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Biographical Sketch

The author of this dissertation pursued a Bachelor of Science degree in Chemical Engineering at Carnegie Mellon University from 2008-2012. He then joined the Chemical Engineering department at the University of Rochester in the fall of 2012. He also received the Frank J. Horton Graduate Research Fellowship from 2013-2017. Research on digital microfluidics was conducted under the supervision of Professor David R. Harding and Professor Thomas B. Jones.

Publications


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Abstract

A requirement for producing fusion energy is the availability of inexpensive fuel capsules. As researchers determine methods to make the fusion process more efficient, the demand for capsules will increase. This dissertation discusses a microfluidics approach using electric fields to produce emulsion droplets and transform them into capsule shells in a continuous process. The goal is to produce shells of high quality with a high throughput. Special attention was given to controlling the size of the droplets; one of which forms the shell wall while another determines the size of the capsule.

Electrowetting-on-dielectric (EWOD) and dielectrophoresis (DEP) forces were used to move conductive and dielectric fluids, respectively. It was demonstrated that water droplets containing a surfactant can be formed using the EWOD force and heating. The droplets had volumes ranging from 0.4 μL to 13 μL, and the variability in the droplet volume was 1 to 5% when a high heater power was used. In addition, oil droplets of various viscosity were dispensed with volumes ranging from 8 nL to 11 μL. The variability in the droplet volume was 2 to 15% depending on the substrate geometry. The dispensing experiments were supplemented by force modeling.

Combining the droplets formed emulsions ranging in volume from 0.2 μL to 16 μL. It was demonstrated that no surfactant was required to form water-in-oil emulsions. Moreover, using a high surfactant concentration allowed oil-in-water emulsions to form. A Gibbs free energy analysis was conducted to determine the effect of surfactant concentration on emulsion formation.

Once the emulsions were formed, they were transported between parallel plates using the EWOD force. The excitation sequence for the electrodes depended on the
emulsion type, the fluids used, and the size of the electrodes. As part of an effort to transport the emulsions to a space with a plate spacing suitable for making capsule shells, large droplets were moved between diverging plates down an inclined surface using gravitational and electrical forces. These forces were adequate to overcome capillary and surface pinning forces that prevented the droplet from moving to a wider plate separation.

To determine if emulsions could be transformed into capsule shells, droplets containing the chemicals required to form polystyrene shells were pipetted into an oil bath. The chemicals were photo-polymerized with ultraviolet light. An electric field was then applied between two electrodes surfaces to center a styrene-based double emulsion.
Contributors and Funding Sources

The professors on my dissertation committee include Dr. David Harding, Dr. Douglas Kelley, Dr. Thomas Jones, and Dr. Matthew Yates. The work discussed in this dissertation was personally conducted with a few exceptions. The electrical force equation (Eqn. 3.20) for moving a droplet was derived by Dr. Weiqiang Wang. The dielectrophoresis force equations (Eqns. 3.32-3.33) were derived by Dr. Zongmin Bei. In addition, the SEM images in Chapter 10 (Figs. 10.6-10.8) were taken by Dr. David Harding and Brian McIntyre. Dr. Harding and Dr. Jones were my collaborators in the journal articles mentioned earlier. Funding for this work came from the Frank J. Horton Graduate Research Fellowship.
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6.13 Top view showing the fluid membrane for a 1x CMC solution being locally heated by a resistive strip (30V\textsubscript{DC} application). The strip had a resistance of 113 $\Omega$. [a-d] The electrode width was 6 mm and the plate spacing was 270 $\mu$m. The membrane ruptured within 0.4 s to separate a $\sim$12.2 $\mu$L droplet.

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6.16 The measured wavelength that destabilized the membrane. The dc voltages used were 20V and 30V. The surfactant concentration ranged from 0.5 to 5x the CMC limit.
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6.18 Length of time that heat was applied to the membrane to rupture it. The electrode width was 6 mm and the plate spacing was 270 µm. The error bars were calculated by determining the average heating time and finding the values that represented one standard deviation.

6.19 Droplet volumes formed with a range of heater powers (0.02 W to 0.15 W) applied to the membrane. The electrode width was 2 mm and the plate spacing was 90 µm. The error bars were calculated by determining the average droplet volume and finding the values that represented one standard deviation.

6.20 Droplet volumes formed with a range of heater powers (0.95 W to 2.1 W) applied to the membrane. The electrode width was 6 mm and the plate spacing was 270 µm. The error bars were calculated by determining the average droplet volume and finding the values that represented one standard deviation.
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Process to dispense a PAA-water droplet using 75 V$_{\text{rms}}$ at 30 kHz on 2-mm square electrodes with a 180 µm plate spacing. A resistive heater was embedded in the electrode pattern. Fluid was: (a) centered on the reservoir electrode, (b) moved onto the droplet electrode, (c) retracted to the reservoir electrode. (d) ~0.15 W of heater power was applied to the membrane, which (e) ruptured after ~0.90 s. The droplet volume was ~0.79 µL.
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6.26 Water droplets containing surfactant at 0 to 5x the CMC limit were transported back-and-forth between two 6-mm square electrodes using 75 or 100 V\textsubscript{rms}. The spacing between plates was 270 µm. One electrode was activated for 6 s while the other was unpowered. The time that the droplet successfully moved from one electrode to the next is presented.

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8.2  Top view showing a water-in-decane emulsion being transported along an electrode pattern using $88 \text{ V}_{\text{rms}}$ at 100 Hz. (a) All electrodes were grounded. (b) The first two electrodes were powered, which pulled the emulsion onto those electrodes. (c) The emulsion moved along the electrode pattern by activating two electrodes at a time. (d) The emulsion reached the top of the electrode pattern.
8.3 Top view showing the formation of a (water-acetonitrile)-in-(styrene-butanol) emulsion from two reservoirs of fluid. The styrene-butanol solution was moved using 133 V$_{\text{rms}}$ at 900 Hz, while the water-acetonitrile solution was moved using 75 V$_{\text{rms}}$ at 100 Hz. (a) One droplet of styrene-butanol rested on a 2-mm square electrode while another was dispensed. (b) Five styrene-butanol droplets rested on the 2 mm-square electrode pattern while the water-acetonitrile solution was centered on its reservoir electrode. (c) The water solution was moved onto the droplet electrode. (d) A water-acetonitrile droplet was dispensed. (e) The water droplet was transported. (f) The combined water and styrene-based droplets formed a water-in-styrene emulsion upon contact.

8.4 Top view showing a water-in-silicone oil emulsion being transported along an array of 6-mm square electrodes using 75 V$_{\text{rms}}$ at 100 Hz. The spacing between plates was 180 μm. The volume of water and oil were 12.5 μL each. (a) The water droplet was centered on the powered electrode. (b) The emulsion advanced. (c) A membrane formed in the silicone oil as the water droplet advanced. (d) The membrane ruptured and a silicone oil droplet was pinched off, which reduced the oil volume surrounding the water droplet.
8.5 Top view showing a water-in-silicone oil emulsion transported along an array of 6-mm square electrodes with a 180μm plate spacing. The volume of water was 12 μL while the volume of oil was 3 μL. (a) Emulsion on an unpowered electrode. (b-d) The emulsion advanced onto the powered electrodes.

8.6 Top view showing a water-in-mineral oil emulsion transported along an array of 6-mm square electrodes with a 180 μm plate spacing. The volume of water was 12 μL while the volume of oil was 4 μL. (a) Emulsion on an unpowered electrode. (b-c) The emulsion advanced to the powered electrode but with the mineral oil lagging behind. As a result, the emulsion could not completely fill the powered electrode in c.
Top view showing the formation of a water-styrene-mineral oil double emulsion. (a) 20 μL of mineral oil, 4 μL of styrene-butanol, and 8 μL of water-acetonitrile were placed on the bottom substrate with the top substrate angled ~1.5° relative to the bottom substrate. The arrow indicates larger spacing. The bottom substrate was also tilted above the horizontal by ~1.3° in the direction of the mineral oil droplet. (b) The styrene and water-based droplets were combined using 120 V_{rms} at 100 Hz. The emulsion was then transported towards the mineral oil. (c) The mineral oil enveloped the water-in-styrene emulsion. (d) The water-based droplet moved to the center of the mineral oil, but the outline of the styrene droplet became indistinguishable from the oil. (e) White particulates formed within the mineral oil and (f) a cloudy solution appeared to envelop the water droplet.
8.8 Top view showing a mineral oil-in-water emulsion being made and transported on 2-mm square electrodes with a 90-μm plate spacing. (a) A surfactant-water droplet was dispensed using 75 V\text{rms} at 10 kHz and 0.15 W of heater power, while a mineral oil droplet was centered on the top electrode using 672 V\text{rms} at 100 Hz. (b) After combining the fluids, the second electrode from the top was activated to center the water phase over it. (c) The water portion of the emulsion advanced to the third electrode while the trailing end of the emulsion had barely moved after 10 s. (d) After 30 s, the trailing end of the emulsion was in the same position. (e) The water droplet advanced onto the 4\textsuperscript{th} electrode, which extended the length of the membrane.

