream will favor the less densely packing *-cis* isomer.

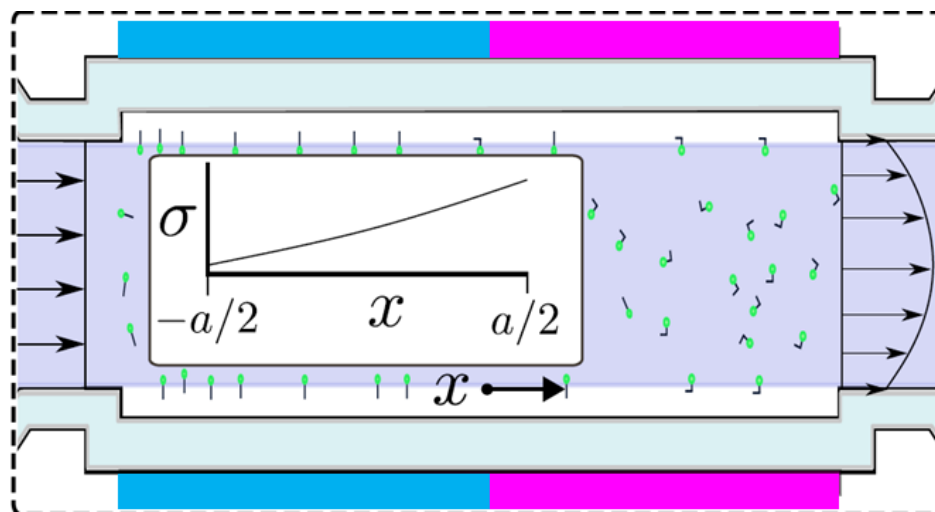


Figure 33: Favorable surface tension gradient induced by active control of the local relative ratio of *-cis* to *-trans* isomers of photosensitive surfactant

Chromocapillary Driven “Racetrack”

Since we expect the chromocapillary induced Marangoni effect to be modest relative to the bulk momentum of driven flow, our experiment demonstrating the effect will be a transient one on initially stationary fluid. Our proposed “racetrack” microfluidic device is shown in Figure 34.

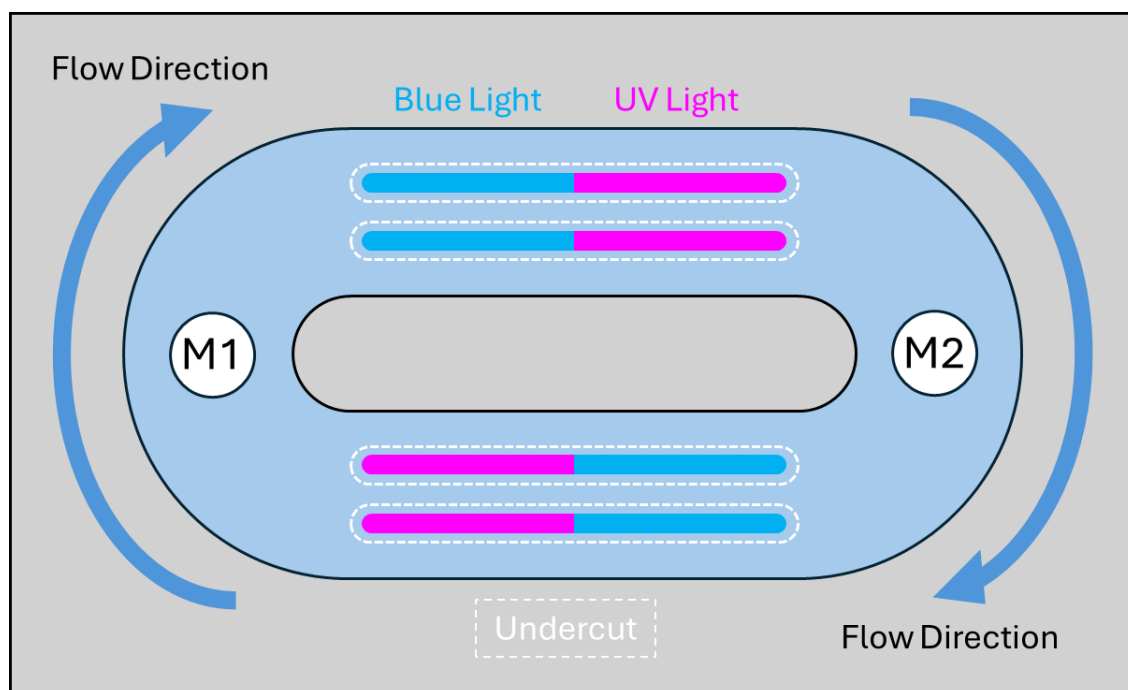


Figure 34: Microfluidic “racetrack” to demonstrate transient flow induced by chromocapillary driven Marangoni stress

We will make the device using multi-layer SU-8 lithography techniques to the project detailed in the previous chapter. But here, the channel will be a closed loop with two sections of reentrant trenches. The channel will be filled using the two ports labeled M1 and M2, fed by vertical glass capillary tubes. Potentially, by comparing the height of the fluid in the tubes after the device is filled, the two tubes could function as a rough manometer. When flow is induced by the chromocapillary effect, the change in pressure should be visible in a corresponding change in liquid rise in the tubes. However, since the chromocapillary effect is modest, we are not expecting to rely on that as means of measuring properties. Particle image velocimetry (PIV) could

potentially be useful as well to visual flow, but we are hesitant to add additional potential sources of surfactants (commonly used to prevent PIV microparticles from flocculating) from contaminating our flow given our modest predictions of the strength of the chromocapillary effect.

We expect the streamwise length scale of the trench sections illuminated by blue or ultraviolet light to be on the order of centimeters, so manual application of opaque masking will be sufficient to create the pattern of light exposure we desire. If this proves unable to induce appreciable chromocapillary driven flow requires micrometer scale patterning, so a process to create masking on the channel at the microscale is shown in the Appendix as well.

Unfortunately, as with the development of the internal flow reentrant channel required designed in the previous chapter, work on this project has been suspended due to the unexpected closure of the Tufts University Micro and Nano Fabrication Facility.

Appendix

Alternative Subtractive Glass Etching Method

As an alternative to our additive SU-8 method, we are also considering a subtractive method using a wet etching process and making the channel predominantly from glass. An all-glass channel is attractive in the surety we would have that there is no contamination from the structure itself, but later required glass-glass bonding may not be possible with the equipment we have at the Tufts Mico and Nano Fabrication Facility.

Etching an isotropic material, like glass, naturally creates an undercut under the etching mask into the material underneath. Wet etching is a common technique for manufacturing microfluid chips on glass, but the mask is typically stripped after etching before bonding. Instead, we want to leave the etching mask and use it as the reentrant structure itself. Figure A1 shows our proposed plan for this process and a complete channel.

If we are unable to wet etch to the desired trench depth without delamination of the etching mask, we will attempt to use a combination of deep reactive ion (DRI) etching with wet etching. The DRI process would not produce the undercuts that we require, but it could reduce the overall time in the etchant bath if the bulk of the material is removed first. Steps A and B of this process are the same as in Figure A1 and the differing steps C through E are shown in Figure A2.

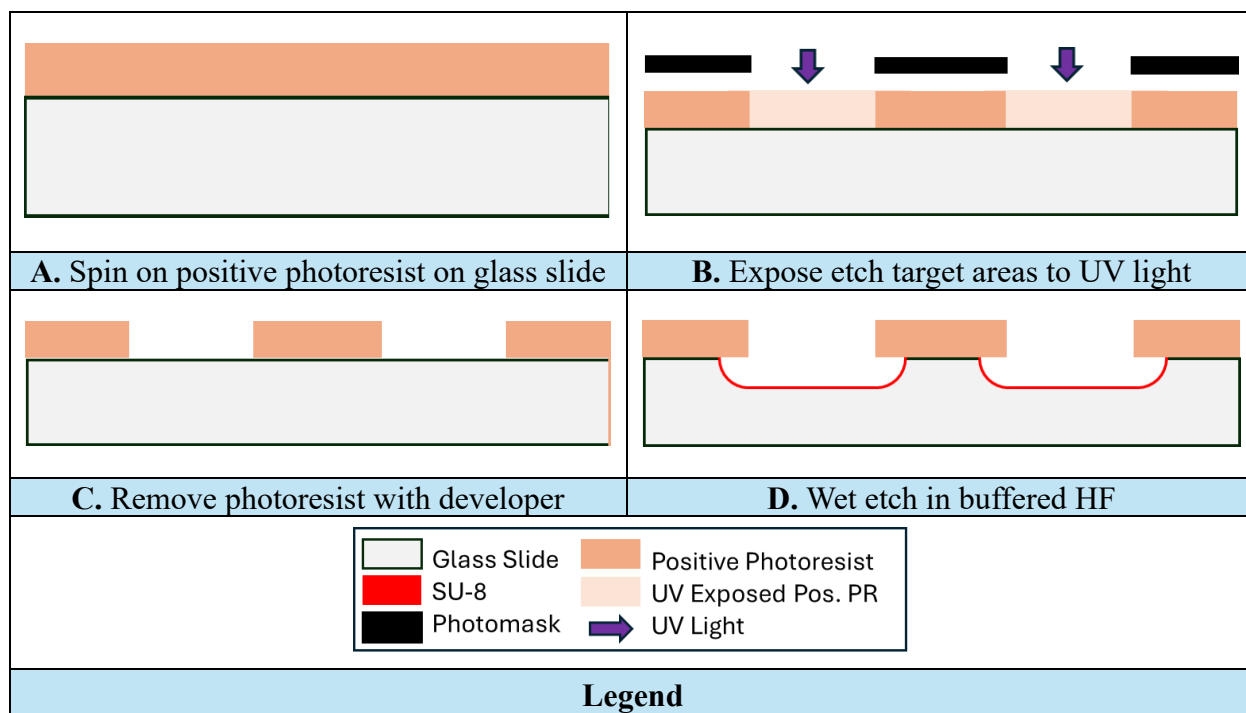


Figure A 1: Alternate microfabrication plan using wet etching

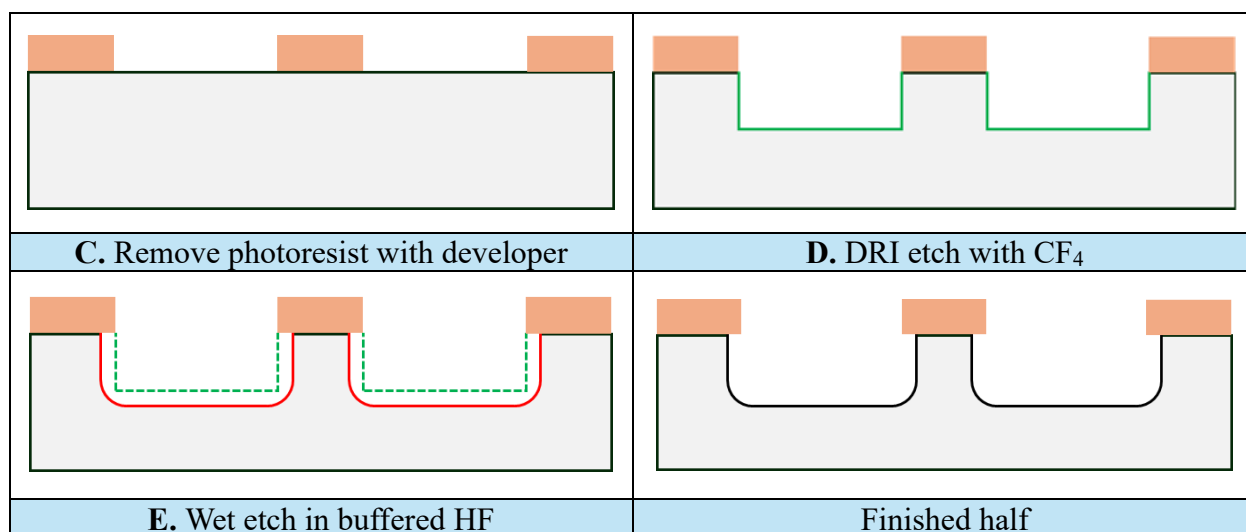


Figure A 2: Combined deep reactive ion and wet etching method

Finally, we have two options to seal this channel. One, perform a lithography process on a second glass slide to make the channel side walls (like the process outlined above). Two, use wet etching again to form the walls and ceiling of the channel out of glass. Both methods are shown in Figure A3.

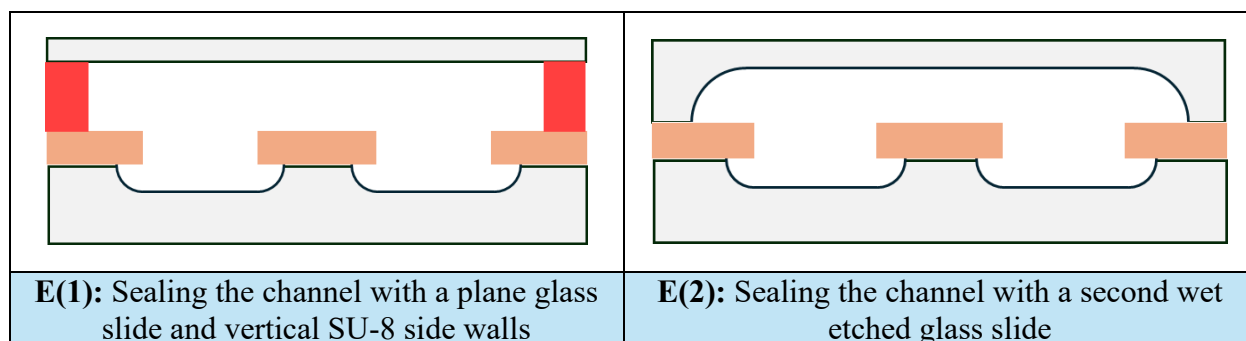


Figure A 3 Options for sealing the wet etched glass channel

Microscale Masking Pattern

We currently expect to perform our transient chromocapillary driven flow experiments under a millimeter scale light patterns but have additional plans for reducing that scale to micrometers, if needed. Our design uses photolithography of positive photoresist (where, opposed to negative SU-8 photoresist, the photoresist exposed to ultraviolet light is removed by the developer) to pattern a mask for sputter deposition of metal that is stripped from the substrate leaving on the desired metal layer behind. This process is shown in Figure A4.

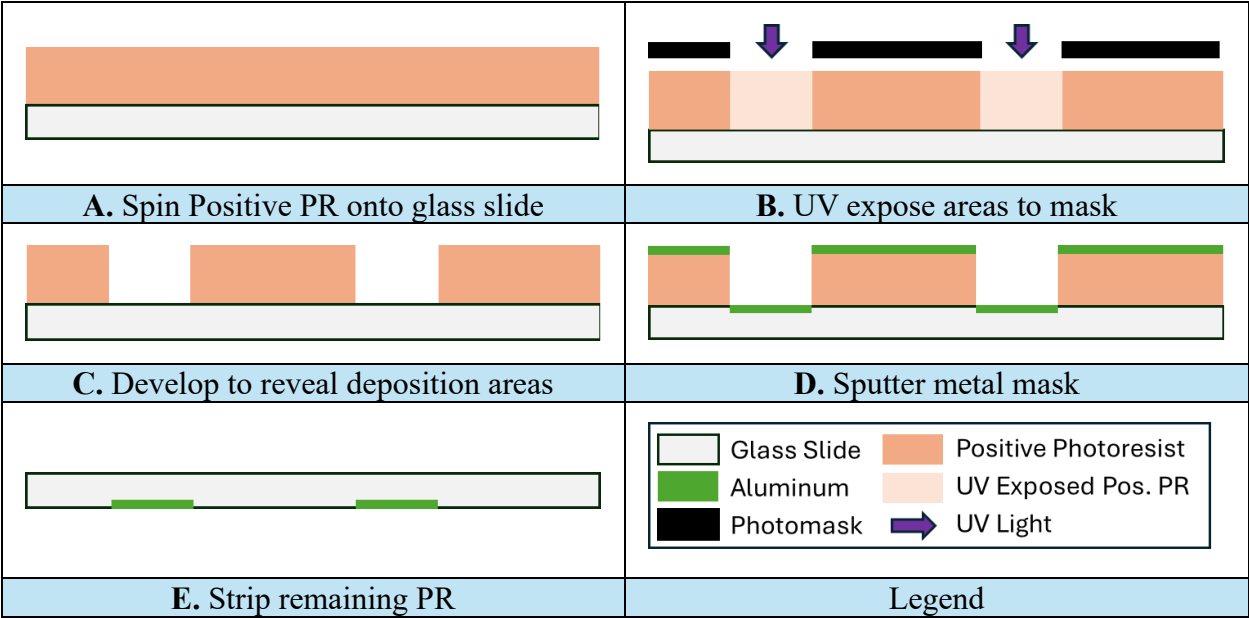


Figure A 4: Proposed microfabrication plan for a microscale masking pattern for period light exposure

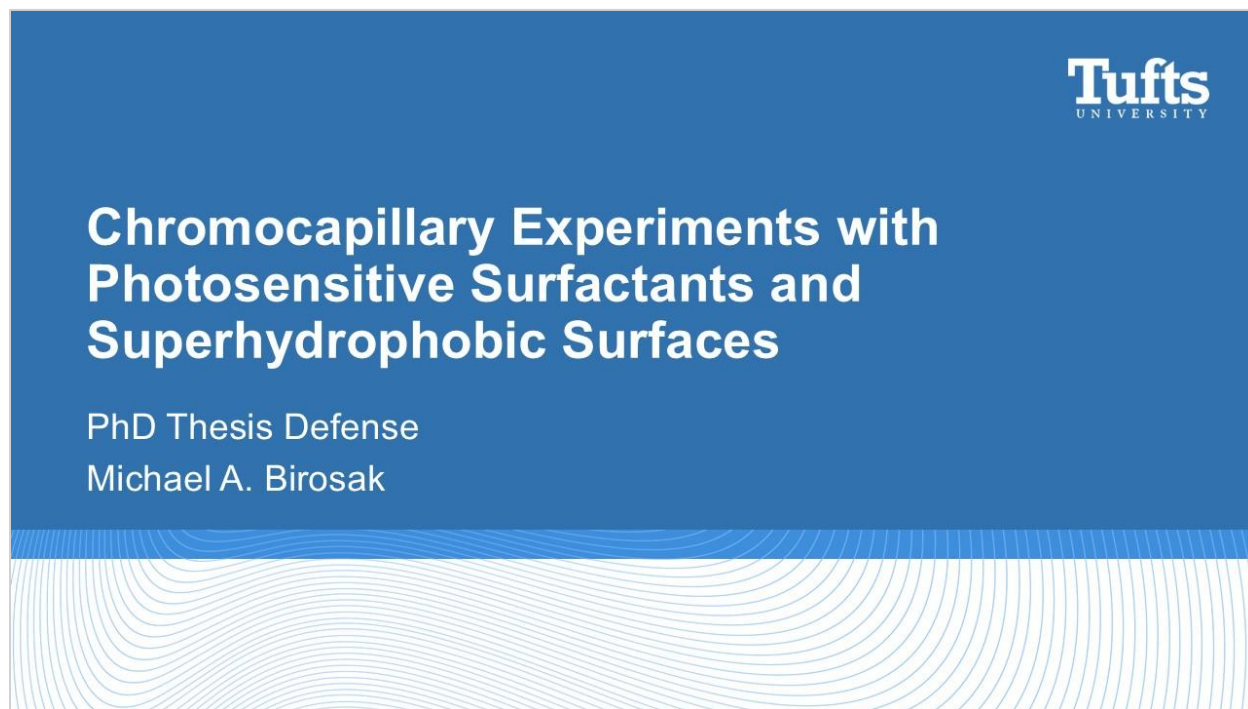
Thesis Defense Presentations

The following images are the two sets of overhead slides presented on December 5, 2025, at the public defense of this thesis. They are not individually captioned for the sake of brevity.