8.9 Top view showing the transport of a mineral oil-in-water emulsion on 2-mm square electrodes with a 180-μm plate spacing. (a) The 2\textsuperscript{nd} electrode (from the top) was energized and occupied by the water portion of the emulsion. (b-e) The 3\textsuperscript{rd} electrode was energized and occupied by the water droplet, forming a membrane between it and the oil droplet. (f-k) Surface tension in the water filament surrounding the oil moved the oil onto the 2\textsuperscript{nd} electrode. (l) The emulsion was transported to the 4\textsuperscript{th} electrode.
Top view showing the formation of a mineral oil-in-water emulsion on 2-mm square electrodes with a 90 μm plate spacing. The mineral oil was moved using 610 V$_{\text{rms}}$ at 100 Hz, while the water was moved using 75 V$_{\text{rms}}$ at 10 kHz. (a) Mineral oil was centered on the reservoir electrode. (b) Mineral oil was moved onto the droplet electrode. (c) A mineral oil droplet was dispensed. (d) The oil droplet was transported to a specific site to be combined with the water droplet. (e) A liquid column was drawn from the reservoir of the 5x CMC solution. (f) 1.0 W of heater power was applied to the membrane after fluid had been retracted to the reservoir electrode. (g) The water droplet was moved along the electrode pattern. (h) The oil and water droplets were combined to form an oil-in-water emulsion.
Top view showing the transport of a mineral oil-in-water emulsion along an electrode pattern. (a) The second electrode from the bottom was powered, which pulled the water droplet onto it. (b) The third electrode was activated, and the majority of the water flowed onto it. (c) The second and third electrodes were powered, which caused the bulk of the water to recombine with the emulsion. (d) The water droplet moved forward after the second electrode was grounded and the third electrode remained active. (e) The front end of the emulsion was pulled back when the second electrode was powered. (f) The water droplet was pulled forward after grounding the second electrode. (g) The emulsion pulled back after the second electrode was powered. (h) The emulsion moved forward after grounding the second electrode. (i) The emulsion moved forward after powering and then grounding the second electrode. (j) The emulsion was transported to the next electrodes. (k) The emulsion was transported across three electrodes. (l) The front of the emulsion reached the end of the electrode pattern, but the rest of the emulsion was left behind.
Top view showing a mineral oil-in-water emulsion being transported using 75 V\textsubscript{rms} at 10 kHz across a rectangular electrode pattern. The electrodes were 2.5 mm x 10 mm, and the plate spacing was 180 μm. The emulsion had 6 μL of mineral oil and 6 μL of water. (a) The water droplet moved onto the powered electrode. (b) The water droplet advanced onto the electrode ahead of the emulsion. (c) The water droplet retracted after powering two electrodes at once. (d) The water droplet advanced after powering the fourth electrode from the right. (e) The water droplet moved backwards after powering the third electrode. (f) The water droplet advanced. (g) The water droplet moved onto the next electrode. (h) The water droplet retracted. (i) The water droplet advanced. (j) The water droplet advanced again. (k) The emulsion advanced to the next electrode. (l) The emulsion advanced to the final electrode.
9.1 Side-view schematic of a concept for making double emulsions. The oil-water emulsion and the encapsulating droplet are formed between narrowly-spaced plates and transported down inclined surfaces. The double emulsion forms when the encapsulating droplet envelops the emulsion.

9.2 Top view showing a 6 µL mineral oil droplet being transported down a 45° incline between two plates separating at an angle of ~0.31°, from a plate spacing of 0.18 mm to 0.45 mm. The applied voltage was 672 V\textsubscript{rms} at 100 Hz. Each electrode was 2.5 mm x 10 mm. The individual images (a-h) show the progression of the droplet as successive electrodes were energized.

9.3 Forces acting on a 6 µL mineral oil droplet moving between two diverging plates. The bottom substrate had a 45° tilt. The applied voltage was 672 V\textsubscript{rms} at 100 Hz. The net force (electrical, gravitational, pinning, and capillary) was calculated for plate separation distances ranging from ~0.2 to 0.42 mm.
9.4 Top view showing a 10 µL mineral oil droplet being transported down a 45° incline between two plates separating at an angle of ~2.3°, from a plate spacing of 0.45 mm to 2.2 mm. The electrical condition was $755 \text{ V}_{\text{rms}}$ at 100 Hz. The electric field was needed to move the droplet a portion of the distance (a-b), thereafter gravity took over as the capillary force decreased and the droplet rolled down the two-plate construction. (c-h).

9.5 Forces acting on a 10 µL mineral oil droplet moving between two diverging plates. The bottom substrate had a 45° tilt. The applied voltage was $755 \text{ V}_{\text{rms}}$ at 100 Hz. The net force (electrical, gravitational, pinning, capillary, and drag) was calculated for spacing ranging from ~0.8 to 1.9 mm.

9.6 Top view showing a 6 µL water droplet with a surfactant concentration of 5x the CMC limit being transported down a 45° incline between two plates separating at an angle of ~0.31°, from a plate spacing of 0.18 mm to 0.45 mm. The electrical condition was $75 \text{ V}_{\text{rms}}$ at 10 kHz. The contact area of the droplet with the substrates decreased with distance traveled. The droplet also became more rounded.
Forces acting on a 6 µL water droplet with a surfactant concentration of 5x the CMC limit moving between two diverging plates. The bottom substrate was tilted 45°. The applied voltage was 75 V_{rms} at 10 kHz. The net force (electrical, gravitational, pinning, and capillary) was calculated for spacing ranging from ~0.2 to 0.43 mm.

Top view showing a 10 µL water droplet with a surfactant concentration of 5x the CMC limit being transported down a 45° incline between two plates separating at an angle of ~2.3°, from a plate spacing of 0.45 mm to 2.2 mm. The electrical condition was 75 V_{rms} at 10 kHz. The electric force controlled the droplet movement initially (a-c), but eventually (d-i) the droplet rolled beyond the activated electrodes. In those frames, the droplet velocity increased due to reduced Laplace pressure and pinning forces.
Forces acting on a 10 µL water droplet with a surfactant concentration of 5x the CMC limit moving between two diverging plates. The bottom substrate was tilted 45°. The applied voltage was 75 V_{\text{rms}} at 10 kHz. The net force (electrical, gravitational, pinning, capillary, and drag) was calculated for spacing ranging from ~0.6 to 2.1 mm. The electrical force only acted on the droplet for the first three data points.

Top view showing a 20 µL water droplet being transported from a plate spacing of ~1 to 1.7 mm. The plates separated at an angle of ~5.5°, and the bottom substrate was horizontal. The electrical condition was 75 V_{\text{rms}} at 100 Hz. In (a)-(d) the droplet became more rounded and had a smaller footprint on the substrates.

Forces acting on a 20 µL water droplet between two diverging plates as a function of plate spacing. The applied voltage was 75 V_{\text{rms}} at 100 Hz. The net force (electrical, pinning, and capillary) was calculated for spacing ranging from ~1 to 1.7 mm.

Process to form a double emulsion. (a) A styrene droplet is pipetted into the silicone oil, forming an emulsion. (b) A silicone oil droplet is pipetted into the styrene droplet to form a double emulsion.
Images of a 1 μL styrene-butanol droplet in mineral oil. The density of the styrene solution was 0.85725 g/cc, while the density of the mineral oil was 0.85665 g/cc. (a) The droplet was pipetted and (b-c) the droplet began to tilt upwards. (d-f) The droplet vertically elongated, presumably an effect of the differences in density between the styrene and butanol.

Images of a 1 μL styrene-DMA droplet in mineral oil taken 4s apart. The density of the styrene-DMA droplet was 0.92857 g/cc. The droplet (a-b) gradually sunk, (c) approached the bottom substrate, and (d) wet the bottom surface.

A 3 μL styrene-polystyrene-DMA-PPO droplet was (a) pipetted onto a glass microscope slide, (b) exposed to UV light for two minutes. The droplet became clear and a solid plate formed in the center with a low viscosity fluid surrounding it.
Images showing a 2 µL droplet containing 37.6 wt% styrene, 7.4 wt% polystyrene, 45 wt% DMA, and 10 wt% PPO being polymerized in silicone oil. The densities of the styrene solution and the silicone oil were 0.95870 g/cc and 0.95827 g/cc, respectively. (a) Prior to exposing the droplet to UV light, the droplet slowly sank. (b) The droplet was exposed to UV light for a minute, resulting in the droplet separating into two volumes. (c) Another minute of UV exposure caused the darker droplet to sink. (d-e) The droplet then approached the bottom surface and (f) after an additional minute of exposure the droplet wet the bottom surface.
SEM image of the surface of a dried polystyrene bead. Small craters exist along the surface.