Surfactant Characterization

This first set of slides focuses on the background, methods, and results described in Chapter 1 (An Inverse Method for Measuring the Adsorption and Desorption Coefficients of Multi-Isotherm Surfactants), and then includes the Acknowledgements of this thesis.

Slides bordered in red contained an embedded video or some other moving graphical element that could not be printed. A description of the moving content is included below each slide as needed. An original copy of this presentation is available upon request from Professor Marc Hodes at Tufts University.



Outline

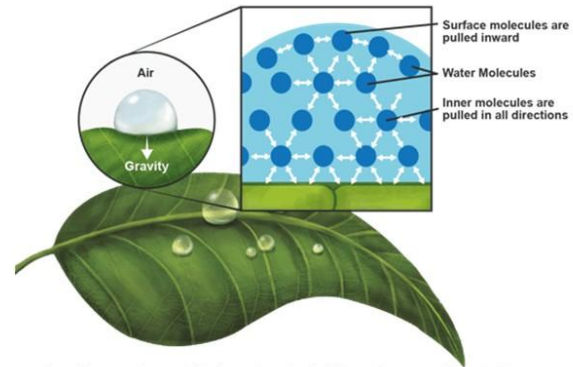
- 01 Inverse Method for Measuring the Adsorption and Desorption Coefficients of Multi-Isotherm Surfactants
- 02 Internal Flow Microfluidic Channel with Reentrant Structures for Low-Surface Tension Liquids (*separate slides*)
- 03 Light-Driven Flow in a Textured Microfluidic Device Using Chromocapillary Marangoni Stress (*separate slides*)
- 04 Acknowledgements and Dedication

Inverse Method for Measuring the Adsorption and Desorption Coefficients of Multi-Isotherm Surfactants

Surface Tension: γ

Liquid-Vapor Surface Tension

Stronger attractive forces between fluid molecules (**cohesion**) than between fluid and air molecules (**adhesion**) pull the interface **inwards**



<https://www.moleer.com/blog/horticulture/nanobubbles-surface-tension-for-soil-infiltration>

Soap Film on an Adjustable Wire Loop

Force and Work

Force

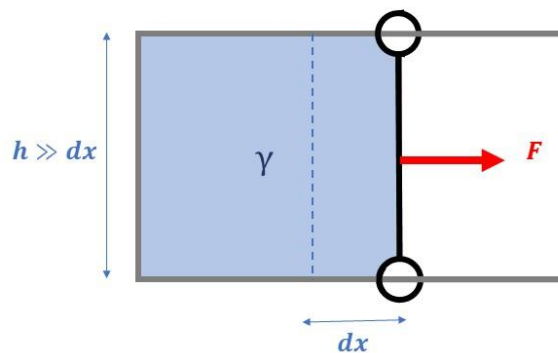
$$\Delta F_x = F - \gamma dx = 0$$

$$\gamma = \frac{F}{dx} = \frac{N}{m} = \frac{\text{Force}}{\text{Length}}$$

Work

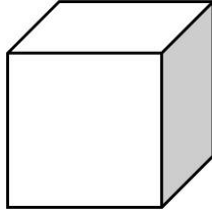
$$W = F dx = (\gamma dx) dx = \gamma dA$$

$$\gamma = \frac{W}{dA} = \frac{J}{m^2} = \frac{\text{Energy}}{\text{Area}}$$



Why are bubbles spherical?

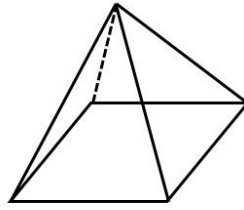
Volume = 1 m^3



Square Cube

$$l = 1$$

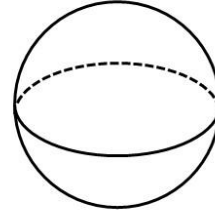
$$A = 6 \text{ m}^2$$



Square Right Pyramid

$$l = 4.5^{1/6}, \quad h = \left(\frac{3}{4.5}\right)^{1/3}$$

$$A \approx 5.68 \text{ m}^2$$



Sphere

$$R = \left(\frac{3V}{4\pi}\right)^{1/3}$$

$$A = 4\pi R^2 \approx 4.84 \text{ m}^2$$

Young-Laplace Equation

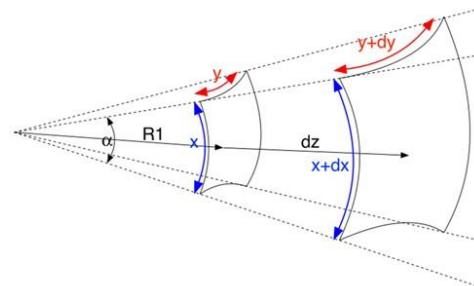
Pressure, Curvature, Surface Tension

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

ΔP : Pressure across the surface

$R_{1,2}$: Principal radii of curvature of the surface

γ : Surface tension



Contact Angle

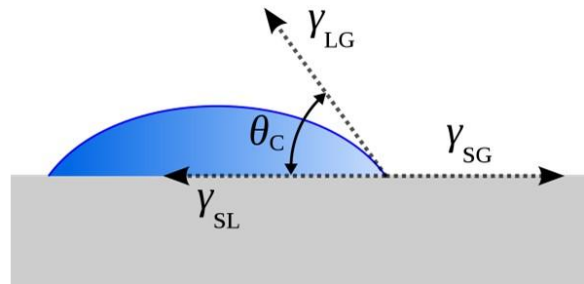
Sessile Droplet

The angle between the forces of the solid-liquid and liquid-gas surface tensions when in the surface free energy is minimized

$$\sum F_x = \gamma_{SG} - \gamma_{SL} - \cos \theta_C \gamma_{LG} = 0$$

$\theta_C < 90^\circ$: Wetting (**hydrophilic**)

$\theta_C > 90^\circ$: Non-wetting (**hydrophobic**)

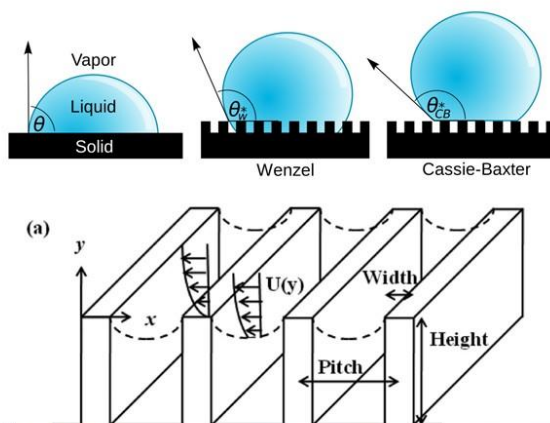


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Hydrophobicity

Shear-Free Flow

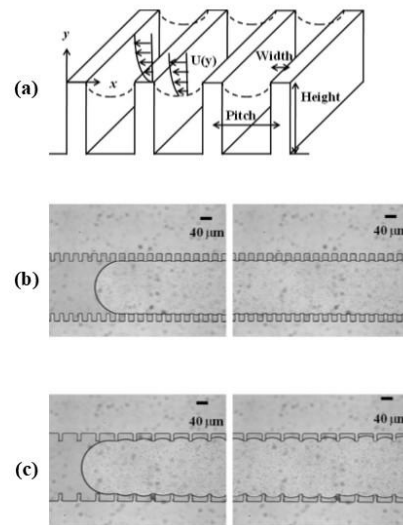
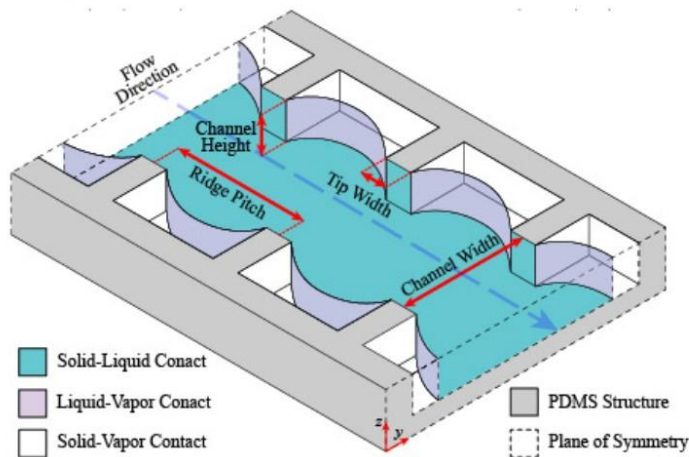


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Missing Video: Water beading up and rolling off the hydrophobic texture of a head of broccoli

Byun et al. 2008

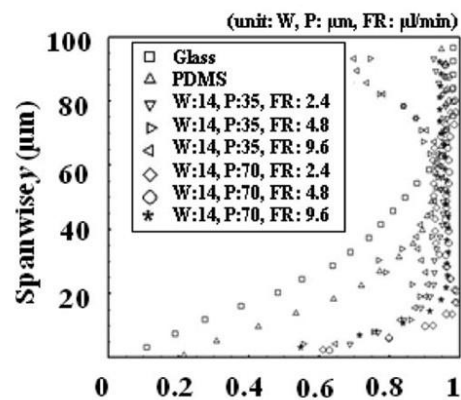
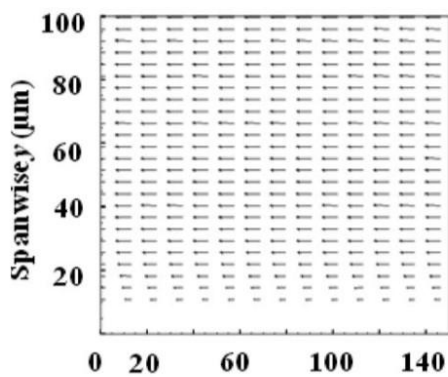


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Byun et al. (2008)

Particle Image Velicimetry



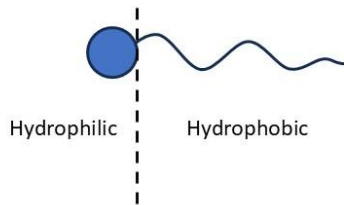
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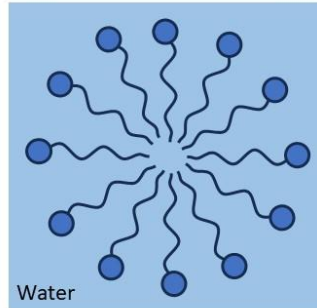
Surfactants

Surface Active Agents

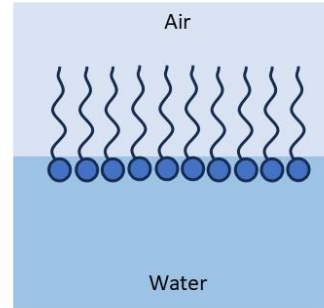
Amphiphilic: a molecule with a hydrophilic head and hydrophobic tail (or vice versa)



Formation of Micelles



Adsorption to Meniscus

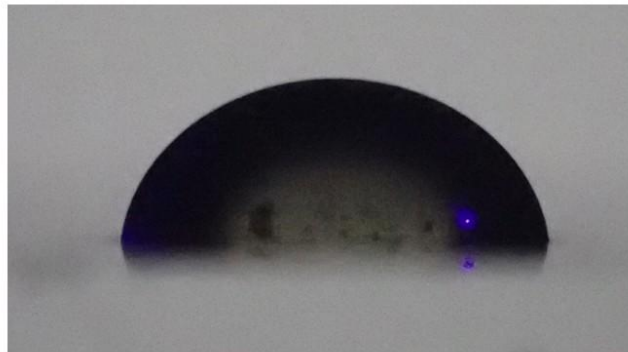


Transient Contact Angle

Surfactant-laden sessile droplet

Surfactant laden DI water dispensed via pipette on a hydrophobic surface. Initially, the meniscus is “fresh” and free of any surfactant

As surfactant adsorbs from the bulk to interface, the liquid-vapor surface tension relaxes, and the contact angle decreases



Missing Video: Transient relaxation of a sessile droplet of surfactant-laden water on a hydrophobized glass slide

Marangoni Stress

Water based food coloring, milk, and dish soap

The dish soap (surfactant) locally lowers the surface tension of the milk when it contacts the meniscus.

This creates a low-to-high gradient of surface tension away from the center of the plate, which creates a stress strong enough to induce flow (visualized by the food coloring).

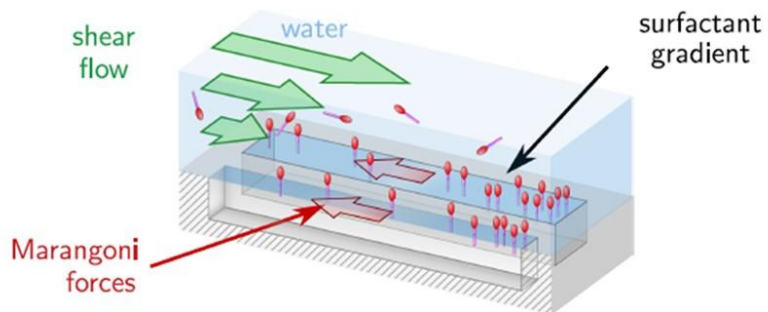


Missing Video: Demonstration of flow induced by Marangoni stress using milk, water-based food coloring, and dish soap

Adverse Marangoni Stress

Peudecref et al. (2012)

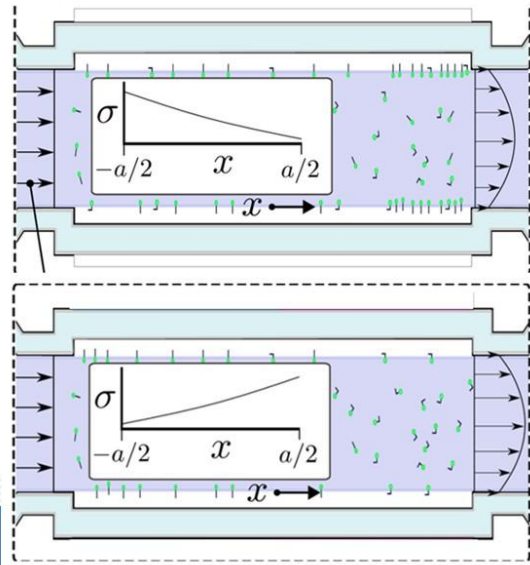
Surfactant accumulation on hydrophobic textures can generate **adverse Marangoni stresses** strong enough to **immobilize** the meniscus and eliminate lubrication



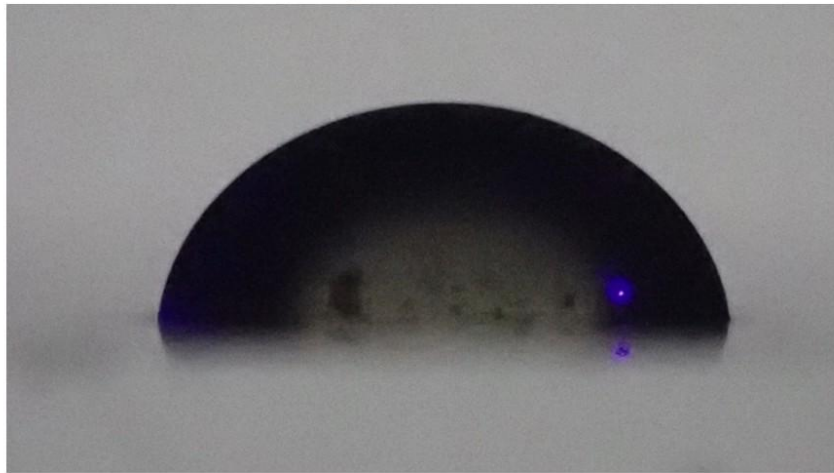
Adverse/Controlled Marangoni Stress

Uncontrolled surfactant accumulation generating **adverse** surface tension gradient and **minimal to no slip**

Actively controlled surface tension gradient generating **favorable** Marangoni stress and **restored or enhanced slip**

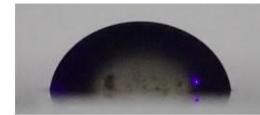
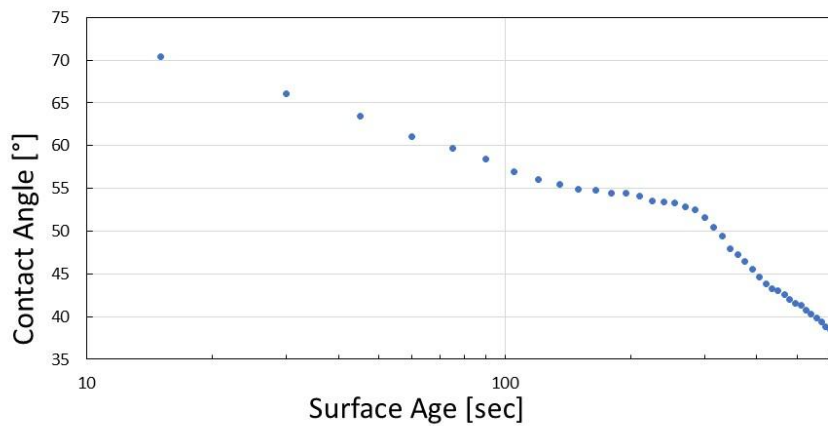


Transient Contact Angle



Missing Video: Transient relaxation of a sessile droplet of surfactant-laden water on a hydrophobized glass slide

Transient Contact Angle



Start: 75.8°



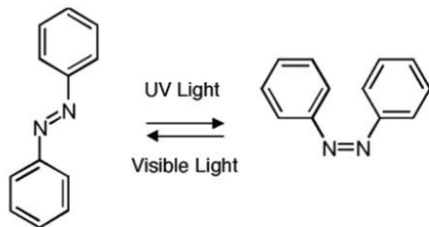
225 sec: 53.4°



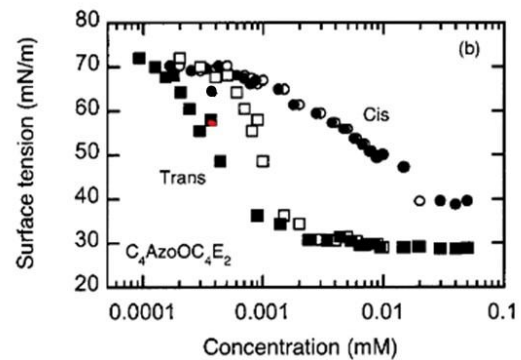
600 sec: 38.4°

Photosurfactants

Photosurfactants undergo controllable, reversible **isomerization** between **-cis** and **-trans** states when exposed to different wavelengths of light.