SEM image of a cross-sectioned dried polystyrene bead. There are voids throughout the polystyrene material.

SEM image of a cross-sectioned dried polystyrene bead. Micron and sub-micron pores exist throughout the polystyrene material.

Images showing a 2 µL droplet containing 58.3 wt% styrene, 11.7 wt% polystyrene, 20 wt% DMA, and 10 wt% PPO photopolymerizing in silicone oil. The density of the styrene solution was 0.95590 g/cc, while the density of the silicone oil was 0.95577 g/cc. (a) Prior to exposing the droplet to UV light, the droplet slowly sank. (b) The droplet was exposed to UV light for one minute, which resulted in a plume forming at the top of the droplet. The droplet turned from clear to opaque. (c) Another minute of UV exposure caused the droplet to sink. (d-f) With three more minutes of UV curing the droplet diameter decreased. Material expelled from the droplet formed ribbon-like-strands in the silicone oil.
Images showing a 2 µL droplet containing 75 wt% styrene, 15 wt% polystyrene, and 10 wt% PPO photo-polymerizing in silicone oil. The density of the styrene solution was 0.95052 g/cc, while the density of the silicone oil was 0.95040 g/cc. (a) Prior to exposing the droplet to UV light, the droplet slowly sank. (b) The droplet was exposed to UV light for one minute, which resulted in a strand of liquid being extruded from the top of the droplet. (c) The droplet then tilted. With three more minutes of UV curing (d-f) the droplet appeared to have flattened or rolled on its side.

Images showing a (silicone oil)-in-(styrene-polystyrene-DMA-PPO)-in-(silicone oil) double emulsion: (a) prior to applying voltage, (b) 1 minute after applying 840 V\text{rms} at 20 MHz, (c) 2 minutes later, (d) 3 minutes later, and (e) 4 minutes later. The density of the inner droplet was 0.95880 g/cc, the density of the styrene solution was 0.96856 g/cc, and the density of the surrounding oil was 0.95821 g/cc.
# List of Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>CMC</td>
<td>Critical micelle concentration</td>
</tr>
<tr>
<td>DAQ</td>
<td>Data acquisition unit</td>
</tr>
<tr>
<td>DT</td>
<td>Deuterium-tritium</td>
</tr>
<tr>
<td>DEP</td>
<td>Dielectrophoresis</td>
</tr>
<tr>
<td>DMA</td>
<td>Dimethylacetamide</td>
</tr>
<tr>
<td>DVB</td>
<td>Divinylbenzene</td>
</tr>
<tr>
<td>DE</td>
<td>Double emulsion</td>
</tr>
<tr>
<td>EWOD</td>
<td>Electrowetting-on-dielectric</td>
</tr>
<tr>
<td>GE</td>
<td>Gibbs free energy</td>
</tr>
<tr>
<td>GDP</td>
<td>Glow discharge polymer</td>
</tr>
<tr>
<td>HMDS</td>
<td>Hexamethyldisilazane</td>
</tr>
<tr>
<td>HMTD</td>
<td>Hydroxyl methyl resorcinol derivative</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium-tin-oxide</td>
</tr>
<tr>
<td>ICF</td>
<td>Inertial confinement fusion</td>
</tr>
<tr>
<td>IFT</td>
<td>Interfacial tension</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl alcohol</td>
</tr>
<tr>
<td>Ma</td>
<td>Marangoni number</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>NIF</td>
<td>National ignition facility</td>
</tr>
<tr>
<td>NC</td>
<td>Non-concentricity</td>
</tr>
<tr>
<td>O/W</td>
<td>Oil-in-water</td>
</tr>
<tr>
<td>PPO</td>
<td>Phenylbis (2,4,6-tri-methylbenzoyl) phosphine oxide</td>
</tr>
<tr>
<td>Symbol</td>
<td>Term</td>
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<tr>
<td>--------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>PuMS</td>
<td>Poly (α-methylstyrene)</td>
</tr>
<tr>
<td>PAA</td>
<td>Poly(acrylic acid)</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly(vinyl alcohol)</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylphenol</td>
</tr>
<tr>
<td>PCB</td>
<td>Printed circuit board</td>
</tr>
<tr>
<td>PMA</td>
<td>Propylene glycol methyl ether acetate</td>
</tr>
<tr>
<td>RF</td>
<td>Resorcinol formaldehyde</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SOG</td>
<td>Spin-on-glass</td>
</tr>
<tr>
<td>SBS</td>
<td>Styrene-butadiene-styrene</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>W/O</td>
<td>Water-in-oil</td>
</tr>
<tr>
<td>$\theta_A$</td>
<td>Advancing contact angle</td>
</tr>
<tr>
<td>$\alpha_{\text{tilt}}$</td>
<td>Angle the bottom substrate is tilted from horizontal</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency</td>
</tr>
<tr>
<td>$P_f'$</td>
<td>Apparent film pressure</td>
</tr>
<tr>
<td>Bi</td>
<td>Biot number</td>
</tr>
<tr>
<td>$C_{\text{air}}$</td>
<td>Capacitance of the air</td>
</tr>
<tr>
<td>$C_{\text{coatings}}$</td>
<td>Capacitance of the coatings</td>
</tr>
<tr>
<td>$C_{\text{fluid}}$</td>
<td>Capacitance of the fluid</td>
</tr>
<tr>
<td>$C_{\text{SOG}}$</td>
<td>Capacitance of the spin-on-glass coating</td>
</tr>
<tr>
<td>$C_{\text{Teflon}}$</td>
<td>Capacitance of the Teflon® coating</td>
</tr>
<tr>
<td>$F_{\text{lap}}$</td>
<td>Capillary force</td>
</tr>
</tbody>
</table>
\( P_c \)  
Capillary pressure

\( \Delta \)  
Center-to-center distance between spheres

\( \mu_{\text{static}} \)  
Coefficient of static friction

\( C_i \)  
Concentration of surfactant in liquid \( i \)