Since the **-trans** isomers pack more densely on the interface, they cause a **greater relaxation** in surface tension.



Shang et al. (2013)

Actively Controlled Surface Gradient

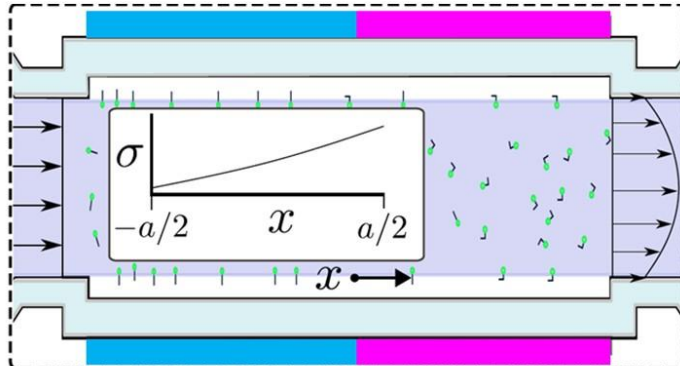
Optically Tunable Surfactants

Controlled Light Exposure:

Blue (430 nm): -cis

Ultraviolet (365 nm): -trans

Actively controlled surface tension gradient generating **favorable** Marangoni stress and **restored or enhanced slip**



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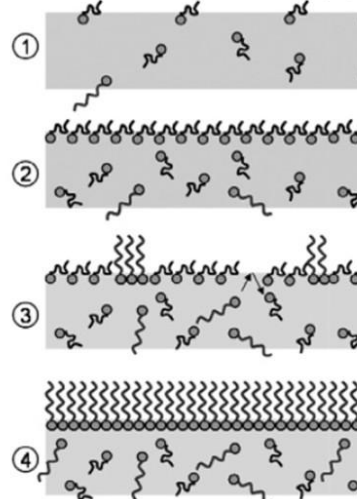
Department of Mechanical Engineering

Competitive Adsorption

Cicciarelli et al. (2006)

The -cis isomers adsorb to the interface more quickly but are then “squeezed off” the surface by adsorbing -trans isomers.

1. -cis isomers begin to adsorb from the bulk to a clean interface
2. Interface saturates with -cis isomers
3. -trans isomers start squeezing off -cis
4. Interface saturates with -trans isomers

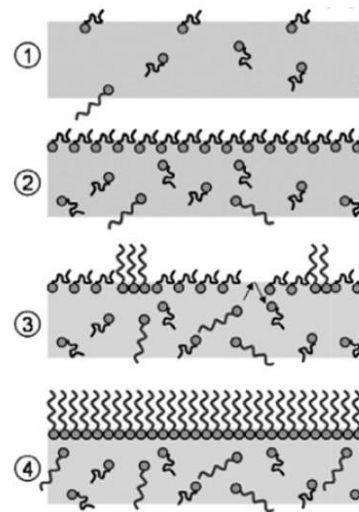
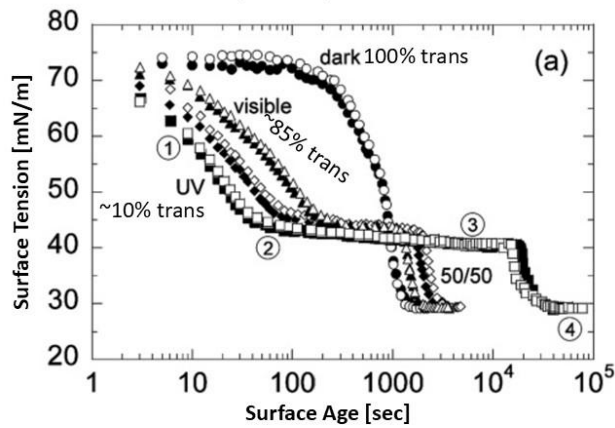


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Competitive Adsorption

Cicciarelli et al. (2006)

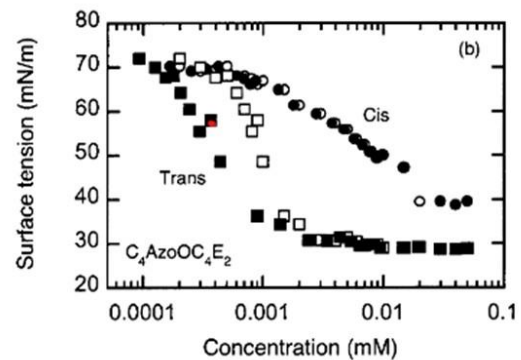
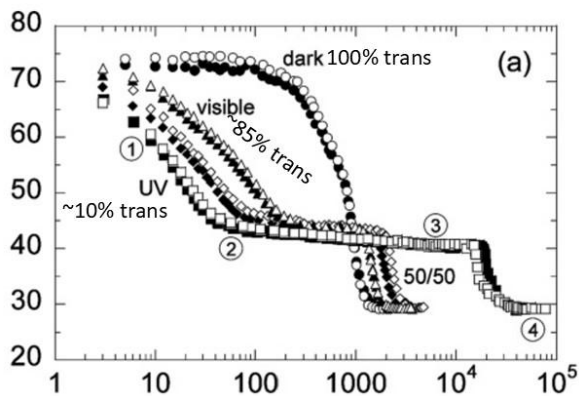


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Shang and Cicciarelli

What's missing?

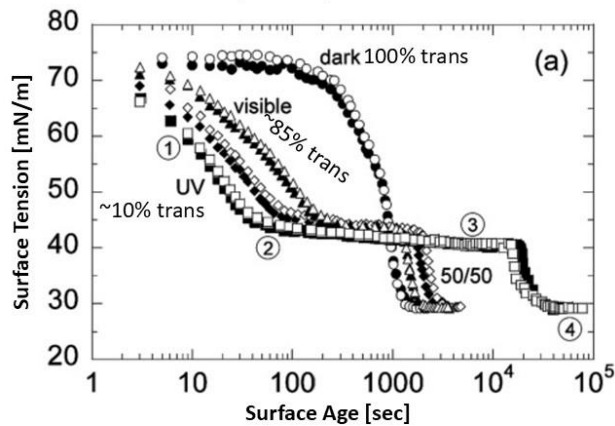


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Modeling Competitive Adsorption

Cicciarelli et al. (2006)

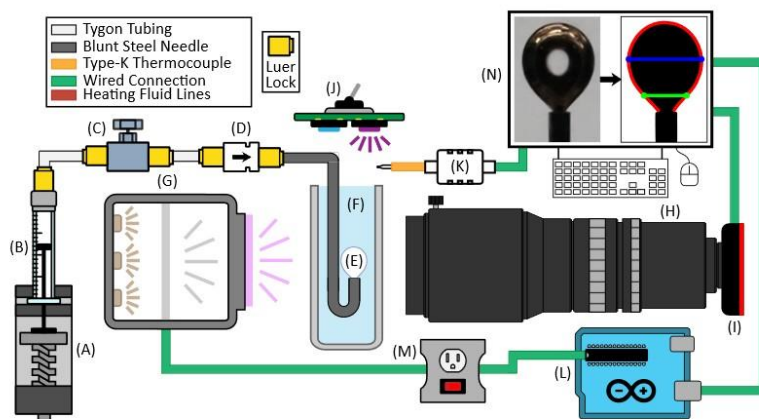


To extract the **adsorption and desorption coefficients** from a model for the transient surface tension of a bubble in a multi-species surfactant-laden liquid we need:

1. Initial ratio of –cis to –trans isomers
2. Surface tension over time

Transient Surface Tension Measurement

Axisymmetric Drop Shape Analysis (ASDA)



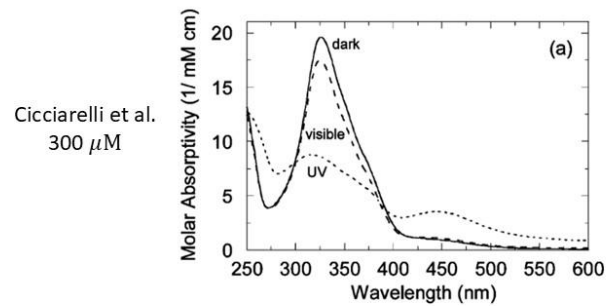
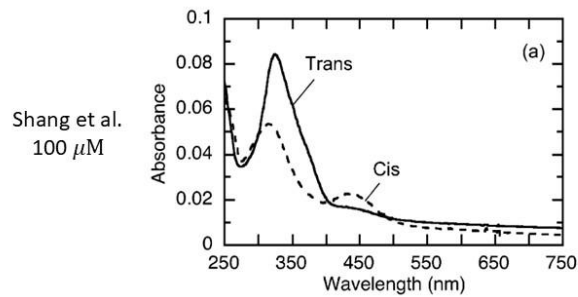
Components

Component Label	Component Name
A	Syringe Pump
B	Glass Micro Syringe
C	Valve
D	Check Valve
E	Pendant Bubble
F	Quartz Cuvette
G	Background Light
H	Zoom Lens
I	Camera
J	Blue/UV LEDs
K	Type K Thermocouple
L	Microcontroller
M	IOT Controlled Relay
N	Computer

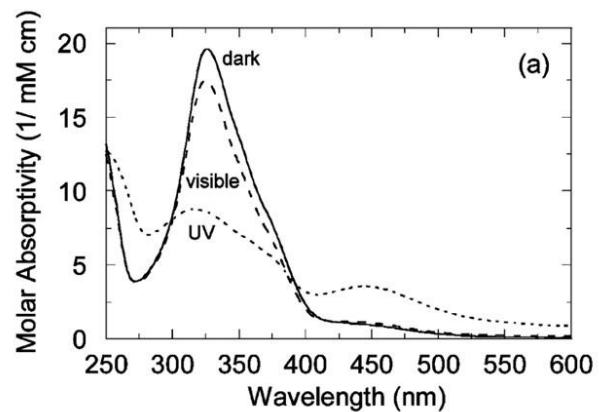
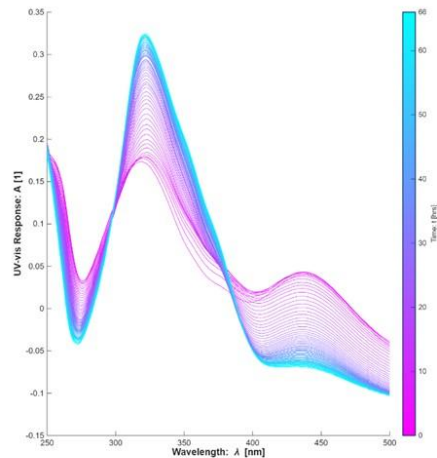
Isomeric Composition

Measuring absorptivity using UV-vis spectroscopy

While possible to directly measure the spectrum of a purely –trans solution by isolating it from light before measurement, it is not possible for $X_{ci} = 1$



Thermodynamic Relaxation



Total Molar Absorptivity

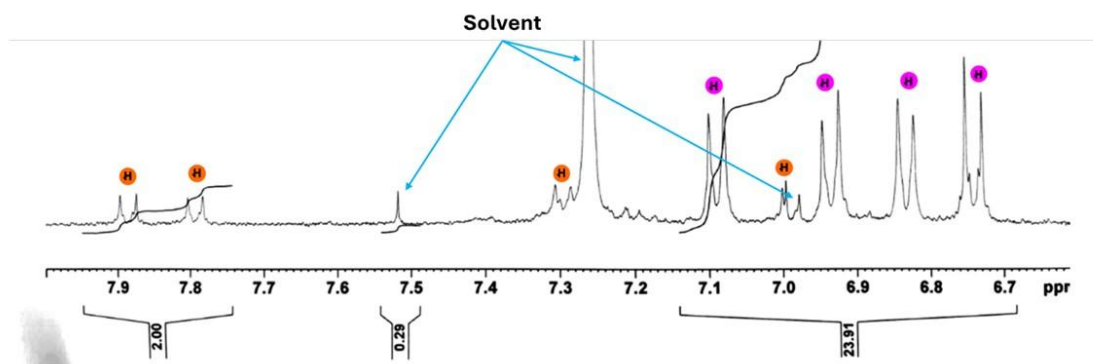
Kang et al. (2000)

$$A_{\text{total}}(\lambda) = [\epsilon_{\text{trans}}(\lambda)X_{\text{trans}} + \epsilon_{\text{cis}}(\lambda)X_{\text{cis}}]bc_{\text{total}}$$

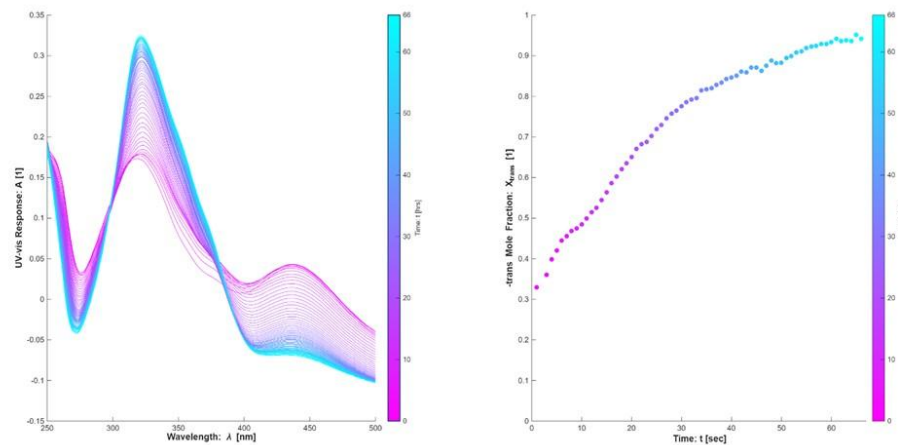
Terms		Subscripts	
$A(\lambda)$	absorption at wavelength λ	total	Of the entire solution
$\epsilon(\lambda)$	molar extinction coefficient at wavelength λ	trans	Of the –trans isomer only
X	mole fraction of isomer	cis	Of the –cis isomer only
b	cell path length		

Nuclear Magnetic Resonance

Identifying the specific isomers

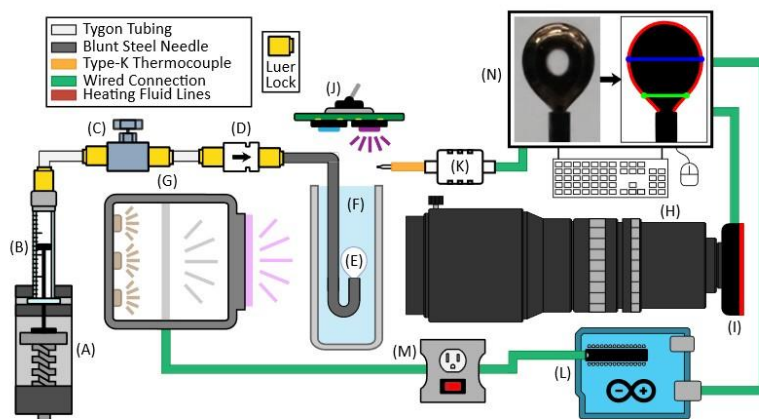


Transient Isomeric Composition



Transient Surface Tension Measurement

Axisymmetric Drop Shape Analysis (ASDA)



Components

A	Syringe Pump
B	Glass Micro Syringe
C	Valve
D	Check Valve
E	Pendant Bubble
F	Quartz Cuvette
G	Background Light
H	Zoom Lens
I	Camera
J	Blue/UV LEDs
K	Type K Thermocouple
L	Microcontroller
M	IOT Controlled Relay
N	Computer

Axisymmetric Drop Shape Analysis

- 01 Bubble creation
- 02 Image preparation and isolated noise removal
- 03 Profile extraction from experimental data
- 04 Generate and optimize a generate drop shape profile to data
- 05 Adhering noise removal using ALFI-S

Bubble Creation

Axisymmetric Drop Shape Analysis

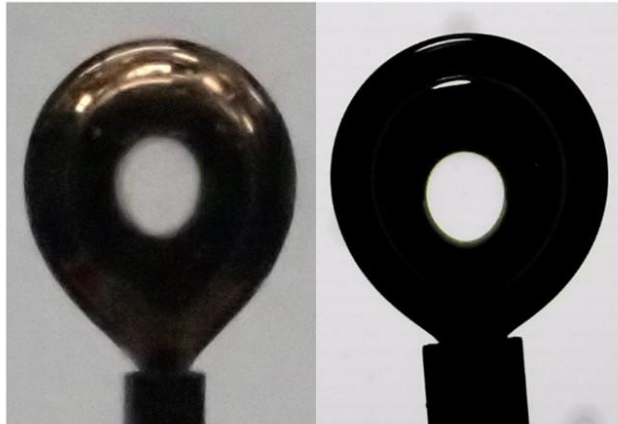
Lighting and Alignment

PROs:

Vertically aligned
Large enough to neck

CONS:

Poorly focused
Extra reflections



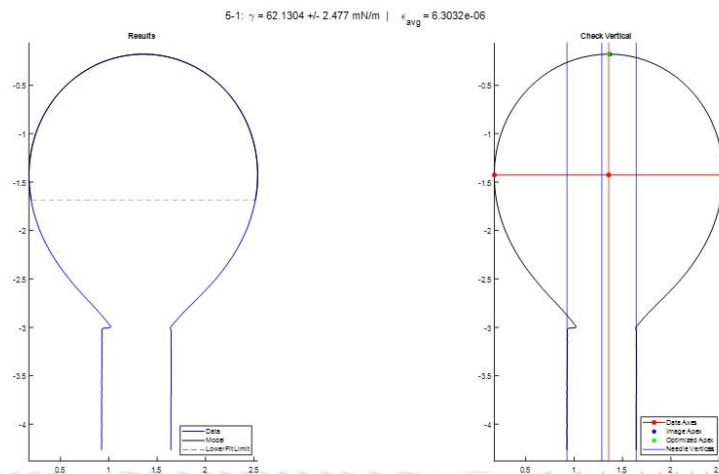
PROs:

Crisp silhouette
Well focused
Minimal reflections

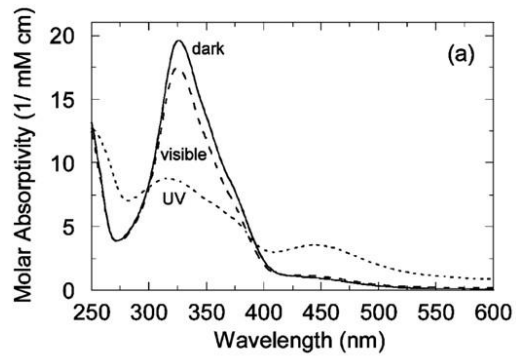
CONS:

Poor vertical alignment

Importance of Vertical Alignment



Background Light Color and Bubble Volume



72.30 ± 0.44 mN/m



31.24 ± 0.03 mN/m

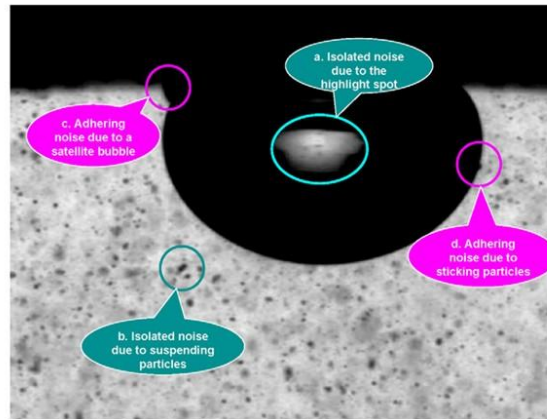
Image Preparation Isolated Noise Removal

Axisymmetric Drop Shape Analysis

Isolated and Adhering Noise

Zuo et al. (2006)

We can remove **isolated** noise **before** analysis

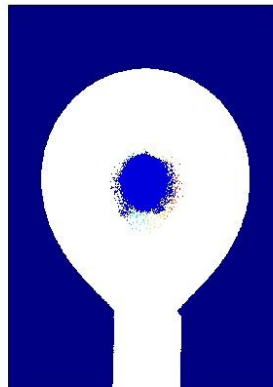


We remove **adhering** noise **during** analysis

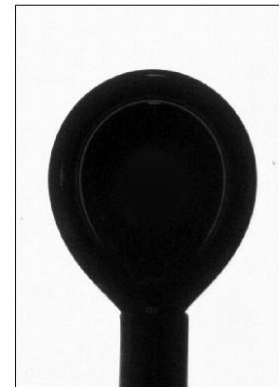
Isolated Noise Removal



Original Image



Binarization / Component Labeling
(Otsu's Method)



Cleaned Image

Profile Extraction

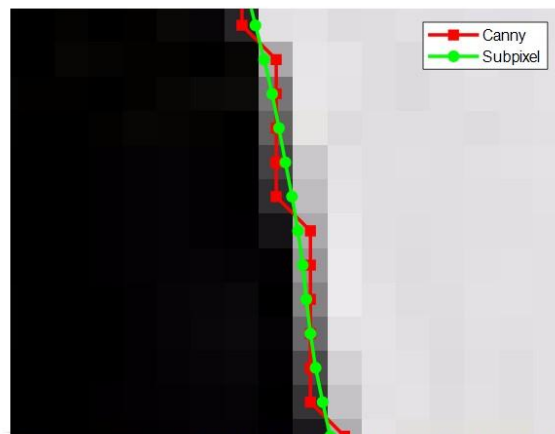
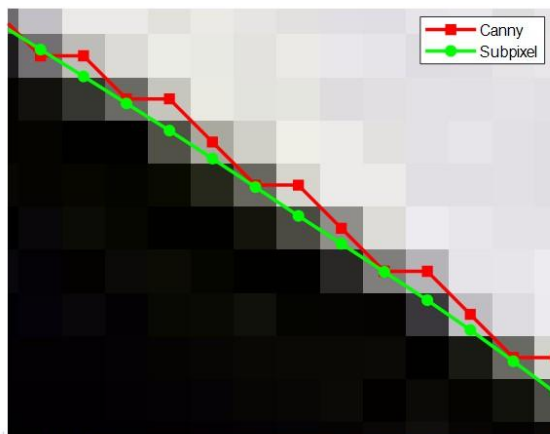
Axisymmetric Drop Shape Analysis

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Sub-pixel Edge Detection

Canny vs Partial Area Methods



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Partial Area Effect

Trullio-Pino et al. (2013)

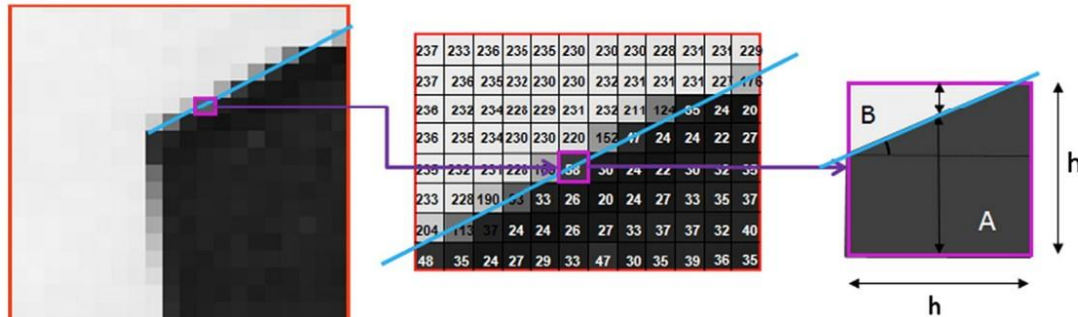


Fig. 1. Our hypothesis assumes that pixel values acquired by light sensors are proportional to the intensities and areas at both sides of the edge.

Profile Generation

Axisymmetric Drop Shape Analysis

Generalizing Capillary Rise in a Tube

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

Radii of curvature $R_1 = R_2$ at the apex: b

The elevation of a general point on the surface: $z = y - h$

At $z = 0$: $\Delta P = \frac{2\gamma}{b}$

Changes in ΔP from $\Delta \rho g z$

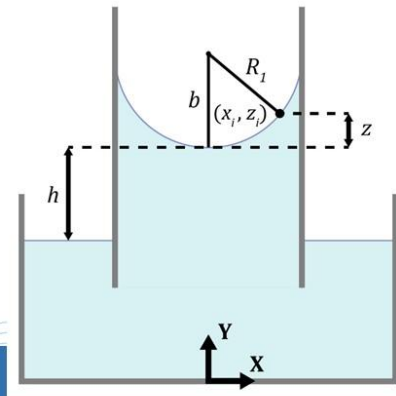
$$\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta \rho g z + \frac{2\gamma}{b}$$

Rearranged and made dimensionless

$$\frac{1}{R_1/b} + \frac{\sin \phi}{x/b} = \beta \frac{z}{b} + 2$$

$$\beta = \frac{\Delta \rho g b^2}{\gamma}$$

$$\beta = \frac{\text{gravity body forces}}{\text{surface tension forces}}$$



Shape Factors

$$\beta = \frac{\Delta \rho g b^2}{\gamma}$$

$$\gamma = \frac{-\Delta \rho g b^2}{\beta} = \frac{-\Delta \rho g d_e^2}{\beta \left(\frac{d_e}{b} \right)^2}$$

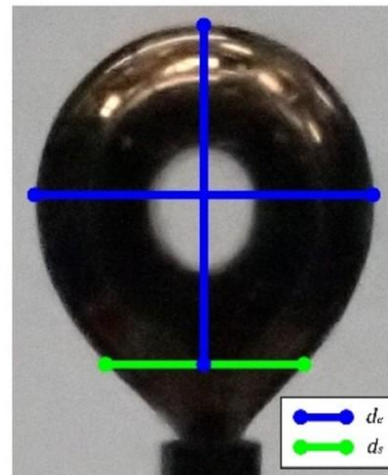
b is difficult to measure, define shape factor H

$$H = -\beta \left(\frac{d_e}{b} \right)^2$$

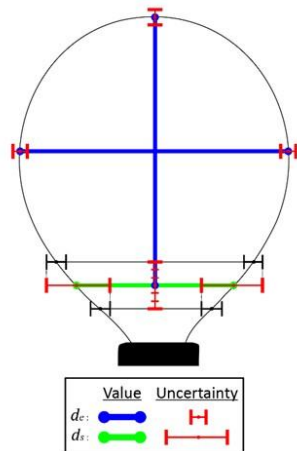
$$\gamma = \frac{-\Delta \rho g d_e^2}{H}$$

$$H = f \left(S = \frac{d_s}{d_e} \right)$$

Tabular Values: S vs. $1/H$



Shape Dependent Uncertainty



$72.30 \pm 0.44 \text{ mN/m}$



$31.24 \pm 0.03 \text{ mN/m}$

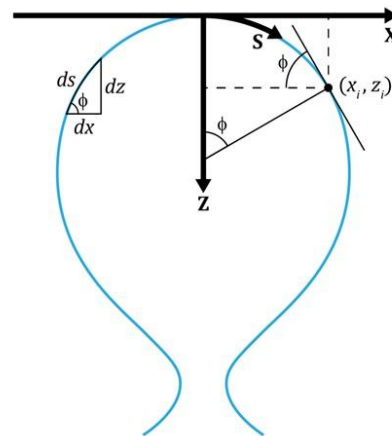
Path Length Parametrized Model

Directions

- S : Along the drop profile
- X : Horizontal
- Z : Vertical

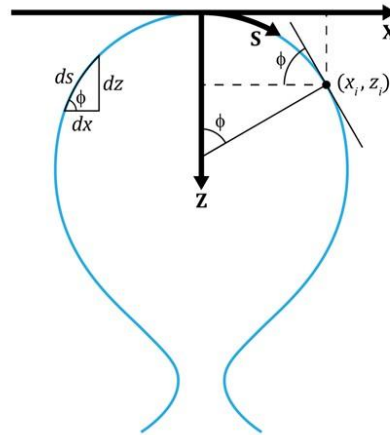
Coordinate Location

- x : Horizontal location
- z : Vertical Location
- ϕ : Angle of rotation/slope of tangent line



Path Length Parametrized Model

- $\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$
 - $\Delta P = \Delta P_0 + \Delta \rho g z$
 - $\Delta P_0 = 2b\gamma$
- $\frac{1}{R_1} = \frac{1}{R_2} = \frac{1}{R_0} = b$
- $ds = R_1 d\phi$
- $x = R_2 \sin \phi$
- $\frac{d\phi}{ds} = 2b + cz - \frac{\sin \phi}{x}$
 - $c = \frac{(\Delta \rho)g}{\gamma}$



Path Length Drop Shape Model

Main Model:

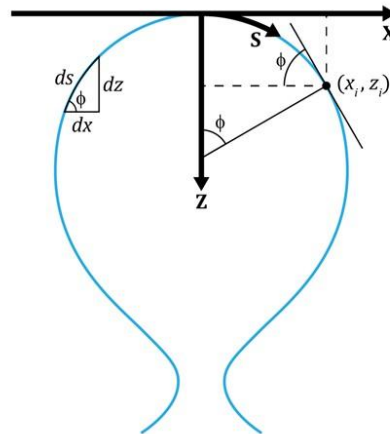
- $\frac{d\phi}{ds} = 2b + cz - \frac{\sin \phi}{x}$
- $\frac{dx}{ds} = \cos \phi$
- $\frac{dz}{ds} = \sin \phi$

Optional : Volume and Surface Area

- $\frac{dV}{ds} = \pi x^2 \sin \phi$
- $\frac{dA}{ds} = 2\pi x$

Boundary Conditions:

- $x(0) = z(0) = \phi(0) = V(0) = A(0) = 0$
- $\frac{d\phi}{ds} = b @ s = 0$



$$c = \frac{(\Delta \rho)g}{\gamma}$$

$$b = 1/R_0$$

Optimization to Match Profiles

Axisymmetric Drop Shape Analysis



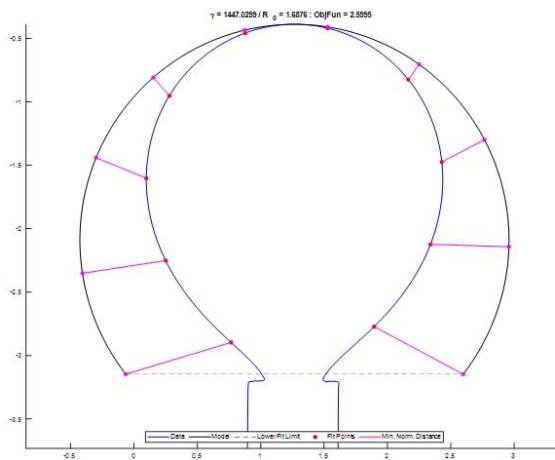
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Optimization Problem

Objective Function:

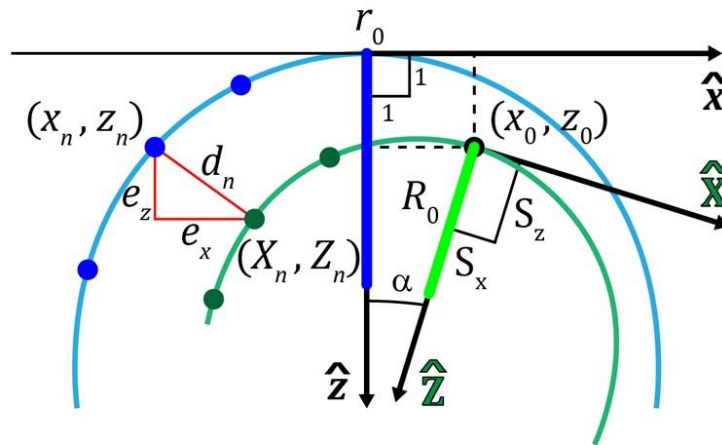
For the n experimental coordinates (x_n, z_n) compared to their nearest respective model coordinates axes at (X_n, Z_n)

$$E = \sum_{n=1}^N e_n$$
$$e_n = \frac{1}{2} d_n^2 = ((x_n - X_n)^2 + (y_n - Y_n)^2)$$



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Difference in Coordinate Axes



Optimization Between Axes

Dropping the n subscript:

$$e = \frac{1}{2} d^2 = \frac{1}{2} (e_x^2 + e_z^2)$$

$$e_x = x - x_0 - S_x X \cos \alpha + S_z Z \sin \alpha$$

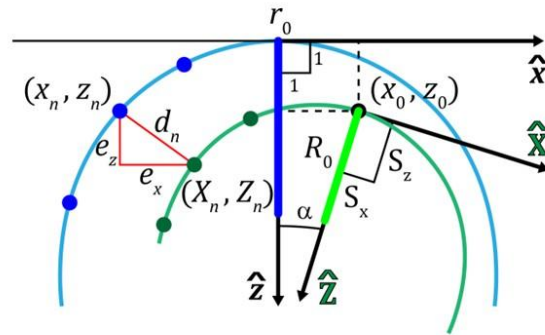
$$e_z = z - z_0 - S_x X \sin \alpha - S_z Z \cos \alpha$$

x_0 : Horizontal translation between origins

z_0 : Vertical translation between origins

α : Angle of rotation between frames

S_x and S_z : linear scaling factor between x and z axes between frames

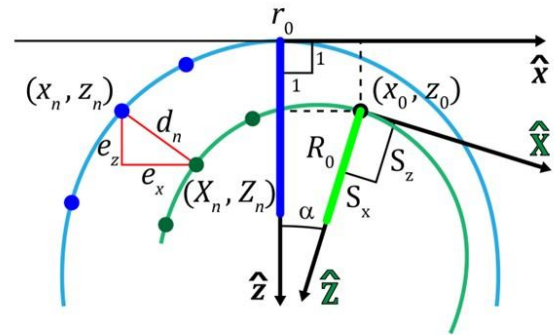


Optimization Between Axes

$$\begin{bmatrix} X \\ Z \\ 1 \end{bmatrix} = \begin{bmatrix} S_x \cos \alpha & -S_z \sin \alpha & x_0 \\ S_x \sin \alpha & S_z \cos \alpha & z_0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} x \\ z \\ 1 \end{bmatrix}$$

Optimization Parameters:

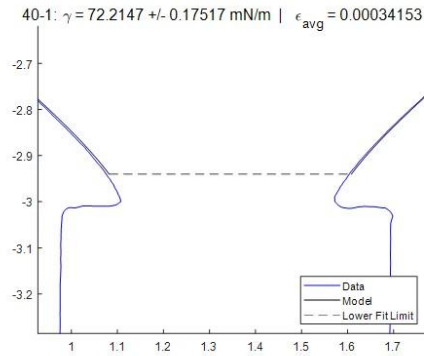
- 1) R_0 : Apex radius of curvature
- 2) γ : Surface tension
- 3) x_0 : Origin horizontal location
- 4) z_0 : Origin vertical location
- 5) α : Angle of axes rotation
- 6) S_z : Scaling factor of vertical axis



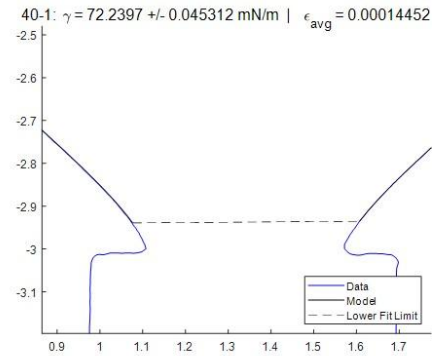
S_x : Measured from needle diameter. Can only optimize TWO of S_x , S_z , and R_0

Inclusion of α and S_z

4 Parameters: x_0 , z_0 , R_0 , and γ

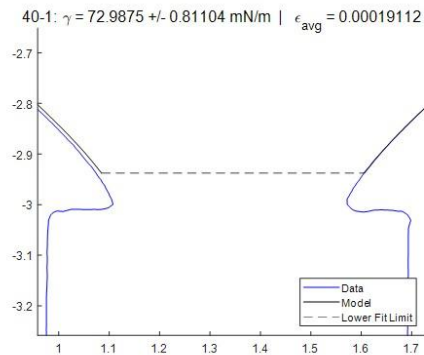


6 Parameters: Including α and S_z

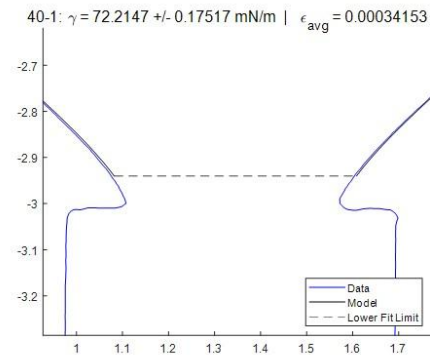


Point Selection

Evenly Spaced: $M = 10 / N = 250$

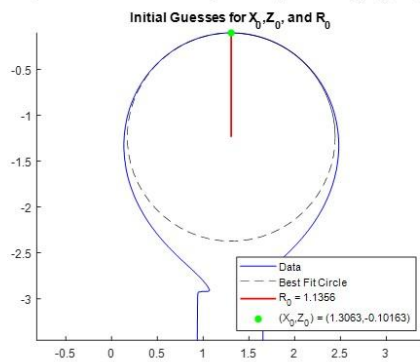


Randomly Selected: $M = 10 / N = 250$

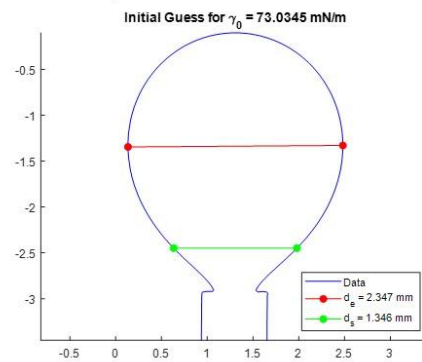


Initial Guesses: x_0 , z_0 , R_0 , and γ

Least squares fit a circle of radius R_0 to the apex of the drop shape at (x_0, z_0)



Measure d_e and d_s to estimate γ using tabular shape factor values



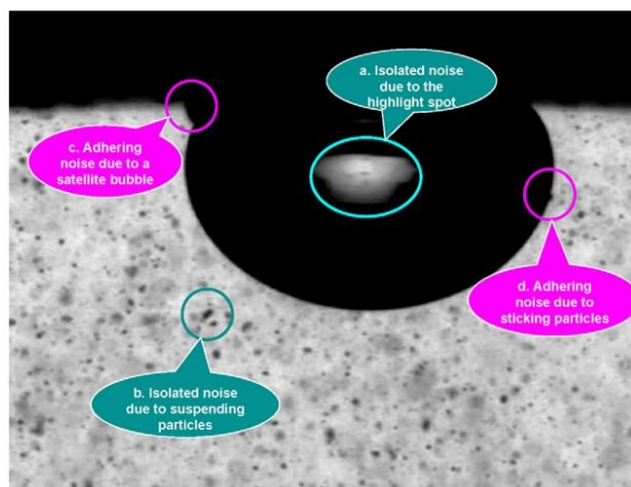
Isolated Noise Removal

Axisymmetric Drop Shape Analysis

Adhering Noise

Zuo et al. (2004)

Isolated noise can be removed by **component labeling**, but **adhering** noise is more difficult to remove since it can be **mistaken as part of the interface** during edge detection

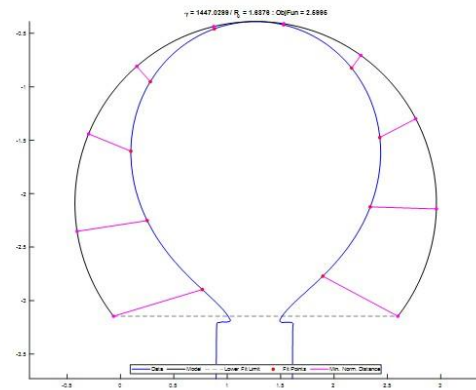


Axisymmetric Liquid Interface Smoothing

Zuo et al. (2004)

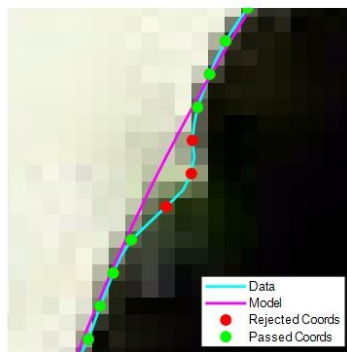
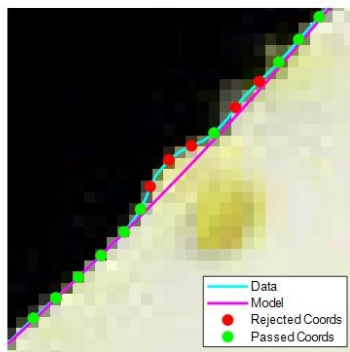
ALFI-S

1. Optimize a model profile to a data set
2. Calculate the standard deviation, σ , of the minimum normal distances, d_n
3. Any coordinate outside 3σ is eliminated as an outlier
4. Repeat (1-3) until no coordinates are rejected



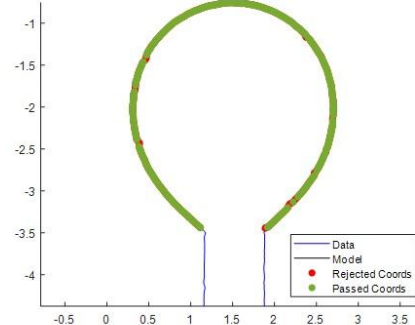
Axisymmetric Liquid Interface Smoothing

1 mM solution with visible floating aggregates



Before ALFI-S: 75.61 mN/m
After ALFI-S: 72.43 mN/m

Every Other - N = 302/328 - ALFI-S Count: 5



Method Validation and Results

Axisymmetric Drop Shape Analysis



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Results

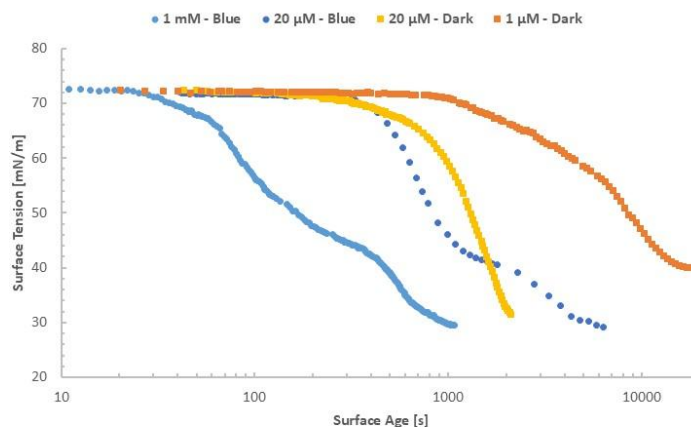
Pure reference fluids and transient surfactant measurements

Distilled Water

- Tufts: 72.45 ± 0.02 mN/m
- NIST: 72.74 mN/m
- 0.4% Difference

Isopropyl Alcohol

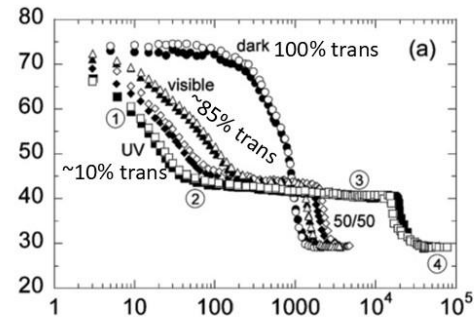
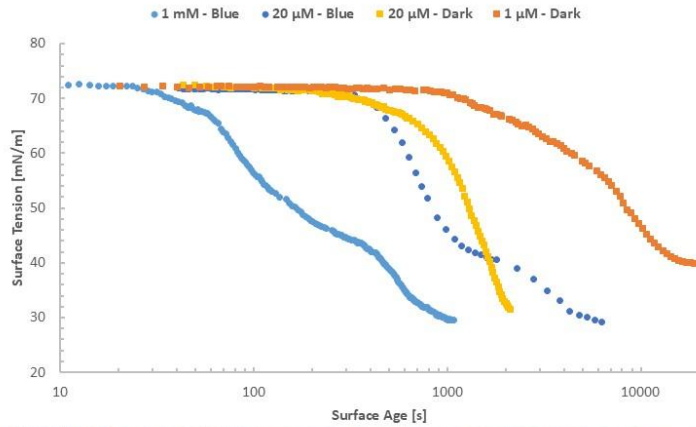
- Tufts: 21.23 ± 0.32 mN/m
- NIST: 21.55 mN/m
- 1.5% Difference



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Results

Compared to Cicciarelli et al (2013)



Internal Flow Microfluidic Channel with Reentrant Structures for Low-Surface Tension Liquids

(Continued in separate slides)

Light-Driven Flow in a Textured Microfluidic Device Using Chromocapillary Marangoni Stress

(Continued in separate slides)



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Acknowledgements

All the faculty and staff at Tufts University



**Robert
White**



**Jeffrey
Guasto**



**Jim
Vlahakis**



**Erica
Kemmerling**



**Georgios
Karamanis**



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Acknowledgements

The staff, students, and equipment (not the waterjet) at Bray Lab



**Nicole
Batrouny**



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Acknowledgements

The coaches and athletes at Community Rowing Inc.



**Aaron
Arnold**



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Acknowledgements

The various heroes and scoundrels of...

Hargrave House, the Scrum, the Players Agency, Thruster Buster, the Heartbreakers,
the Murder Mavens, the investigators of Bright Falls, the Nebulous Knights,
Xtra-Thiquenessé, and the No-Names



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Acknowledgements

My mother, Elisabeth, and grandmother, Mary Louise



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Dedication

Michael Joseph Birosak (June 15, 1943 - August 29, 2011)



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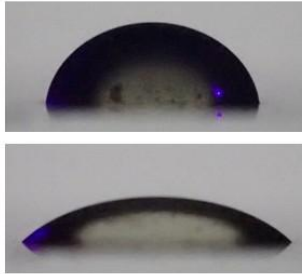
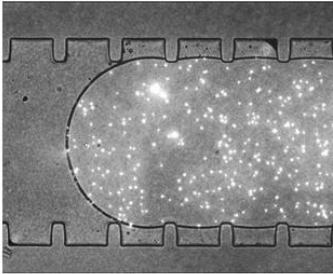
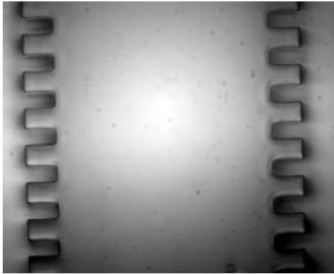
Reentrant Microfluidic Channels for Chromocapillary Demonstration

This second set of slides covers the combined materials of Chapters 2 (Internal Flow Microchannels with Reentrant Structures for Low-Surface Tension Liquids) and 3 (Light Driven Flow Using Chromocapillary Marangoni Stress).

Slides bordered in red contained an embedded video or some other moving graphical element that could not be printed. A description of the moving content is included below each slide as needed. An original copy of this presentation is available upon request from Professor Marc Hodes at Tufts University.

Enhanced Lubrication of Superhydrophobic Surfaces Via Chromocapillary Marangoni Stress

Michael Birosak
Department of Mechanical Engineering, Tufts University

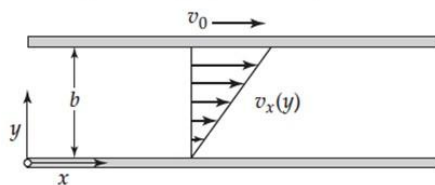




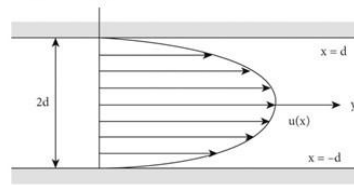
Surface Tension and Hydrophobicity

Boundary Conditions

- **Solid-Fluid:** Liquid velocity equals velocity of solid at interface ("no-slip")

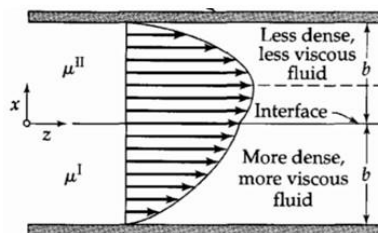


Parallel Plate Flow (Couette)

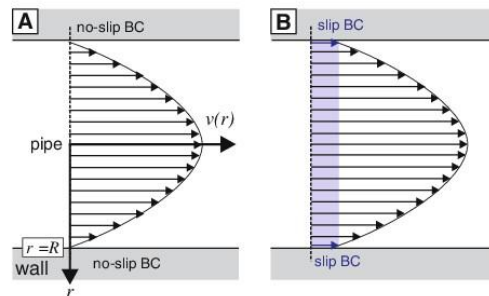


Pipe Flow (Poiseuille)

- **Liquid-Liquid:** Tangential velocity and interfacial molecular stresses ($p + \tau_{xx}$, τ_{xy} , and τ_{xz}) are equal

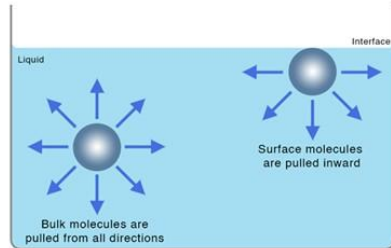


- **Liquid-Gas:** Shear interfacial stresses are zero ("shear free")



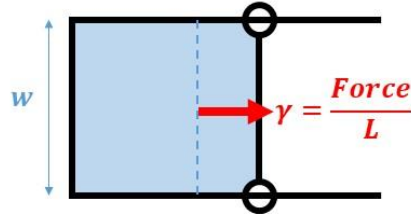
Surface Tension

- **Liquid-Vapor Surface Tension:** Greater attractive forces between fluid molecules (cohesion) than to air molecules (adhesion) pulls the interface inwards



Soap film on a wire frame with movable side

$$\text{Work} = \gamma L dx = \gamma dA$$



- **Surface Tension vs Surface Free Energy**

$$\text{Work} = \gamma L dx = \gamma dA$$

$$\gamma = \frac{\text{Force}}{\text{Length}} = \frac{N}{m} = \frac{\text{Energy}}{\text{Area}} = \frac{J}{m^2}$$

Soap Bubble

$$\Delta P = \frac{2\gamma}{r}$$



Contact Angle and Hydrophobicity

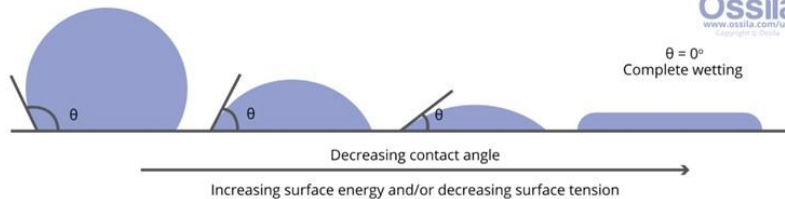
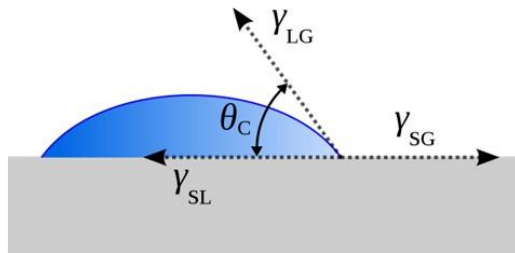
- **Contact Angle**

- The angle between the forces of the solid-liquid and liquid-gas surface tensions
- Determined by the minimum total surface free energy

$$\sum F_x = \gamma_{SG} - \gamma_{SL} - \cos \theta_C \gamma_{LG} = 0$$

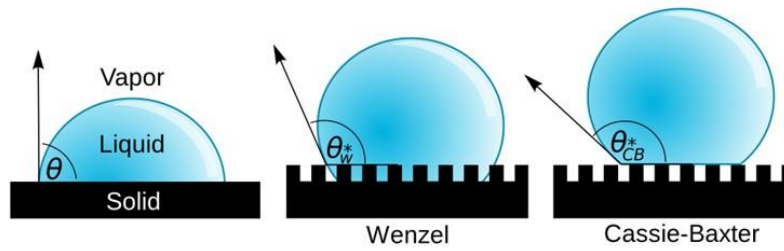
$\theta_C < 90^\circ$: Wetting (**hydrophilic**)

$\theta_C > 90^\circ$: Non-wetting (**hydrophobic**)

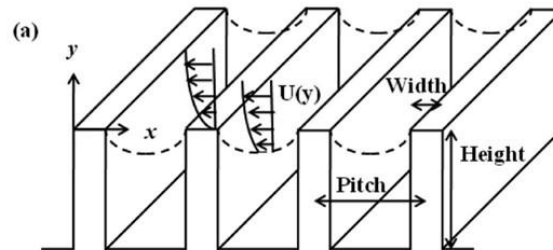


Mixed Boundary Conditions

• Contact Angle and Wetting

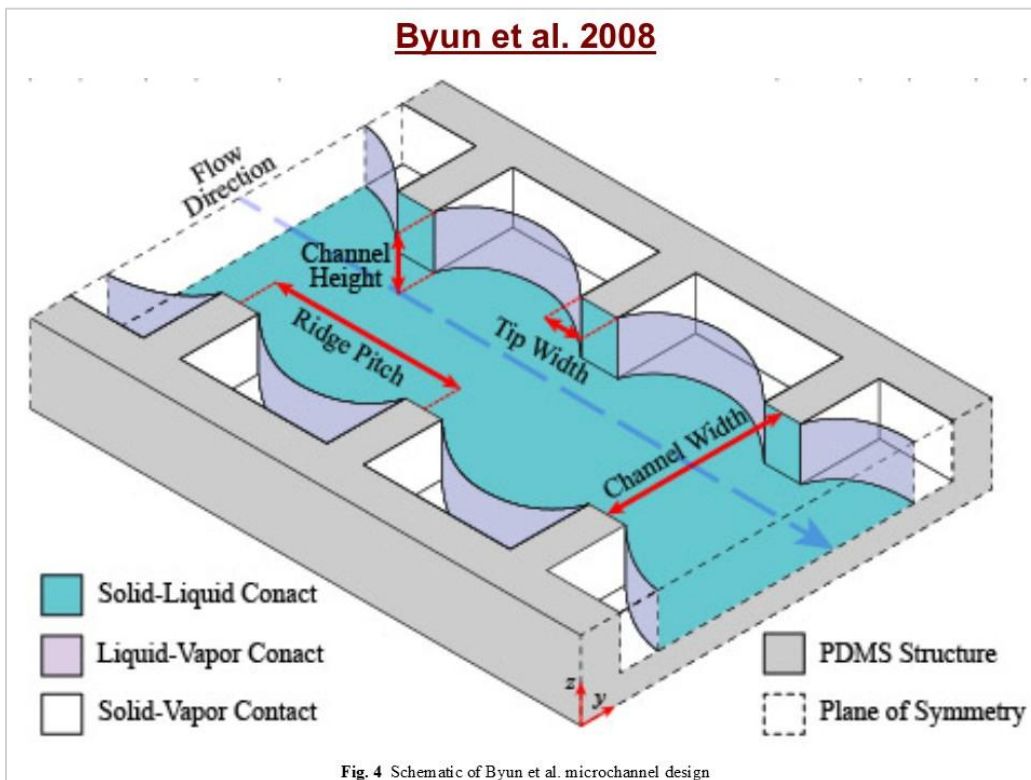


• Texture Driven Hydrophobicity

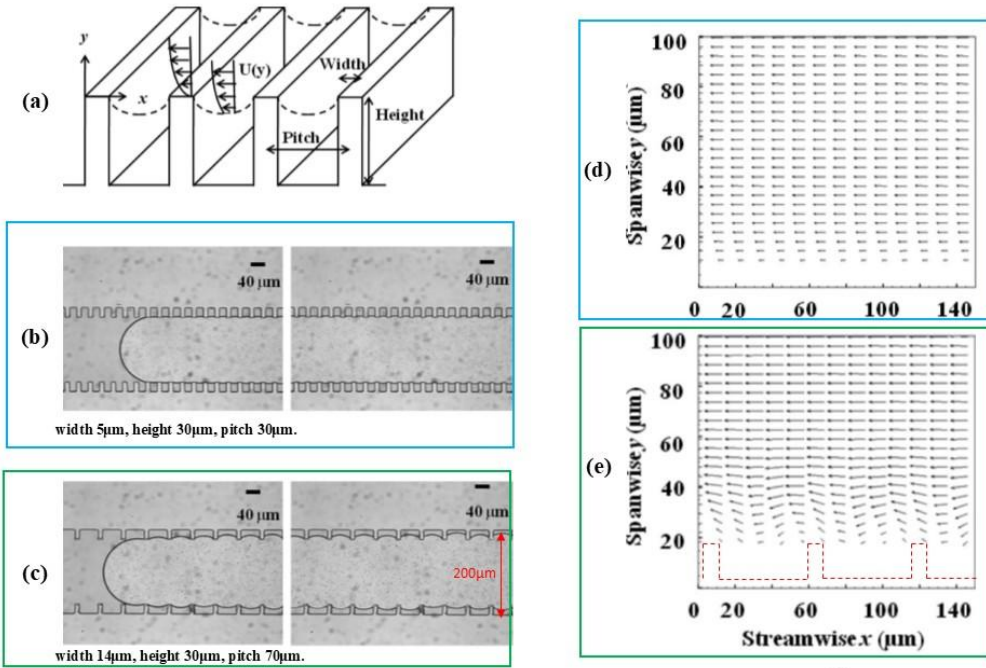


Missing Video: Water beading up and rolling off the hydrophobic texture of a head of broccoli