\( g_{\text{fluid}} \)  
Conductance of the fluid

\( \sigma_{\text{cond}} \)  
Conductivity of the fluid

\( F_{\text{hysteresis}} \)  
Contact angle hysteresis force

\( \theta_0 \)  
Contact angle with no voltage

\( \theta_V \)  
Contact angle with voltage applied

\( f_c \)  
Critical frequency between the EWOD and DEP mechanisms

\( f_{c,\text{DEP}} \)  
Critical frequency to center droplets

\( \lambda_{\text{crit}} \)  
Critical wavelength to destabilize the membrane

\( A_{\text{cross}} \)  
Cross sectional area

\( I \)  
Current

\( \rho_{\text{amb}} \)  
Density of the ambient fluid

\( \kappa_L \)  
Dielectric constant of the liquid

\( \kappa_{\text{air}} \)  
Dielectric constant of the air

\( F_{\text{DEP}} \)  
Dielectrophoretic force

\( V_{\text{DC}} \)  
Direct current voltage

\( \Pi \)  
Disjoining pressure

\( \delta z \)  
Displacement in \( z \) direction

\( x \)  
Distance along an electrode of length \( L \)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>$l_{\text{path}}$</td>
<td>Distance from the point where the plate spacing would have been 0 to the back section of the droplet</td>
</tr>
<tr>
<td>$C_d$</td>
<td>Drag coefficient</td>
</tr>
<tr>
<td>$D$</td>
<td>Droplet diameter</td>
</tr>
<tr>
<td>$v$</td>
<td>Droplet velocity at a given time</td>
</tr>
<tr>
<td>$V$</td>
<td>Droplet volume</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Eccentricity</td>
</tr>
<tr>
<td>$\kappa_{\text{eff}}$</td>
<td>Effective dielectric constant</td>
</tr>
<tr>
<td>$m_{\text{eff}}$</td>
<td>Effective mass</td>
</tr>
<tr>
<td>$F_{\text{elec}}$</td>
<td>Electric force</td>
</tr>
<tr>
<td>$w$</td>
<td>Electrode width</td>
</tr>
<tr>
<td>$\Pi_{\text{elec}}$</td>
<td>Electrostatic component of disjoining pressure</td>
</tr>
<tr>
<td>$F_{\text{EWOD}}$</td>
<td>Electrowetting-on-dielectric force</td>
</tr>
<tr>
<td>$X$</td>
<td>Elongation ratio</td>
</tr>
<tr>
<td>$C_V$</td>
<td>Empirical drag constant</td>
</tr>
<tr>
<td>$E$</td>
<td>Energy</td>
</tr>
<tr>
<td>$H$</td>
<td>Film thickness</td>
</tr>
<tr>
<td>$\sigma_{\text{fluid}}$</td>
<td>Fluid conductivity</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Fluid density</td>
</tr>
<tr>
<td>$V_x$</td>
<td>Fluid velocity in the direction of drainage</td>
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<tr>
<td>$F_{\text{form drag}}$</td>
<td>Form drag force</td>
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<tr>
<td>$F_{\text{fric}}$</td>
<td>Frictional interaction force</td>
</tr>
<tr>
<td>$g$</td>
<td>Gravity constant</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$F_{grav}$</td>
<td>Gravity force</td>
</tr>
<tr>
<td>$h$</td>
<td>Half of the plate spacing</td>
</tr>
<tr>
<td>$A$</td>
<td>Hamaker-van der Waals constant</td>
</tr>
<tr>
<td>$P_{hyd}$</td>
<td>Hydrodynamic pressure in the film</td>
</tr>
<tr>
<td>$j$</td>
<td>Imaginary component</td>
</tr>
<tr>
<td>$Z_{air}$</td>
<td>Impedance of air</td>
</tr>
<tr>
<td>$Z_{coating}$</td>
<td>Impedance of the coating</td>
</tr>
<tr>
<td>$Z_{fluid}$</td>
<td>Impedance of the fluid</td>
</tr>
<tr>
<td>$I_{laser}$</td>
<td>Laser intensity</td>
</tr>
<tr>
<td>$L_i$</td>
<td>Length of component $i$</td>
</tr>
<tr>
<td>$L$</td>
<td>Length of electrode</td>
</tr>
<tr>
<td>$l_{drop}$</td>
<td>Length-wise diameter of the droplet</td>
</tr>
<tr>
<td>$Y_{LL}$</td>
<td>Liquid-liquid interfacial tension</td>
</tr>
<tr>
<td>$Y_{LS}$</td>
<td>Liquid-solid interfacial tension</td>
</tr>
<tr>
<td>$n$</td>
<td>Neutrons</td>
</tr>
<tr>
<td>$f_{burn}$</td>
<td>Overall burn fraction</td>
</tr>
<tr>
<td>$K_p$</td>
<td>Partition coefficient</td>
</tr>
<tr>
<td>$V_{peak}$</td>
<td>Peak implosion velocity</td>
</tr>
<tr>
<td>$P$</td>
<td>Perimeter of the droplet on a substrate</td>
</tr>
<tr>
<td>$\epsilon_0$</td>
<td>Permittivity of free space</td>
</tr>
<tr>
<td>$h_D$</td>
<td>Plate spacing at which the droplet width is measured</td>
</tr>
<tr>
<td>$P_{back}$</td>
<td>Pressure at the back section of the droplet in motion</td>
</tr>
<tr>
<td>$P_{front}$</td>
<td>Pressure at the front section of the droplet in motion</td>
</tr>
</tbody>
</table>
\( \Delta P \)  \hspace{1cm} \text{Pressure difference between the air and the film} \\
\( P_{\text{air}} \)  \hspace{1cm} \text{Pressure of the air} \\
\( r \)  \hspace{1cm} \text{Radius of curvature of a liquid droplet suspended between two plates} \\
\( R \)  \hspace{1cm} \text{Radius of droplet} \\
\( \theta_{\text{R}} \)  \hspace{1cm} \text{Receding contact angle} \\
\( R_i \)  \hspace{1cm} \text{Resistance of component i} \\
\( R_{\text{meas}} \)  \hspace{1cm} \text{Resistance of the entire heater electrode} \\
\( \text{Re} \)  \hspace{1cm} \text{Reynolds number} \\
\( V_{\text{rms}} \)  \hspace{1cm} \text{Root mean square voltage} \\
\text{SEM}  \hspace{1cm} \text{Scanning electron microscope} \\
\( a \)  \hspace{1cm} \text{Semi-major axis} \\
\( b \)  \hspace{1cm} \text{Semi-minor axis} \\
\( \beta \)  \hspace{1cm} \text{Separation angle between the top and bottom substrates} \\
\( S_i \)  \hspace{1cm} \text{Solubility in liquid i} \\
\( Z \)  \hspace{1cm} \text{Spacing between the top and bottom substrates} \\
\( C_p \)  \hspace{1cm} \text{Specific heat capacity} \\
\( S \)  \hspace{1cm} \text{Spreading coefficient} \\
\( \sigma \)  \hspace{1cm} \text{Standard deviation} \\
\( P_{\text{liquid}} \)  \hspace{1cm} \text{Static liquid pressure} \\
\( P_i \)  \hspace{1cm} \text{Static pressure at region i} \\
\( U \)  \hspace{1cm} \text{Steady-state velocity of a droplet} \\
\( \Pi_{\text{structural}} \)  \hspace{1cm} \text{Structural component of disjoining pressure} \\
\( A_{\text{LL}} \)  \hspace{1cm} \text{Surface area for the liquid/liquid interface}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$A_{LS}$</td>
<td>Surface area for the liquid/solid interface</td>
</tr>
<tr>
<td>$A_{LV}$</td>
<td>Surface area for the liquid/vapor interface</td>
</tr>
<tr>
<td>$F_{st}$</td>
<td>Surface pinning force</td>
</tr>
<tr>
<td>$\gamma_{LV}$</td>
<td>Surface tension of liquid with air</td>
</tr>
<tr>
<td>$\Delta T$</td>
<td>Temperature difference between two points</td>
</tr>
<tr>
<td>$k$</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>$d'$</td>
<td>Thickness of spin-on-glass layer</td>
</tr>
<tr>
<td>$d$</td>
<td>Thickness of Teflon® layer</td>
</tr>
<tr>
<td>$t$</td>
<td>Thickness of the dielectric layer on a substrate</td>
</tr>
<tr>
<td>$\Pi_{VDW}$</td>
<td>Van der Waals component of disjoining pressure</td>
</tr>
<tr>
<td>$\mu_{amb}$</td>
<td>Viscosity of the ambient fluid</td>
</tr>
<tr>
<td>$\mu_d$</td>
<td>Viscosity of the droplet</td>
</tr>
<tr>
<td>$F_{drag}$</td>
<td>Viscous drag force</td>
</tr>
<tr>
<td>$V_i$</td>
<td>Voltage drop across component $i$</td>
</tr>
<tr>
<td>$w_i$</td>
<td>Width of component $i$</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction

There is a constant search for alternative technologies to replace burning fossil fuels. One promising alternative is fusion as it has the potential to provide cheap energy on a large scale while having minimal impact on the environment. The goal is to capture the fusion energy and use it to produce electricity.

The fusion reaction that is easiest to achieve (Eqn. 1.1) combines deuterium and tritium atoms at temperatures in excess of $10^7$ °C to produce inert helium atoms, neutrons (n), and energy.$^{1,2}$ During this process, the fuel density increases to 1000x its liquid density. A complete reaction of a 50:50 mixture of deuterium-tritium (DT) fuel releases $3.38*10^5$ MJ per gram.$^2$

$$^2\text{H} + ^3\text{H} \rightarrow ^4\text{He} + n + 17.6 \text{ MeV} \tag{1.1}$$

Deuterium ($^2\text{H}$) is abundant in sea water, where its concentration is ~40g per metric ton of water.$^1$ The worldwide inventory of tritium ($^3\text{H}$) is limited, but additional tritium can be bred on-site and recycled rapidly through the fusion reaction process. Tritium is replenished by reacting neutrons produced by the fusion process with beryllium and/or lithium atoms.$^1$

There are two main approaches to fusion energy: magnetic confinement fusion and inertial confinement fusion (ICF). Research efforts in ICF primarily use lasers to directly or indirectly compress the DT fuel contained in a capsule shell. The indirect-drive method uses laser beams aimed at a spherical hohlraum housing the target (Fig. 1.1).$^3$ The vessel absorbs the laser energy and emits x-rays that are absorbed by the target. The direct-drive method uses lasers to illuminate the target symmetrically; the absorbed energy from the laser radiation compresses the DT fuel.
Figure 1.1: Indirect or direct-drive illumination of a target capsule with DT fuel. Absorbed laser energy causes the capsule shell to “blowoff” and the fuel to compress. The fuel ignites at ~10⁷ °C, and products from the reaction are absorbed by the remaining fuel to produce additional energy.

The more feasible approach for harnessing fusion energy is direct-drive implosion. The targets generally consist of a thin capsule shell comprised of plastic, carbon, or beryllium that encloses either a thin layer of cryogenic DT ice or DT gas. The implosion process is started by using the laser energy to heat the capsule shell via an inverse Bremsstrahlung process. The temperature increase at the surface vaporizes the shell material to form plasma, and the resulting rocket effect drives the DT fuel inwards with an implosion velocity of ~3*10⁷ cm/s. This compresses the fuel to reach the required density and temperature for the fusion reaction. The initial input of laser energy must be long enough for ~20% of the fuel to react, which allows the reaction to become self-
sustaining. The process results with very little long-life radioactivity, avoiding the risks associated with fission reactors.

The plastic shells used in fusion experiments are either foam or fully-dense. Tests using foam shells show higher energy yields. This is attributed to two factors: the coatings placed over the foam shells that help manage the Rayleigh-Taylor instability during the fusion process; and the DT fuel wicking into the porous structure of the foam shells. Even so, the emphasis is on fully-dense shells made of polystyrene due to the ability to match experimental data with simulations.

**Fusion-energy considerations**

It is estimated that a facility producing 1GW of electricity needs to implode ~500,000 DT targets daily. Each target needs to cost < $0.30 to produce affordable electricity at 4 to 7 cents per kilowatt hour. Note that targets currently cost ~$2500.

Producing energy at low cost requires the energy output from the fusion reaction to be several times greater than the total energy used to react the DT fuel. This is quantified in terms of energy gain. The gain is proportional to the overall burn fraction for the DT fuel ($f_{\text{burn}}$), the fuel density ($\rho$), the capsule radius ($R$), the peak implosion velocity of the capsule ($V_{\text{peak}}$), and the laser intensity ($I_{\text{laser}}$):

$$Gain \propto f_{\text{burn}}(\rho R)/(V_{\text{peak}}^{5/4}I_{\text{laser}}^{1/4}).$$ (1.2)

The current objective is to reach a gain of one. Increasing the burn fraction (and thus the gain) requires shells that contain the fuel to have consistent diameter and wall thickness. This requires a shell manufacturing process that is highly controlled, rapid, and deterministic. The goal of this thesis is to contribute to the process of making such suitable shells.
Dissertation outline

This dissertation discusses an electric-field based microfluidics approach to produce emulsion droplets and form capsule shells. The premise is to develop a new manufacturing process that addresses the effects of surface energy and chemistry. The following chapters address the different aspects of this work.

Chapter 2 discusses the current process to produce shells, the different types of shells, and the remaining problems. Digital (droplet-based) microfluidics is introduced as a method to replace the existing process.

Chapter 3 discusses the electric-field mechanisms used in digital microfluidics to form droplets, make emulsions, and center the emulsions to form spherical shells.

Chapter 4 discusses the necessary steps to make electric-field-coupled microfluidics a viable process. The electrical, chemical, and physical requirements are addressed.

Chapter 5 discusses the electrode designs used to transport the fluids, the process to create the microfluidic device, the fluids used, and the electrical circuitry used to operate the device.

Chapter 6 discusses dispensing water droplets and the mechanisms involved. The effect of adding a surfactant is examined.

Chapter 7 discusses dispensing oil droplets that have different electrical and physical properties. The conditions that are needed to move droplets are reported.

Chapter 8 discusses forming and transporting emulsion droplets that meet OMEGA and NIF (National ignition facility) requirements.
Chapter 9 discusses a method for transporting droplets between differently-spaced sections of a microfluidic device, so that spherical capsule shells can be made. Gravitational and electrical forces allow droplets to be transported.

Chapter 10 discusses a series of steps to form double emulsions containing the chemicals needed to form polystyrene shells. Tests were conducted in an aquarium-like setup.

Chapter 11 provides a conclusion of the first ten chapters. Future directions for the research are suggested.
Chapter 2: Background and motivation

Introduction

Forming high-quality ICF shells at a rapid rate will require a new fabrication process. Each shell must have a non-concentricity (NC) less than 2% but preferably less than 1%. They must also be spherical to within 0.2%.\textsuperscript{11,12} These parameters are defined as:

\[
\text{NC} = \frac{\text{Distance between the centroids of the spheres defined by the inner and outer surfaces of the shell}}{2 \times \text{avg shell thickness}}
\]

\[
\text{Sphericity} = 1 - \frac{a}{b}
\]

where ‘a’ and ‘b’ are the semi-major and semi-minor axes for the shell.

To develop the new process, there needs to be an understanding of the current processes. This chapter examines the current methods for producing shells, the types of shells produced, the limitations with the current shells, and a novel approach to form shells using electric-field based microfluidics.

2.1 Current methods to create shells

Current methods to fabricate shells for laser targets utilize a triple-nozzle generator to produce double emulsion (DE) droplets (step 1 in Fig. 2.1).\textsuperscript{11} The flow of the shell fluid in the annulus squeezes the inner phase flow to form droplets. The outer phase then squeezes the inner and shell fluids to form double emulsions. The fluid velocities and cylinder dimensions can be tuned to produce a specific target size. Chemicals needed to form the shell wall are present in the shell phase, while the outer phase contains a surfactant to prevent the emulsions from agglomerating.
For the processing of resorcinol formaldehyde (RF) shells, the double emulsions are transferred to a vessel, stirred, and heated to 70°C (step 2 of Fig. 2.1). The rotation centers the innermost fluid relative to the shell fluid using hydrodynamic shear to form a concentric foam shell. The chemicals in the shell fluid polymerize to form a rigid shell wall with a density between 50 and 200 mg/cc.

For the processing of poly (α-methylstyrene) [PaMS] and polystyrene shells, they are made by dissolving the polymer in fluorobenzene. The formed emulsion is then cured while being rotated. During the curing process, the fluorobenzene in the shell fluid diffuses into the outer phase leaving behind a polymer shell. The diffusion rate is controlled by the partial pressure of the solvent in the vessel.

Once the polymerization / curing process is complete, the shells are dried by exchanging the liquids from the innermost droplet and the shell with a miscible solvent, such as isopropyl alcohol (step 3). The solvent is then removed using supercritical CO₂ or air (step 4).
Types of shells and coatings

Three main types of plastic shells are used in ICF experiments: foam (open pore) shells, fully-dense shells, and mandrels that are coated with other materials to form targets. For example, PaMS mandrels with a 1 to 2 mm diameter are first coated with glow discharge polymer (GDP) to a thickness of 2 to 300 µm. The shells are pyrolyzed to depolymerize the α-methyl polystyrene, leaving a GDP shell.13

RF foam shells range in diameter from 0.9 to 4 mm with densities ranging from 100 to 250 mg/cc. RF shells are coated with a GDP layer that is 3 to 4 µm thick to retain deuterium-tritium fuel. An issue with these targets is that the outer coating is not always continuous and the target can leak its fuel: tests using argon gas and X-ray fluorescence show that only 60 to 70% of the coated shells are leak-proof.12,14

Foam shells made using divinylbenzene (DVB) chemistry are coated with polyvinylphenol (PVP) using an interfacial condensation process and then GDP. The PVP overcoats the larger pore structure of the DVB. GDP is added to make the shells leak-proof. The coatings result in a ~70% yield of acceptable targets from the coated batch.

Problems with the current method

The target-making process improved greatly in the 18 years (1992-2010) it was studied, but the overall yield of acceptable targets remains low at less than thirty percent. Problems include non-uniformly thick shells and surface damage when the rotation mechanism is used. The first problem is attributed to using rotation to center the layers of the emulsion. Using this method, it is difficult to keep the emulsion centered for the time needed to form the shell. The centering process is further complicated by the steadily
increasing density of the shell fluid with time. The second problem is attributed to the emulsions contacting each other or the container surface during the polymerization and drying processes. This leads to shells that are scratched or ruptured.\footnote{15}

A third problem is that vacuoles are often present in the capsule shells. During the agitation step, small emulsions form within the shell fluid due to solubility properties. These emulsions turn into vacuoles as the shell is dried.\footnote{15} Polystyrene shells, in particular, have a long curing time that allows water to diffuse into the shell. Defects have diameters up to several micrometers, which become enlarged when coatings for RF, DVB, and P\textsubscript{a}MS shells are placed over the surface. Dust particles or residue on the shells also cause defects in the GDP / PVP coatings. As a result, each shell must be manually inspected to select undeformed, unscratched shells with the desired dimensions.

A fourth problem is that the yield of good shells decreases as the foam density increases. Paguio\footnote{11} noted that RF shells with a $\approx$100 mg/cc density had a 30\% yield, while at $\approx$200 mg/cc the yield dropped to 5\%. Lower yields require intensive inspection to find acceptable shells. Such low yields indicate that shell production must become more efficient to meet target needs in the future.