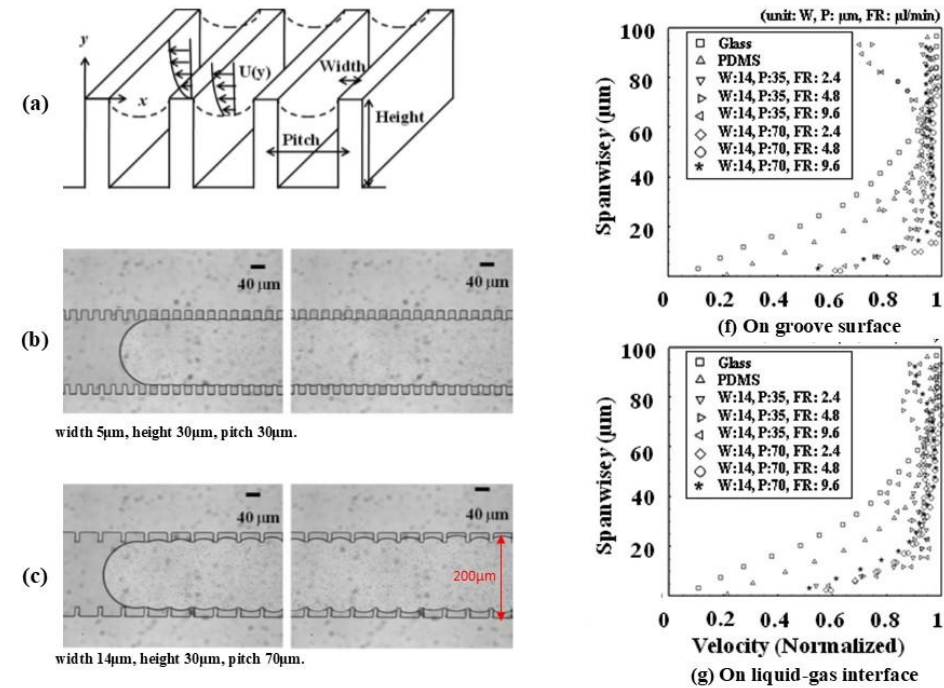
Byun et al. 2008



Byun et al. 2008



Byun et al. 2008



Surfactants and Interfacial Effects

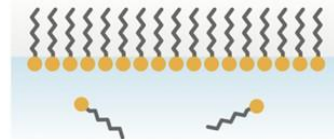
Surfactants and Marangoni Stress

- **Surfactant:** A chemical **surface-active agent** that decreases interfacial tension

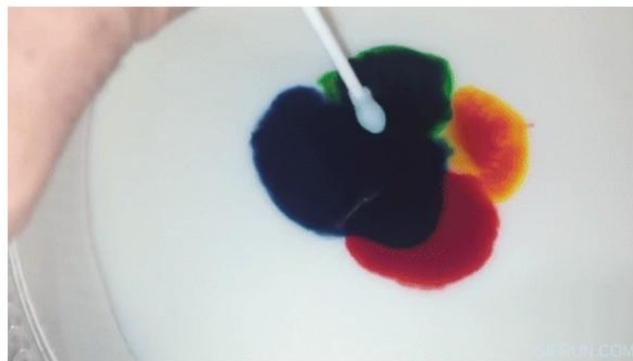
Low concentration ($\ll$ CMC)
Moderate surface tension



Surface saturation ($\leq$ CMC)
Low surface tension, no micelles



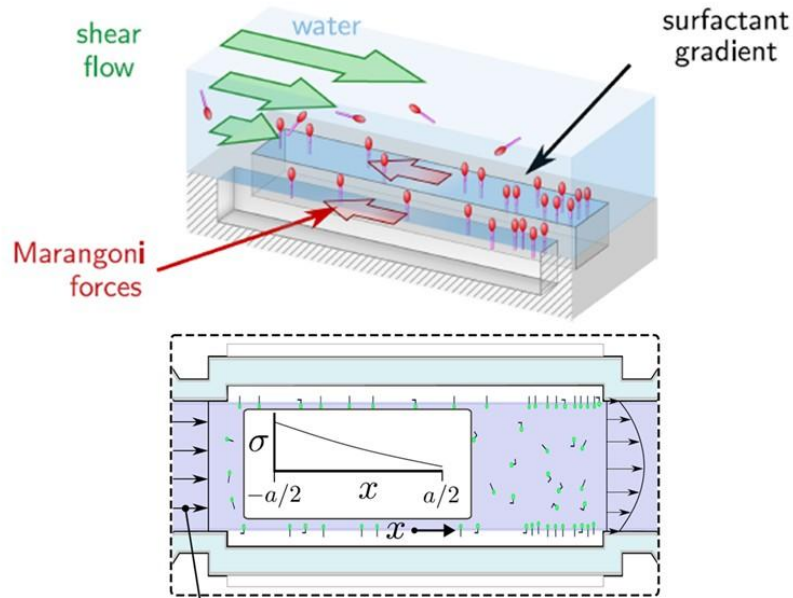
- **Marangoni Effect:** Flow induced by a surface tension gradient



Missing Video: Demonstration of flow induced by Marangoni stress using milk, water-based food coloring, and dish soap

Adverse Marangoni Stress

- **Surfactant accumulation** on hydrophobic textures can generate **adverse Marangoni stresses** strong enough to **immobilize** the meniscus and eliminate lubrication

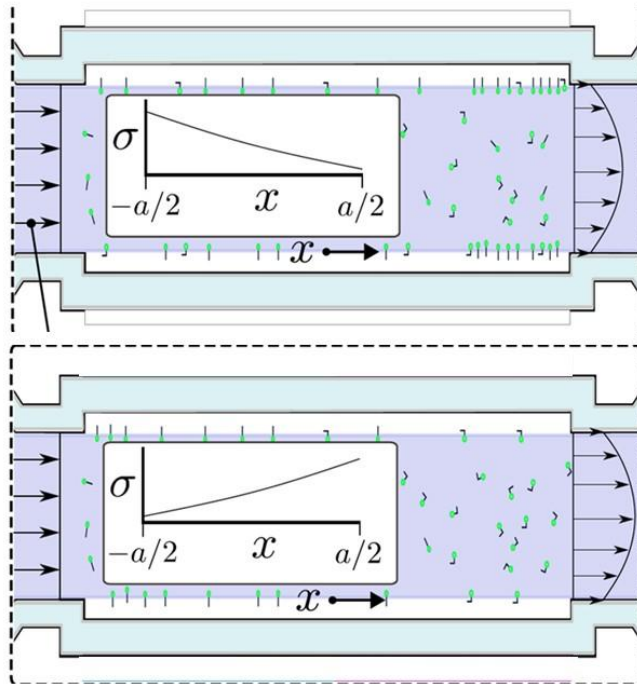


Peaudecerf, François J., et al. "Traces of surfactants can severely limit the drag reduction of superhydrophobic surfaces." Proceedings of the National Academy of Sciences 114.28 (2017): 7254-7259.

Controlled Marangoni Stress

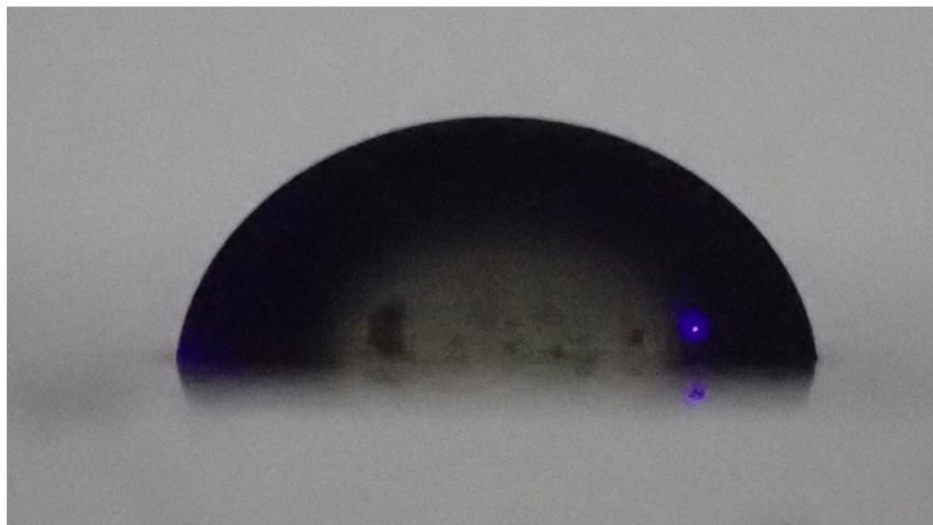
Uncontrolled surfactant accumulation generating **adverse** surface tension gradient and **minimal to no slip**

Actively controlled surface tension gradient generating **favorable** Marangoni stress and **restored or enhanced slip**



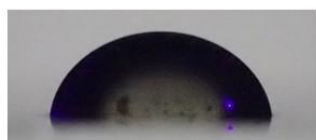
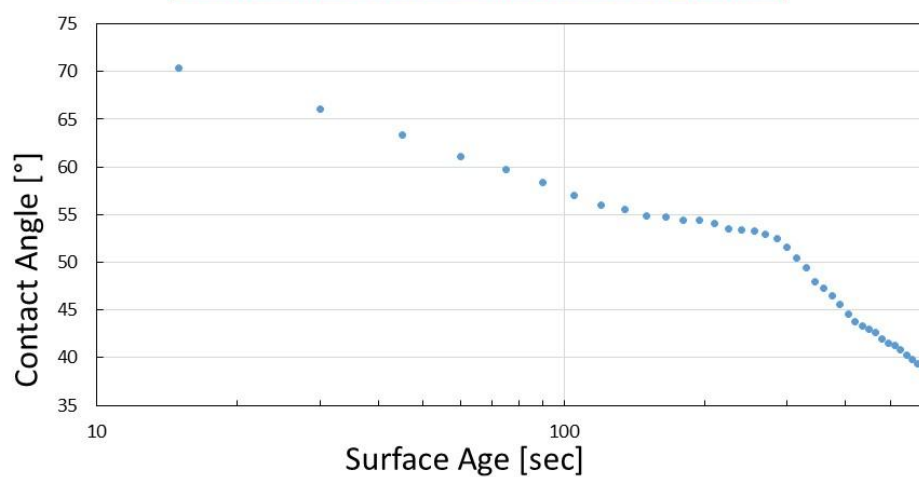
Transient Surface Tension Relaxation

- Surfactant laden DI water dispensed via pipette on a hydrophobic surface. Initially, the meniscus is “fresh” and free of any surfactants.
- As surfactant adsorbs from the bulk to interface, the liquid-vapor surface tension relaxes and the contact angle decreases



Missing Video: Transient relaxation of a sessile droplet of surfactant-laden water on a hydrophobized glass slide

Transient Surface Tension Relaxation



Start: 75.8°



225 sec: 53.4°

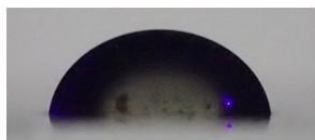
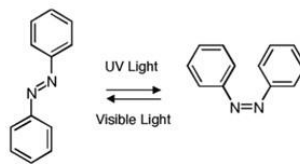
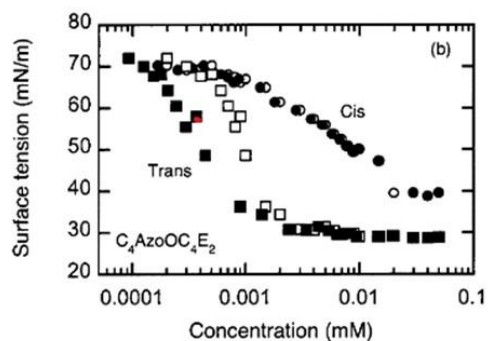


600 sec: 38.4°

Photosurfactants

Photosurfactants

- **Photosurfactants** undergo controllable, reversible **isomerization** between -cis and -trans states when exposed to different wavelengths of light
- The two isomers **adsorb** and **desorb** at different rates and have different **maximum packing densities** on the interface. An interface saturated with more densely packing –trans isomers has a lower surface tension than when it is saturated with –cis



Start: 75.8°



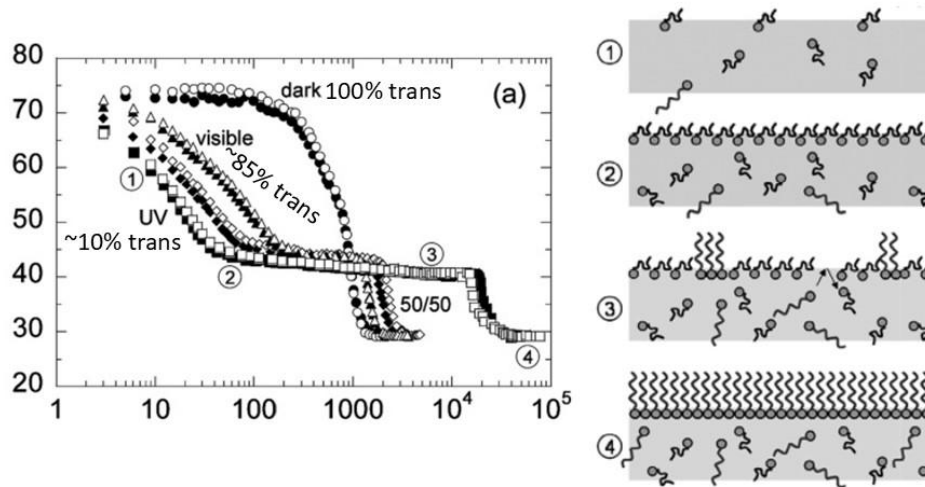
225 sec: 53.4°



600 sec: 38.4°

Cicciarelli et al. (2006)

- Competitive absorption of cis vs trans surfactant
- Cis isomers adsorb more rapidly to fresh meniscus before being squeezed out by trans

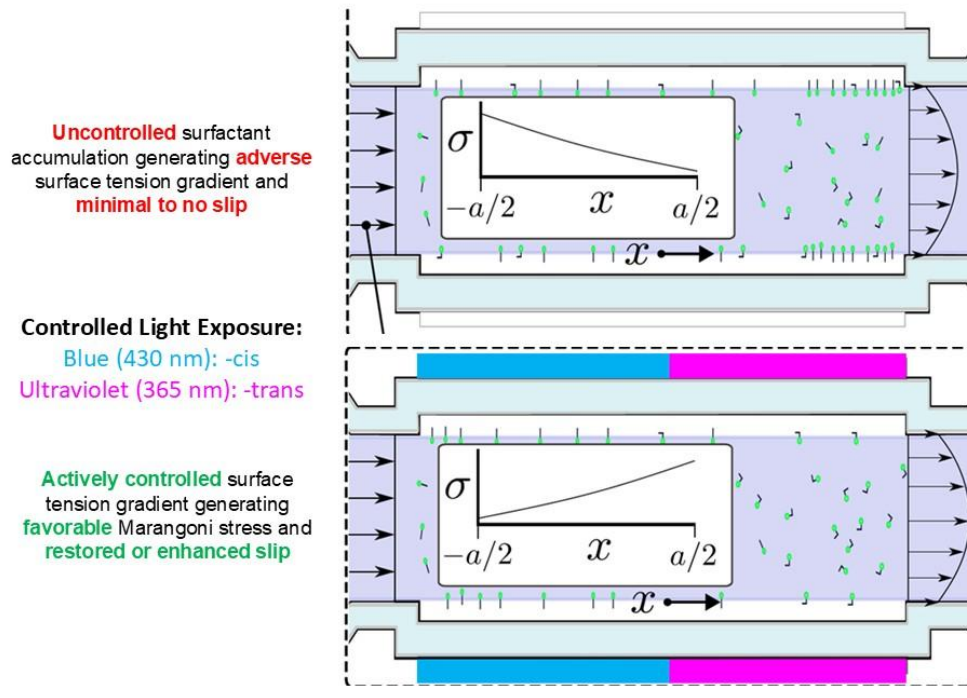


Dynamic Surface Tension Behavior in a Photoresponsive System

Cicciarelli et al. (2006)

Cis: 40.6 mN/m Trans: 29.5 mN/m

Controlled Marangoni Stress



Microfabrication

Byun et al. 2008

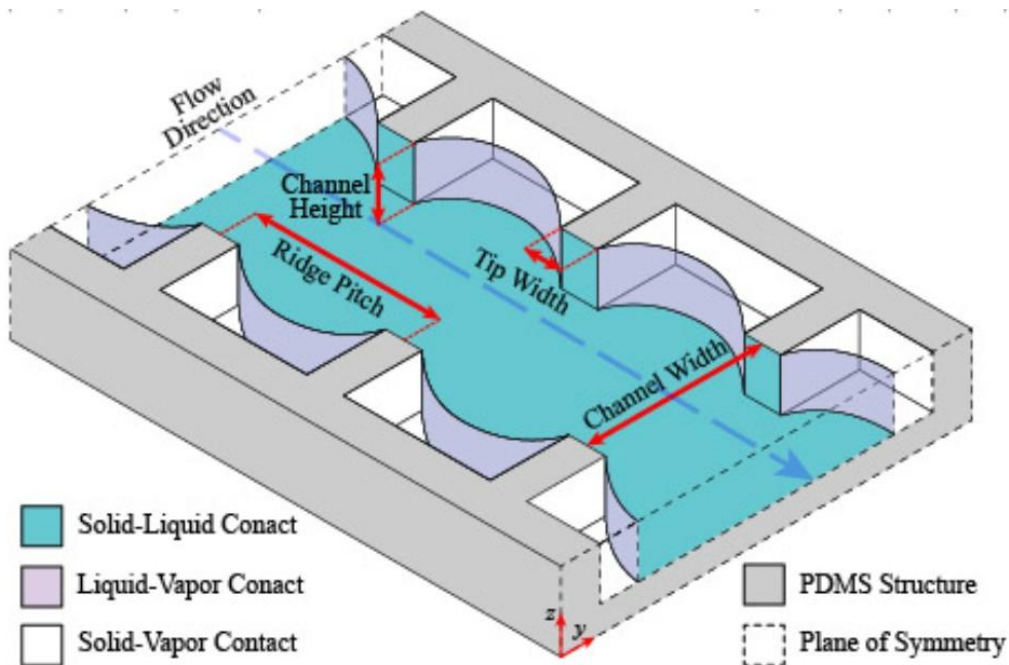
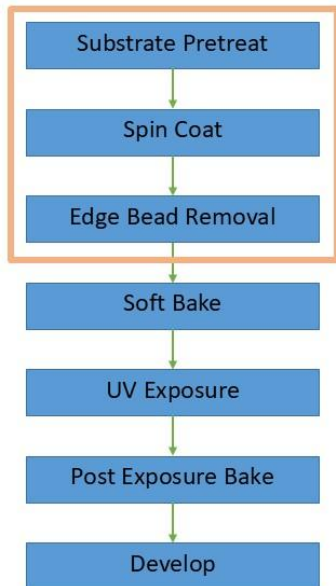