\subsection*{2.2 Alternative method for making shells using electric fields (digital microfluidics)}

To increase the throughput of polymer shells with desired specifications, a microfluidics-based process using electric fields has been proposed.\footnote{16} The microfluidics approach is attractive because the process can be rapid, repeatable, and automated for mass production.\footnote{16-17}
Lab-on-chip digital microfluidic concept

The envisioned process (Fig. 2.2) consists of four main steps: (i) dispensing individual droplets of oil and water, (ii) combining them to form an oil-water emulsion, (iii) forming the double emulsion, and (iv) centering the innermost fluid while the shell is forming / polymerizing. To achieve these steps, the bottom substrate is patterned with individually addressable electrodes while the top substrate serves as a ground electrode. The first step is achieved by selectively dispensing a droplet from a reservoir and moving the droplet from one electrode to another by applying voltage sequentially. The size of the droplets dispensed depends on the surface area of the electrodes, the separation of the powered and grounded electrode plates, and the applied voltage. The oil and water droplets, mutually immiscible, are then moved to a common site to form the initial emulsion.

![Figure 2.2: Side-view schematic of the electric-field based process for creating foam shells. Individual droplets of oil and water are combined to form the double emulsion, which can be electrically centered using DEP and polymerized with UV light.](image)

Combining the emulsion with another droplet creates the desired double emulsion. To achieve this, there are several options: (1) eject the droplets from the closely-spaced parallel electrodes to an open structure, and then combine them, or (2)
combine them in a closed system. Next, the emulsion is transferred to a parallel plate system where the separation between the plates is larger than the diameter of the spherical emulsion. Once there, an electric field is used to center the innermost droplet before exposing the emulsion to ultraviolet light. Past experiments\textsuperscript{18} utilized a fully-enclosed system with the powered and grounded electrodes immersed in the outer fluid. The oil-in-water emulsion, suspended in an immiscible oil phase, was made concentric by applying an electric field for \textasciitilde 1 minute. Irradiating the concentric emulsion with ultraviolet light polymerized the chemical reactants in the shell fluid to form a fully-dense diacrylate shell.\textsuperscript{19}

**Potential benefits of the electric-field based method**

The electric-field based approach allows individual droplets to be produced, combined, and transported on command. One benefit is the use of small inventories of fluid to meet target specifications for the OMEGA and NIF (National ignition facility) laser facilities. With a small footprint for each emulsion-forming structure, multiple electrode patterns can be lined up in parallel to meet target quotas.

A second benefit is the ability to electrically center the double emulsion. Presumably, this will help to produce shells of uniform thickness, avoiding the variability associated with the current batch process. The shells may also have better surface quality as each one would be produced individually.
**Chapter 3: Electric field-induced movement of fluid**

**Introduction**

The proposed microfluidic process uses electric fields to form and center emulsion droplets. There are two electric-field mechanisms used: electrowetting-on-dielectric (EWOD) and dielectrophoresis (DEP). Establishing the electric field induces the electrical force that moves the fluid. This chapter discusses the EWOD and DEP mechanisms, derivations of the electrical force, and pinning and drag forces that inhibit the fluids from being moved.

**3.1 Electrowetting and dielectrophoresis**

Electrowetting-on-dielectric is an electromechanical mechanism used to move and manipulate conductive droplets such as water at low ac voltages (<100 V\text{rms}) and low frequencies (100 Hz). As shown in Fig. 3.1a, the electric field is created between the energized electrode and the liquid surface near the dielectric-liquid-air contact line. The electric field acts on the surface charge near the contact line and the electromechanical force pulls the liquid across the activated electrode.\(^{20,21}\) The apparent contact angle (\(\theta_V\)) of the fluid near the energized electrode also decreases. This decrease can be modeled using the Lippmann-Young equation:

\[
\cos \theta_V = \cos \theta_0 + \varepsilon_o \kappa_L V_{\text{rms}}^2 / 2 \gamma_{LV} t
\]  

(3.1)

where \(\theta_0\) is the equilibrium contact angle, \(\varepsilon_o\) is the permittivity of free space, \(\kappa_L\) is the dielectric constant of the liquid, \(\gamma_{LV}\) is the surface tension of the fluid, and \(t\) is the dielectric thickness.
Figure 3.1: Side-view schematic of a fluid bounded by two substrates. When a potential is applied across a particular electrode on the bottom (in red) and the top (ground) electrode, fluid moves onto that powered electrode if the fluid has a higher dielectric constant than the surrounding medium (e.g. air). The path of the electric field differs in (a) where the field lines originate from the surface of the energized electrode and terminate on the liquid surface near the contact line and (b) where the field lines permeate the fluid.

The dielectrophoresis force is distinct from the electrowetting force. The DEP force results from a non-uniform electric field acting on a dielectric liquid. Electric-field lines permeate the fluid, generating a force in the liquid bulk (Fig. 3.1b). The liquid advances onto the energized electrode because the dielectric constant of the liquid is greater than the surrounding fluid. This is a positive-DEP phenomenon. If the liquid’s dielectric constant is lower, the liquid will be repulsed from the region with the energized electrode; this is negative-DEP. The work presented here utilizes only positive-DEP.

Dielectrophoresis requires higher voltages to move a fluid than does EWOD. Polarizable fluids, such as oil, are moved using voltages ranging from 400 to 800 V$_{\text{rms}}$ at 100 Hz. This is attributed to the low dielectric constant of oil. Water can also be moved using DEP when the frequency is increased to ~100 kHz, though voltage needs vary.

Water solutions containing a surfactant can be actuated using either EWOD or DEP frequencies. Previous work with surfactant-water solutions used EWOD frequencies of 1 to 3 kHz to dispense droplets. DEP frequencies of 10 to 500 kHz were used to control the behavior of surfactant micelles.
There is a critical charge-relaxation frequency ($f_c$) at which the electrical force transitions from a EWOD to a DEP mechanism. This critical frequency depends on the conductance of the fluid ($g_{\text{fluid}}$), the conductivity of the fluid ($\sigma_{\text{fluid}}$), the capacitance of the fluid ($C_{\text{fluid}}$), and the capacitance of the dielectric coatings ($C_{\text{coatings}}$) [Eqns. 3.2-3.6].

$$f_c = \frac{g_{\text{fluid}}}{2\pi(C_{\text{fluid}} + C_{\text{coatings}})}$$

$$g_{\text{fluid}} = \frac{\sigma_{\text{fluid}}xw}{Z}$$

$$C_{\text{fluid}} = \frac{\varepsilon_0\kappa_{\text{fluid}}xw}{Z}$$

$$C_{\text{coatings}} = \left(\frac{1}{C_{\text{Teflon}}} + \frac{1}{C_{\text{Teflon}}} + \frac{1}{C_{\text{SOG}}}\right)^{-1}$$

$$C_{\text{Teflon}} = \frac{\varepsilon_0\kappa_{\text{Teflon}}xw}{d}; C_{\text{SOG}} = \frac{\varepsilon_0\kappa_{\text{SOG}}xw}{d'}$$

where $x$ is the electrode length, $w$ is the electrode width, $Z$ is the spacing between the top and bottom plates, $d$ is the thickness of the Teflon® layer, $d'$ is the thickness of the spin-on-glass (SOG) layer.

Operating in the EWOD regime is preferable to operating in the DEP regime as the electric force is larger using the EWOD mechanism. However, using EWOD frequencies is impractical for insulating dielectric fluids. This is evident from calculations for the critical frequency for ethanol, pentane, and water. The parameters used to calculate the frequency are listed in Table 3.1.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>Electrode length</td>
<td>2 mm</td>
</tr>
<tr>
<td>w</td>
<td>Electrode width</td>
<td>2 mm</td>
</tr>
<tr>
<td>Z</td>
<td>Spacing between plates</td>
<td>90 µm</td>
</tr>
<tr>
<td>d</td>
<td>Thickness of Teflon® coating</td>
<td>0.9 µm</td>
</tr>
<tr>
<td>d'</td>
<td>Thickness of SOG coating</td>
<td>0.3 µm</td>
</tr>
<tr>
<td>κ_{Ethanol}</td>
<td>Ethanol dielectric constant</td>
<td>24.5</td>
</tr>
<tr>
<td>κ_{Pentane}</td>
<td>Pentane dielectric constant</td>
<td>1.84</td>
</tr>
<tr>
<td>κ_{Water}</td>
<td>Water dielectric constant</td>
<td>78</td>
</tr>
<tr>
<td>κ_{Teflon}</td>
<td>Teflon AF dielectric constant</td>
<td>1.93</td>
</tr>
<tr>
<td>κ_{SOG}</td>
<td>Spin-on-glass dielectric constant</td>
<td>4.5</td>
</tr>
<tr>
<td>ε_o</td>
<td>Permittivity of free space</td>
<td>8.85*10^{-12} F/m</td>
</tr>
<tr>
<td>σ_{Ethanol}</td>
<td>Conductivity of ethanol</td>
<td>1.35*10^{-3} S/m</td>
</tr>
<tr>
<td>σ_{Pentane}</td>
<td>Conductivity of pentane</td>
<td>&lt;2.0*10^{-8} S/m</td>
</tr>
<tr>
<td>σ_{Water}</td>
<td>Conductivity of water</td>
<td>5.49*10^{-6} S/m</td>
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</table>

Table 3.1: Values for fluid and dielectric coatings, electrode size, and spacing

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>Pentane</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical frequency (Hz)</td>
<td>2.12*10^3</td>
<td>&lt;3.91</td>
<td>5.87*10^2</td>
</tr>
</tbody>
</table>

Table 3.2: Critical frequency for ethanol, pentane, and water

Table 3.2 shows that the critical frequency is highest for ethanol (2.1 kHz), followed by water (0.59 kHz), and followed by pentane (3.9 Hz). A purely EWOD-based mechanism requires the operating frequency to be much less than the critical frequency. Therefore,
operating in the EWOD regime for ethanol and water is practical but is virtually impossible for pentane because the use of direct current leads to other problems with insulative fluid behavior.

3.2 Electromechanical force modeling

Applying voltage to an electrode (Fig. 3.2) causes a droplet to move across that electrode. The electrical force ($F_{elec}$), equivalent to the change in electrostatic energy ($E$) per unit distance traveled, can be modeled using capacitors. The change in capacitance ($C$) with respect to the horizontal distance ($x$) along an energized electrode represents the electrical force mechanism that acts on a fluid droplet (Eqn. 3.7). $^{21}$

$$F_{elec} = \frac{\partial E}{\partial x} = \frac{\partial}{\partial x} \left( \sum \frac{1}{2} C_i V_i^2 \right) = \frac{V_{rms}^2}{2} \left( \frac{dC}{dx} \right)$$  \hspace{1cm} (3.7)

The total electrical force does not depend on the profile of the advancing liquid as long as the chord length is fixed. If the shape changes due to the electrode width changing with distance $x$, it needs to be taken into account in the capacitance term. The electrical force is present until the fluid completely covers the energized electrode.

Figure 3.2: Top-view schematic of a fluid droplet being transported from a non-powered electrode (black) to a powered electrode (red) by the electric force.
The electrical force differs for the EWOD and DEP regimes due to the distribution of the electric field. To derive expressions for the force in each case, consider the following circuit model that categorizes the system into capacitors and resistors (Fig. 3.3).

\[ C_{\text{air}} = \frac{\varepsilon_o \kappa_{\text{air}} x (L-x) W}{Z} \]  

(3.8)

\[ C_{\text{coating}} = \frac{\varepsilon_o \kappa_d \kappa_t x W}{2d\kappa_d + \kappa_t d'} \]  

(3.9)

\[ C'_{\text{coating}} = \frac{\varepsilon_o \kappa_d \kappa_t (L-x) W}{2d\kappa_d + \kappa_t d'} \]  

(3.10)

where \( C_{\text{coating}} \) is the capacitance of the dielectric coatings in contact with the liquid, \( C'_{\text{coating}} \) is the capacitance of the dielectric coatings not in contact with the liquid, \( L \) is...
the full length of the bottom electrode, \( x \) is the length of the bottom electrode covered by the droplet, and \( \kappa_L \) is the dielectric constant of the fluid.

Using Eqns. 3.4 and 3.8-3.10, the electric force is written as:

\[
F_{\text{electric}} = \frac{1}{2} \varepsilon_o w \left[ \frac{\kappa_L}{Z} V_1^2 + \frac{\kappa_{\text{eff}}}{2d+d'} V_2^2 - \frac{\kappa_{\text{air}}}{Z} V_3^2 - \frac{\kappa_{\text{eff}}}{2d+d'} V_4^2 \right].
\]  

(3.11)

The effective dielectric constant:

\[
\kappa_{\text{eff}} = \kappa_t \kappa_d (2d + d') / (\kappa_t d' + 2\kappa_d d)
\]  

(3.12)

accounts for the dielectric constants of the Teflon (\( \kappa_t \)) and SOG (\( \kappa_d \)) layers.\textsuperscript{25}

\( V_1, V_2, V_3, V_4 \) are the voltage drops across the liquid, the dielectric coatings in contact with the liquid, the air, and the dielectric coatings not in contact with the liquid, respectively. The voltage drops (\( V_i \)) are functions of impedance (\( Z_i \)) and the total voltage drop (\( V \)):

\[
V_i = \frac{Z_i}{\sum Z_i} V.
\]  

(3.13)

If alternating current is used, the voltage has a sinusoidal waveform given by:

\[
V(t) = \text{Re}[V e^{j\omega t}] \text{ where } \omega = 2\pi f.
\]  

(3.14)

t is time, \( \omega \) is angular frequency, and \( j \) is an imaginary number.

The impedances of the fluid, the dielectric coatings, and the air are given by:

\[
Z_{\text{fluid}} = \frac{1}{\varepsilon_{\text{fluid}} + j \omega \varepsilon_{\text{fluid}}}
\]  

(3.15)

\[
Z_{\text{coating}} = \frac{1}{j \omega \varepsilon_{\text{coating}}}; \quad Z'_{\text{coating}} = \frac{1}{j \omega \varepsilon'_{\text{coating}}}; \quad Z_{\text{air}} = \frac{1}{j \omega \varepsilon_{\text{air}}}
\]  

(3.16)

If the system is purely capacitive, the voltage drop across each component simplifies to:

\[
V_1 = \frac{Z_{\kappa_{\text{eff}}}}{Z_{\kappa_{\text{eff}}} + \kappa_L (2d+d')} V
\]  

(3.17)
\[ V_2 = \frac{\kappa_L (2d+d')}{Z \kappa_{\text{eff}} + \kappa_L (2d+d')} V \]  
(3.18)

\[ V_3 = \frac{Z \kappa_{\text{eff}}}{Z \kappa_{\text{eff}} + \kappa_{\text{air}} (2d+d')} V \]  
(3.19)

\[ V_4 = \frac{(2d+d') \kappa_{\text{air}}}{Z \kappa_{\text{eff}} + \kappa_{\text{air}} (2d+d')} V. \]  
(3.20)

Substituting \( V_3 \) and \( V_4 \) into Eqn. 3.11 gives the electric force:

\[ F_{\text{electric}} = \frac{1}{2} \varepsilon_0 W \left[ \frac{\kappa_L}{Z} V_1^2 + \frac{\kappa_{\text{eff}}}{2d+d'} V_2^2 - \frac{\kappa_{\text{air}} \kappa_{\text{eff}}}{Z \kappa_{\text{eff}} + \kappa_{\text{air}} (2d+d')} V_2^2 \right]. \]  
(3.21)

At EWOD frequencies, the capacitance of the fluid does not factor into the electric force because the electric field does not permeate the conducting fluid. Therefore, \( V_1 = 0, V_2 = V \), and the electric force reduces to:

\[ F_{\text{EWOD}} = \frac{1}{2} \varepsilon_0 W V^2 \left[ \frac{\kappa_{\text{eff}}}{2d+d'} - \frac{\kappa_{\text{air}} \kappa_{\text{eff}}}{(Z \kappa_{\text{eff}} + \kappa_{\text{air}} (2d+d'))^2} \right]. \]  
(3.22)

Typically \( Z \gg 2d + d' \), so the EWOD force can be further simplified:

\[ F_{\text{EWOD}} \approx \frac{\varepsilon_0 W}{2} V_{\text{rms}}^2 \left( \frac{\kappa_{\text{eff}}}{(2d+d')} \right) \]  
(3.23)

The EWOD force is calculated for a water droplet moving on a 6-mm square electrode with the plates spaced 30 to 990 \( \mu \)m apart (Fig. 3.4). The dielectric thicknesses and coatings are the same as specified in Table 3.1. Using 75 \( V_{\text{rms}} \) at 100 Hz, the electric force is constant at \( \sim 149 \mu \text{N} \) over the specified range of plate spacing. This suggests that moving droplets with the EWOD force is a good option, regardless of the plate spacing.
Figure 3.4: Electric force as a function of plate spacing when moving a droplet on 6-mm square electrodes using (a) EWOD at 100 Hz to move water; (b) DEP at 100 kHz to move water; (c) DEP at 100 Hz to move decane, and (d) DEP at 100 Hz to move mineral oil. The voltages chosen for the different fluids are based on the anticipated conditions needed to dispense and transport the droplets.