Fig. 4 Schematic of Byun et al. microchannel design

Photolithography



Piranha (3:1)

96% H_2SO_4 :
30% H_2O_2

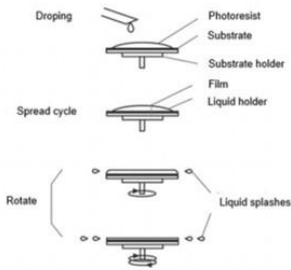


Fig. 5.1 Spin coating process

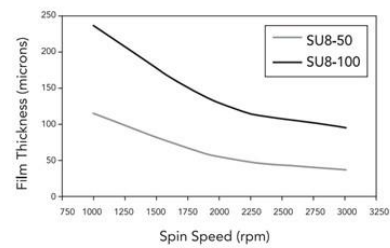
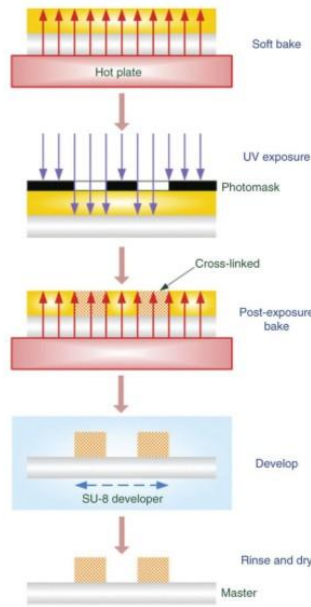
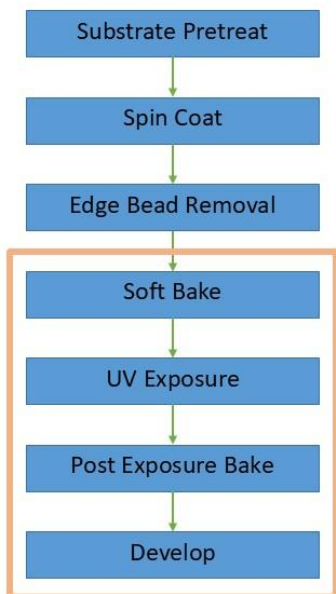


Fig. 5.3 Spin Speed vs. Thickness plot



Fig. 5.2 A spin coater

Photolithography



Drive off excess solvent using hotplate

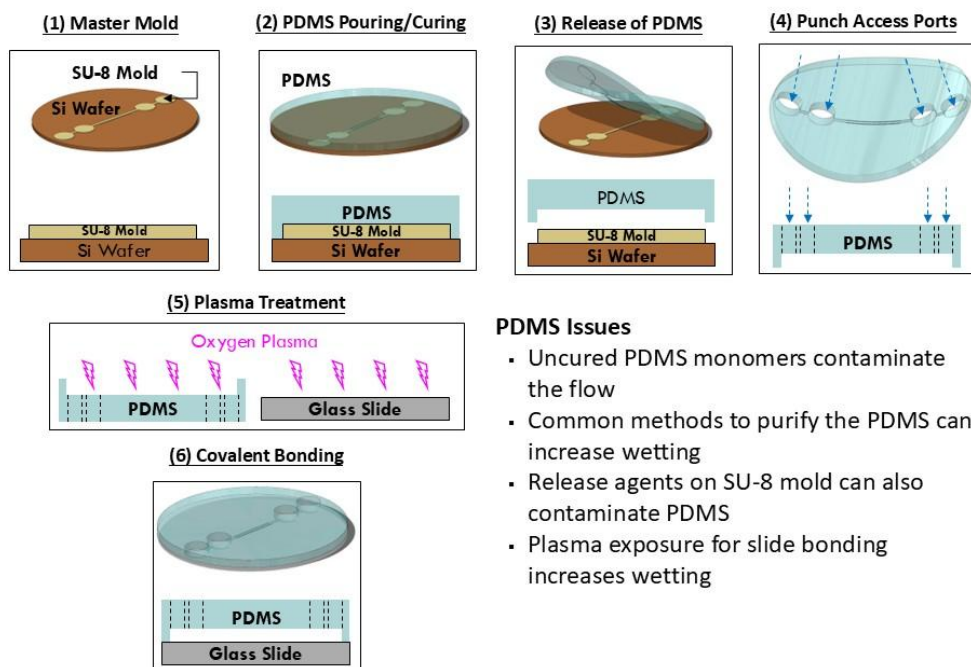
Cross-link with UV light using mask aligner

Heat again to complete cross linking

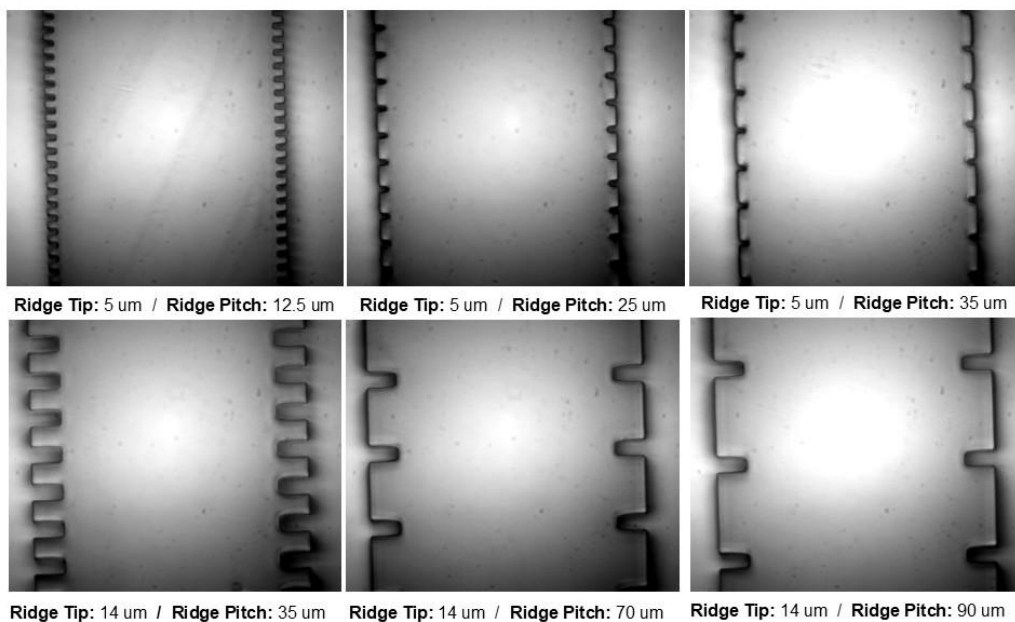
Rinse off non-cross-linked PR by agitating with solvent

Fig. 5.4 Baking and development

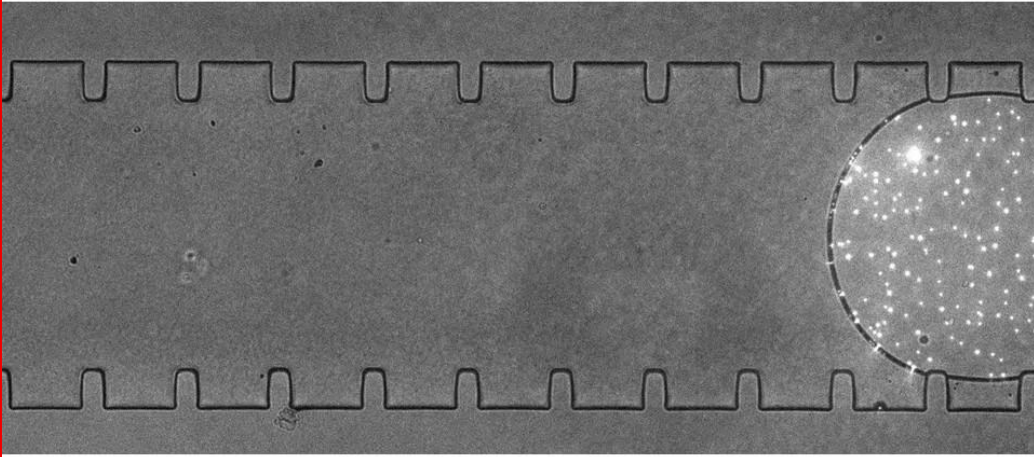
PDMS Casting



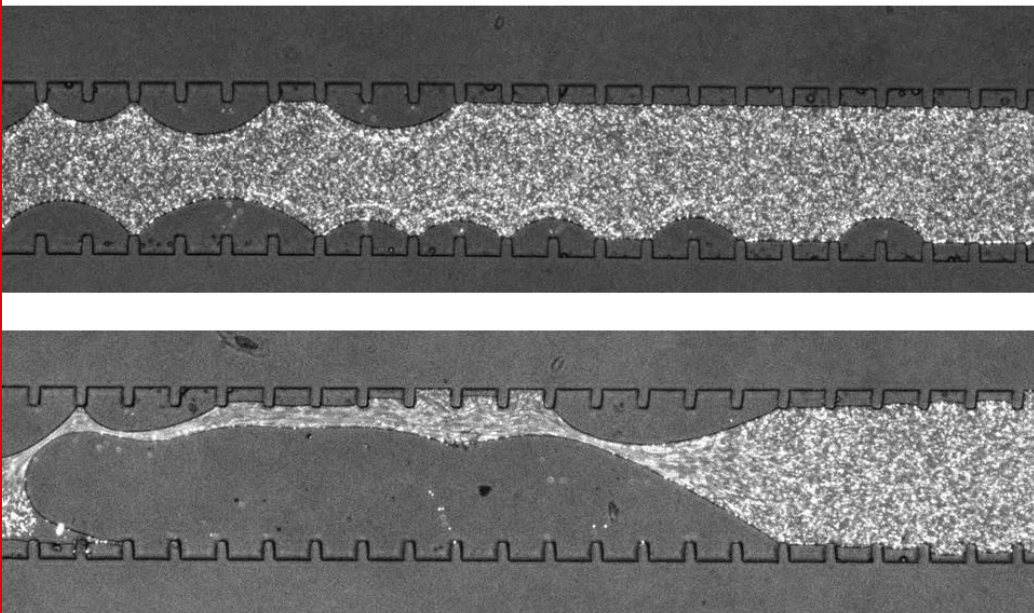
SU-8 2015 Mold on Silicon Wafer



Tufts PDMS Channels

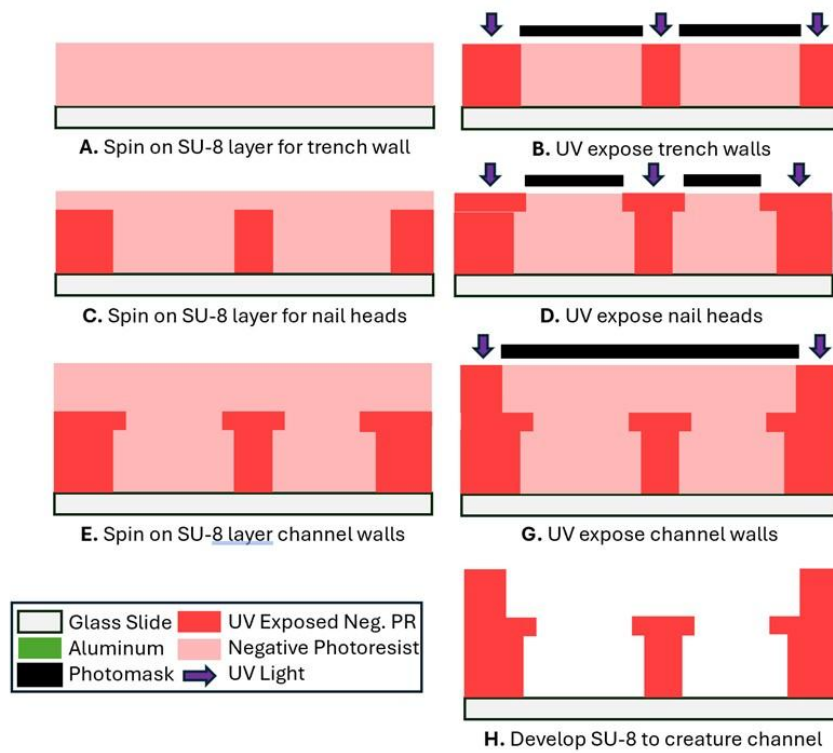
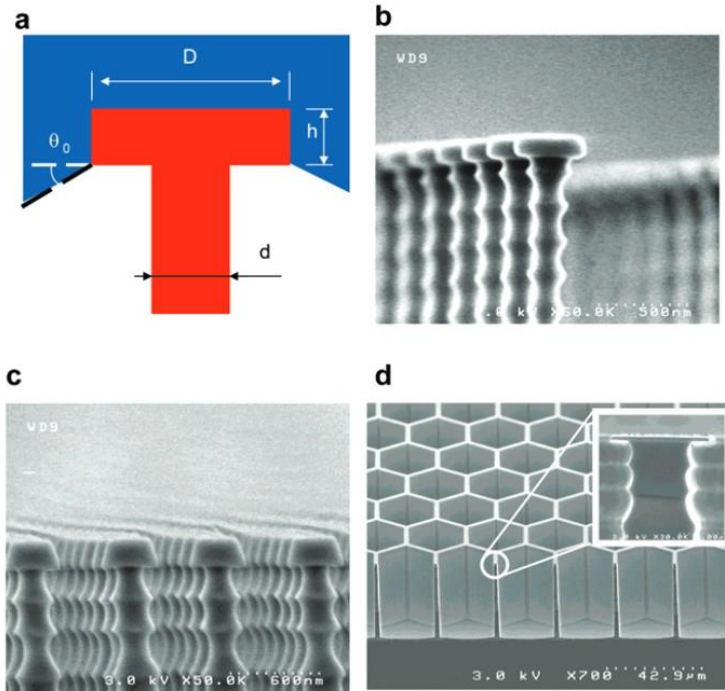


Tufts PDMS Channels

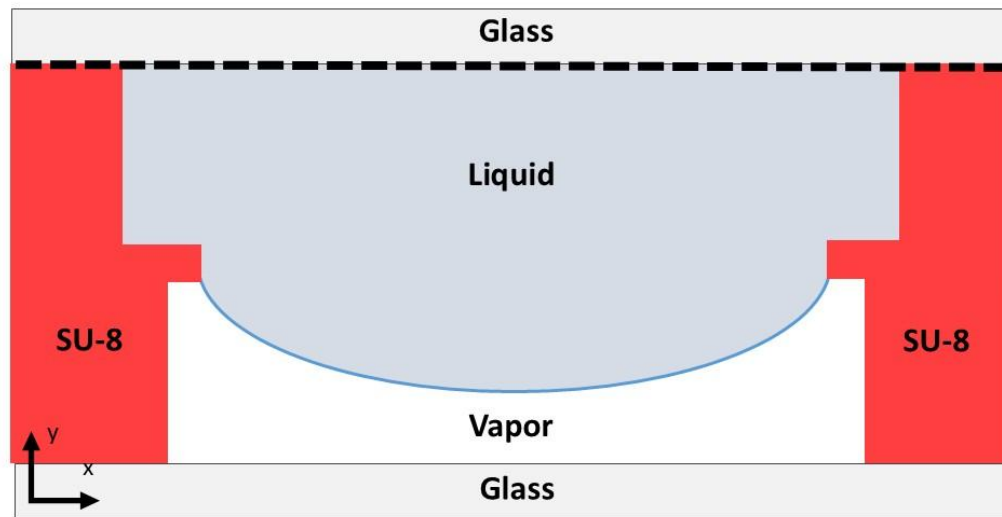


Missing Video: Water seeded with fluorescent PIV microparticles filling a transversely ridged hydrophobic microchannel (**top**) uncontrolled menisci shape during flow (**bottom**)

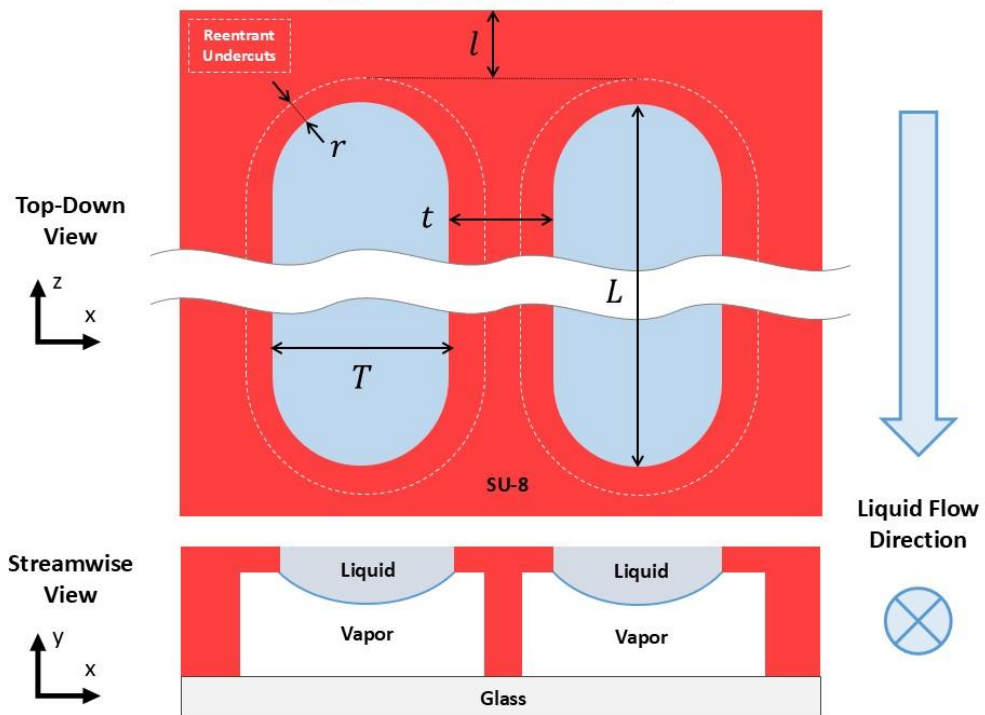
Reentrant Structures



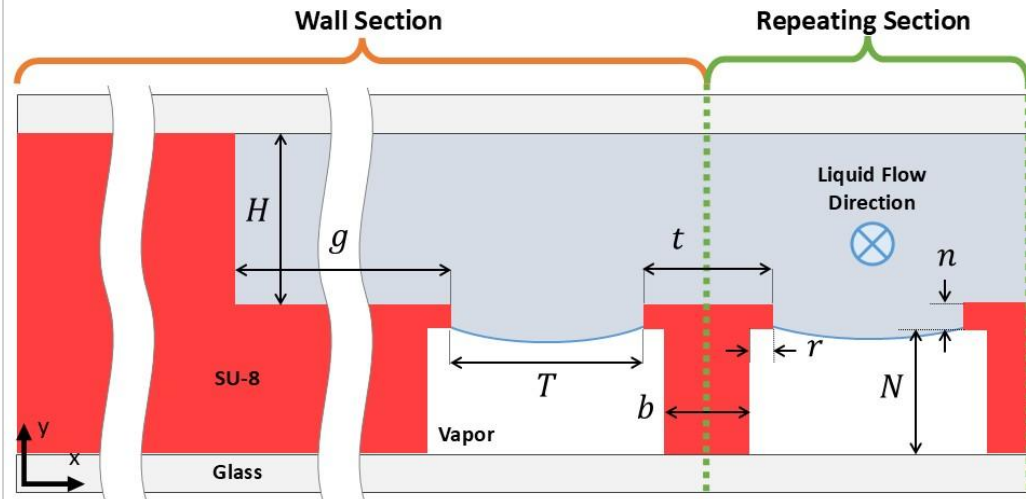
Reentrant Structures



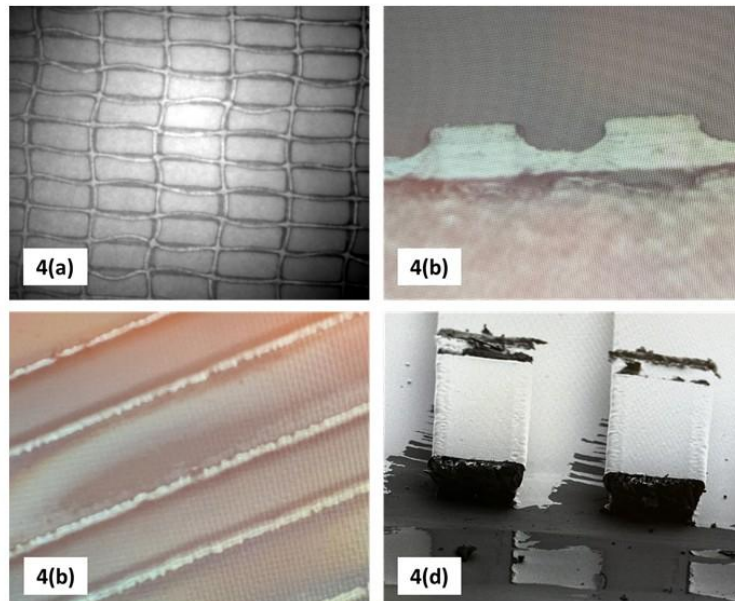
Reentrant Structures



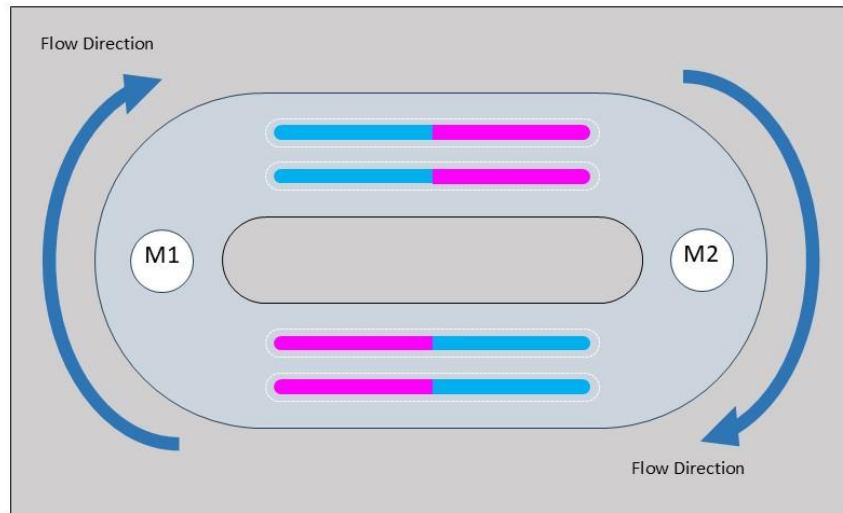
Reentrant Structures



Reentrant Structures

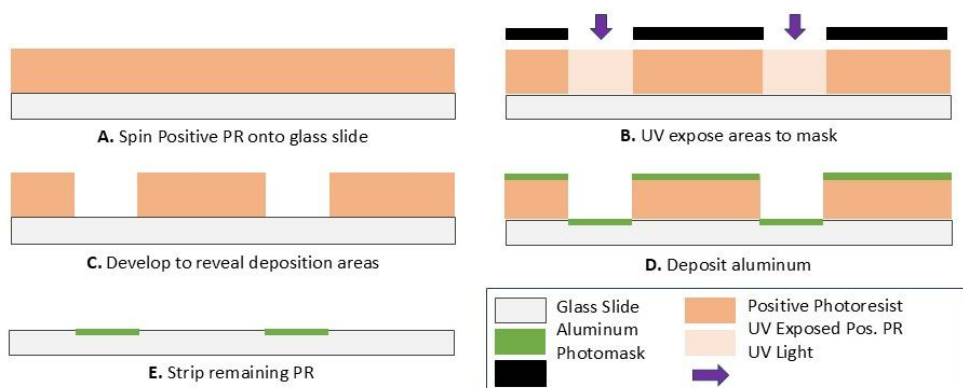


Racetrack Transient Experiment



Micro Masking

Masking Slides



Raw Data

This following is an ASCII formatted tabular record of the data shown in Fig. 21. Archived data (not explicitly included for the sake of brevity) from additional, redundant, or less comprehensive experiments using photosurfactants, and data from experiments using pure water or isopropanol to validate our methods are available upon request from Professor Marc Hodes of Tufts University. The pendant bubble images themselves and the MATLAB code used to analyze them are also available upon request as well.

1 μ M – 100% -*trans*

Time [sec]	Surface Tension [mN/m]	Time [sec]	Surface Tension [mN/m]
20.21	72.32	1347.42	69.15
27.01	72.15	1381.63	68.75
33.82	72.21	1449.46	68.42
40.22	72.16	1488.08	68.27
46.42	71.93	1557.91	68.17
52.62	72.14	1591.73	68.01
58.63	72.09	1663.76	67.76
64.83	72.20	1734.00	67.19
67.63	72.20	1801.63	67.19
74.43	72.25	1874.66	66.88
81.24	72.09	1909.88	66.70
88.04	72.06	2085.16	66.23
94.84	72.04	2153.79	65.95
101.65	72.17	2261.04	65.61
107.85	72.28	2330.07	65.30
114.05	72.13	2436.72	65.00
120.06	72.09	2539.97	65.14
132.46	72.08	2647.81	64.77
135.46	72.10	2749.86	64.51
142.27	72.09	2858.31	63.88
154.87	72.06	2964.96	63.48
162.47	72.09	3102.22	63.04
175.08	72.04	3244.49	62.66
182.88	72.05	3386.55	62.20
195.49	71.98	3527.42	62.18
203.09	72.04	3668.08	61.81

215.70	72.11	3840.36	61.42
223.50	72.02	3982.63	60.90
236.11	71.96	4158.71	60.38
243.71	72.01	4368.80	59.99
261.32	72.10	4544.89	59.60
276.53	71.93	4968.88	58.54
291.13	71.89	5179.98	58.16
304.74	71.80	5425.49	57.63
318.35	71.75	5918.72	56.81
337.35	71.89	6197.64	56.12
352.16	71.87	6481.77	55.60
365.77	71.81	6797.92	54.74
382.98	71.97	7078.05	54.05
398.18	71.81	7430.21	52.98
433.40	71.71	7781.37	52.08
467.21	71.83	8132.93	50.84
501.23	71.62	8519.51	49.69
538.85	71.70	8906.29	49.06
574.06	71.72	9326.88	48.13
609.28	71.62	9786.09	47.19
643.49	71.59	10241.30	46.22
677.31	71.46	10735.73	45.19
749.54	71.48	11263.77	44.30
784.56	71.50	11791.21	43.54
819.58	71.39	12353.67	42.83
853.39	71.27	12950.54	42.13
887.21	71.12	13584.23	41.60
925.22	71.17	14251.14	41.09
960.24	70.96	14920.65	40.76
995.46	71.00	15658.38	40.46
1029.47	70.75	16432.14	40.17
1063.29	70.69	17204.29	40.06
1136.32	70.15	18050.68	39.97
1171.54	69.89	18931.29	39.97
1205.55	69.88	19879.72	39.89
1239.57	69.81	20834.76	39.81
1312.20	69.23		

20 μ M – 100% -*trans*

Time [sec]	Surface Tension [mN/m]	Time [sec]	Surface Tension [mN/m]
43.02	72.49	435.80	68.66
49.82	72.36	449.41	68.59
56.63	72.28	456.21	68.30
63.43	72.07	469.82	68.46
69.83	72.10	480.22	68.03
76.03	71.99	495.43	67.89
82.44	72.09	510.43	67.85
88.64	72.03	523.84	67.68
94.84	72.01	541.45	67.45
101.05	71.93	556.65	67.41
104.05	72.11	571.26	67.30
110.85	71.93	584.87	67.05
117.45	71.88	602.28	66.75
124.26	71.98	617.68	66.45
131.06	71.90	632.29	66.35
137.86	71.62	666.10	65.79
144.67	71.69	700.12	65.34
151.07	71.59	738.54	64.55
157.47	71.59	773.76	63.92
163.67	71.54	808.37	63.33
169.88	71.30	842.19	62.64
176.08	71.70	876.20	61.72
182.28	71.57	914.82	61.03
185.28	71.64	950.23	60.36
192.09	71.48	984.45	59.38
198.89	71.37	1018.47	58.54
205.49	71.38	1056.08	57.58
212.30	71.39	1091.30	56.65
219.10	71.11	1126.52	55.57
225.90	70.83	1160.53	54.61
232.51	71.22	1194.55	53.51
238.91	71.05	1232.36	52.19
245.11	70.76	1267.58	51.07
251.32	70.87	1302.80	49.85
257.52	70.94	1336.81	48.67
263.92	70.67	1370.63	47.78
273.33	70.36	1408.65	46.77
280.13	70.72	1443.86	45.81
286.93	70.55	1478.88	44.91

293.73	70.37	1512.89	43.99
300.34	70.38	1546.71	43.18
307.14	70.46	1584.93	42.04
313.74	70.28	1620.14	41.10
319.95	70.08	1655.16	40.15
326.35	69.96	1688.97	39.25
332.55	70.02	1722.79	38.28
338.76	70.03	1761.21	37.25
344.96	69.83	1796.42	36.42
354.56	69.77	1831.24	35.59
361.36	69.81	1865.06	34.80
368.17	69.74	1898.87	34.11
374.97	69.38	1937.29	33.42
387.38	69.46	1972.51	32.86
395.18	69.30	2007.32	32.52
407.99	69.22	2041.14	32.14
415.59	68.96	2074.95	31.91
428.80	68.83	2113.57	31.54

20 μ M – 85% -*trans*

Time [sec]	Surface Tension [mN/m]	Time [sec]	Surface Tension [mN/m]
40.82	71.99	128.48	71.62
42.09	71.91	129.73	71.61
43.36	71.81	131.00	71.54
44.89	71.82	132.27	71.65
46.26	71.67	133.57	71.54
47.52	71.89	134.85	71.48
48.78	71.80	136.14	71.77
50.04	71.78	137.43	71.56
51.29	71.83	138.71	71.50
52.57	71.71	140.00	71.47
53.87	71.73	141.31	71.48
55.15	71.80	142.65	71.35
56.42	71.88	143.94	71.63
57.68	71.82	145.32	71.42
58.93	71.85	146.61	71.42
60.20	71.66	147.95	71.50
61.48	71.96	149.22	71.51
62.80	71.82	150.59	71.61
64.04	71.81	151.91	71.47
65.30	71.62	153.38	71.51
66.55	71.91	155.14	71.47
67.80	71.72	156.91	71.43
69.07	71.68	158.69	71.54
70.36	71.70	160.46	71.40
71.64	71.84	162.22	71.49
72.90	71.76	163.98	71.50
74.16	71.74	165.73	71.51
75.43	71.75	167.47	71.33
76.70	71.84	169.23	71.57
77.97	71.71	170.97	71.59
79.24	71.77	181.72	71.57
80.48	71.79	192.47	71.43
81.73	71.87	203.25	71.48
82.99	71.76	214.00	71.41
84.29	71.84	224.75	71.39
85.55	71.71	235.52	71.37
86.82	71.69	246.32	71.31
88.09	71.76	257.07	71.32
89.36	71.72	267.83	71.17

90.64	71.82	278.60	71.22
91.91	71.75	329.36	70.68
93.16	71.77	380.11	69.61
94.41	71.68	430.88	68.40
95.67	71.90	481.64	66.39
96.92	71.72	532.39	64.29
98.17	71.71	583.14	61.94
99.43	71.77	633.89	59.32
100.68	71.66	684.64	56.39
101.94	71.61	735.41	53.87
103.22	71.67	786.19	51.73
104.47	71.70	886.98	48.27
105.74	71.75	987.76	46.04
107.00	71.77	1088.53	44.35
108.27	71.66	1189.31	43.08
109.52	71.47	1290.06	42.41
110.78	71.73	1390.82	41.82
112.03	71.59	1491.58	41.43
113.30	71.55	1592.34	41.00
114.59	71.54	1693.11	40.65
115.84	71.58	1793.90	40.56
117.09	71.73	2294.67	39.07
118.34	71.62	2795.45	37.03
119.60	71.62	3296.22	34.90
120.88	71.71	3796.97	33.07
122.16	71.72	4297.73	31.17
123.43	71.59	4798.57	30.49
124.68	71.58	5299.32	30.15
125.93	71.68	5800.06	29.53
127.18	71.79	6300.82	29.22

1 mM – 100% -trans

Time [sec]	Surface Tension [mN/m]	Time [sec]	Surface Tension [mN/m]
2.76	72.58	397.69	42.30
4.10	72.43	403.28	42.09
5.48	72.88	408.86	41.99
6.81	72.99	420.01	41.85
8.22	72.70	425.59	41.86
9.56	72.78	431.18	41.59
10.98	72.52	436.75	41.21
12.56	72.64	442.34	41.02
14.13	72.42	447.92	40.89
15.69	72.21	453.50	40.75
17.26	72.34	459.08	40.42
18.82	72.33	464.69	40.17
20.39	72.27	470.27	39.89
21.97	72.33	475.84	39.71
23.54	72.31	481.42	39.61
25.11	71.92	486.99	39.32
26.70	71.79	492.56	39.19
28.27	71.43	498.14	39.04
29.84	71.14	503.71	38.81
31.43	71.13	509.28	38.59
33.00	70.76	514.86	38.52
34.58	70.30	520.44	38.23
36.15	70.13	526.01	38.03
37.72	69.98	531.61	37.72
39.29	69.57	537.20	37.48
40.87	69.40	542.77	37.37
42.46	69.28	548.36	37.09
44.03	68.77	553.93	36.87
45.62	68.42	559.52	36.58
47.26	68.42	565.10	36.37
48.83	68.05	570.68	36.18
50.42	67.75	576.26	35.89
52.04	67.71	587.45	35.61
53.76	67.57	593.02	35.40
55.34	67.48	598.60	35.09
57.02	67.32	604.18	34.87
45.33	68.61	609.76	34.71
47.39	68.66	615.34	34.46
51.37	67.94	620.92	34.40

53.28	67.60	626.49	34.27
57.42	67.24	632.07	33.99
59.37	66.79	637.64	33.84
61.49	66.22	643.23	33.69
63.46	65.78	648.81	33.61
65.61	65.52	654.41	33.60
67.75	64.49	659.98	33.38
69.75	63.83	665.56	33.30
71.89	63.59	671.14	33.22
73.88	62.81	676.71	33.07
76.05	62.15	682.30	32.96
78.10	61.54	692.87	32.84
80.32	60.80	703.44	32.72
82.33	60.23	714.06	32.55
84.54	59.64	724.63	32.35
86.58	59.09	735.22	32.14
88.74	58.82	745.82	31.96
90.94	58.39	756.43	31.88
93.17	57.81	767.01	31.81
95.24	57.50	777.59	31.81
97.41	56.97	788.17	31.79
99.70	56.38	798.75	31.55
101.80	56.00	809.33	31.36
104.05	55.80	819.90	31.31
106.16	55.75	830.49	31.18
108.48	55.27	841.07	31.21
110.60	54.83	851.66	30.96
112.97	54.22	862.25	30.74
115.13	54.10	872.82	30.51
117.47	53.75	883.40	30.55
119.65	53.37	893.98	30.34
121.93	53.14	904.56	30.39
124.22	52.99	915.13	30.42
129.80	52.65	925.70	30.23
135.41	52.07	936.30	30.15
146.56	51.60	946.88	30.09
152.14	50.97	957.45	30.07
157.72	50.38	968.03	29.90
163.30	50.28	978.60	29.83
168.86	49.70	989.19	29.75
174.44	49.26	999.79	29.66
180.02	48.75	1010.37	29.62
185.60	48.41	1020.95	29.56

191.18	48.14	1031.53	29.65
196.77	47.65	1042.12	29.54
202.37	47.48	1052.69	29.52
207.94	47.23	1063.29	29.60
213.51	47.04	1073.87	29.52
219.10	46.79	1084.45	29.75
224.68	46.60	1095.03	29.63
230.28	46.47	1105.61	29.51
235.86	46.22	1116.20	29.43
252.62	45.98	1126.78	29.45
258.22	45.74	1137.37	29.38
263.79	45.39	1147.95	29.34
269.37	45.29	1158.52	29.31
274.95	45.16	1169.10	29.29
280.52	45.04	1179.68	29.30
286.10	44.95	1190.27	29.39
291.69	44.72	1200.85	29.29
297.27	44.61	1211.42	29.24
302.85	44.49	1222.00	29.17
308.43	44.40	1232.58	29.15
314.00	44.33	1243.16	29.16
319.58	44.17	1253.75	29.11
330.75	44.09	1264.33	29.11
336.33	43.96	1274.91	29.11
341.91	43.63	1285.50	29.08
347.48	43.75	1296.08	29.11
353.05	43.64	1306.66	29.05
358.62	43.56	1317.24	29.02
364.21	43.43	1327.81	29.01
369.79	43.21	1338.39	28.99
375.37	42.95	1348.97	29.14
380.95	42.74	1359.54	29.11
386.53	42.55	1370.13	29.06
392.11	42.48		

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