At DEP frequencies, the capacitance of the fluid is accounted for in the electrical force because the electric field permeates the fluid. Thus,

\[
F_{\text{DEP}} = \frac{\varepsilon_0 \kappa_{\text{eff}} w}{2} V_{\text{rms}}^2 \left( \frac{\kappa_L}{\kappa_L(2d+d') + \kappa_{\text{eff}} Z} - \frac{\kappa_{\text{air}}}{\kappa_{\text{air}}(2d+d') + \kappa_{\text{eff}} Z} \right). \tag{3.24}
\]

Consider the DEP force acting on a water droplet using 75 V\text{rms} at 100 Hz (Fig. 3.4). The electrical force decreases from ~108 to 69 to 45 μN when the plate spacing is increased from 30 to 90 to 180 μm. The DEP force is much weaker than the EWOD force for the same plate spacing, suggesting that higher voltages are required to transport the droplet using the DEP mechanism.

Consider the DEP force exerted on a decane droplet (κ~2) when 460 V\text{rms} at 100 Hz is applied. The DEP force decreases from 350 to 122 to 62 μN when the plate spacing
is increased from 30 to 90 to 180 μm. The sharp decrease in electrical force indicates there is a limited range of plate spacings for which the DEP mechanism can be used.

The DEP force applied to a mineral oil droplet (κ~2.2) also decreases with plate spacing using 672 V_{rms} at 100 Hz. The force decreases from 818 to 145 μN when the plate spacing increases from 30 to 180 μm. It may appear from the force calculations that mineral oil (using 672 V_{rms}) should transport more quickly than decane (using 460 V_{rms}), however, drag forces are larger when the more viscous mineral oil is moved. The effect of drag on droplet movement is discussed in the next section.

### 3.3 Effect of drag and contact angle hysteresis

The speed that a droplet moves across an electrode surface depends on the electrical, drag, and contact angle hysteresis forces acting on the droplet. The drag and hysteresis forces inhibit the droplet’s motion. The drag force is comprised of two components: form and viscous drag. Form drag is present when the droplet moves through an ambient fluid such as air or silicone oil. It takes the form:

\[ F_{\text{form drag}} = \frac{1}{2} C_d A_{\text{cross}} \rho_{\text{amb}} v^2 \]  

(3.25)

where

\[ C_d = \frac{24}{Re} \left[ 1 + 10.189 Re^{0.632} \right] \]  

(3.26)

and

\[ Re = \frac{\rho_{\text{amb}} v D}{\mu_{\text{amb}}} \]  

(3.27)

\( C_d \) is the drag coefficient, \( A_{\text{cross}} \) is the projected surface area of the droplet in the direction of flow, \( \rho_{\text{amb}} \) is the density of the ambient fluid, \( v \) is the velocity of the droplet, \( Re \) is the Reynolds number, \( D \) is the diameter of the droplet in the direction of flow, and \( \mu_{\text{amb}} \) is the viscosity of the ambient fluid. Form drag is larger when the fluid surrounding the droplet...
is more viscous. If the ambient fluid is air, the force resulting from form drag is negligible.

The viscous drag force is a result of the droplet imparting a shear stress on the parallel plates. The force is given as:

$$ F_{\text{viscous drag}} = 2C_v \frac{\mu_d U}{Z} A_{LS} $$

(3.28)

where $C_v$ is an empirical constant, the factor of two accounts for the two substrates, $\mu_d$ is the viscosity of the moving droplet, $U$ is the average fluid velocity, $Z$ is the plate spacing, and $A_{LS}$ is the surface area for the liquid-solid interface. The viscous drag force decreases at a large plate spacing due to the decrease in shear stress; the force increases when larger electrodes are used.

The contact angle (CA) hysteresis force ($F_{\text{hysteresis}}$) is a result of the fluid randomly pinning on the electrode surfaces. The advancing droplet does not wet the surface uniformly; the front of the droplet has a greater contact angle ($\theta_A$) than the equilibrium contact angle and the back of the droplet has a contact angle ($\theta_R$) less than the equilibrium contact angle. The force is given as:

$$ F_{\text{hysteresis}} = 2D \gamma_{LV} (\cos \theta_A - \cos \theta_R) $$

(3.29)

where $D$ is the droplet diameter and $\gamma_{LV}$ is the surface tension. If the substrates are coated with a low-surface-energy polymer such as Teflon®, pinning is reduced but not eliminated.

The combined effect of the electrical, drag, and hysteresis forces determines how fast a droplet moves across an interface. Assuming form drag is negligible and then combining Eqns. 3.21, 3.28, and 3.29, the steady-state velocity ($U$) of the droplet is approximated by:
Increasing the electrical force or decreasing the fluid’s viscosity are just two ways to increase the velocity of the droplet.

### 3.4 Dielectrophoretic centering of double emulsions

The DEP force can also be used to center a droplet within an emulsion (Fig 3.5). If the dielectric constant of the shell fluid is greater than that of the surrounding fluid ($\kappa_2 > \kappa_1$), the innermost droplet moves to the center forming a concentric emulsion.³¹

![Figure 3.5: Side view of a double emulsion with an applied electric field, where the inner layers of the emulsion are (a) uncentered (b) centered.](image)

The DEP force ³² exerted on the inner droplet in the z and x directions is:

\[
F_{\text{DEP} \ z \text{axis}} = -(\kappa_2 - \kappa_1) \left( 432 \pi \varepsilon_o \kappa_1^2 \kappa_2 R_{\text{inner}}^6 R_{\text{outer}}^6 (\kappa_2 - \kappa_3)^2 (3\kappa_2 + 2\kappa_3) E_0^2 \right) \delta z / M^2 N
\]

where

\[
M = 2R_{\text{inner}}^3 (\kappa_1 - \kappa_2)(\kappa_2 - \kappa_3) + R_{\text{outer}}^3 (2\kappa_1 + \kappa_2)(2\kappa_2 + \kappa_3)
\]

\[
N = 6R_{\text{inner}}^5 (\kappa_1 - \kappa_2)(\kappa_2 - \kappa_3) + R_{\text{outer}}^5 (3\kappa_1 + 2\kappa_2)(3\kappa_2 + 2\kappa_3)
\]

\[
F_{\text{DEP} \ x \text{axis}} = -(\kappa_2 - \kappa_1) \left( 324 \pi \varepsilon_o \kappa_1^2 \kappa_2 R_{\text{inner}}^6 R_{\text{outer}}^6 (\kappa_2 - \kappa_3)^2 (3\kappa_2 + 2\kappa_3) E_0^2 \right) \delta x / M^2 N.
\]

The centering force is \( \sim 1.3 \)-fold stronger in the z direction versus the x direction. Note that the equation for \( F_{\text{DEP}} \) in the y direction is the same as in the x direction.
Figure 3.6 shows the DEP force exerted on the inner droplet in the x and z directions as a function of the eccentricity ($\zeta$) for a water-in-fluorobenzene-in-hexylene double emulsion proposed for making polystyrene shells. Eccentricity is given by:

$$\zeta = \frac{\Delta}{R_{outer} - R_{inner}}$$  

(3.33)

where $\Delta$ is the center-to-center distance between the innermost droplet and the shell fluid. The radii of the shell and the innermost droplet are set to OMEGA specifications where $R_{shell}=460$ µm and $R_{inner}=452$ µm. The dielectric constants for fluorobenzene and hexylene are 4.8 and 2.0, respectively. The applied voltage is 490 V$_{rms}$ and the plate spacing is 7 mm.

*Figure 3.6: DEP force (in x and z directions) exerted on a water-in-fluorobenzene-in-hexylene double emulsion as a function of the eccentricity.*
The centering force on the innermost droplet is measured in nano-newtons. This is attributed to the small difference in dielectric constants between the shell and the surrounding fluid.

Using a (silicone oil)-in-(styrene-dimethylacetamide)-in (silicone oil) double emulsion increases the DEP force by two orders of magnitude (Fig. 3.7). The silicone oil and the styrene-dimethylacetamide solution are assumed to have dielectric constants of 2.6 and 37.8, respectively. Dimethylacetamide (DMA) is soluble in styrene and may be a suitable replacement for fluorobenzene. The only uncertainty to using dimethylacetamide is its unknown solubility with water and organic compounds.

![Figure 3.7: DEP force (in x and z directions) exerted on a (silicone oil)-in-(styrene-dimethylacetamide)-in-(silicone oil) double emulsion as a function of the eccentricity.](image)
Resorcinol-formaldehyde shells can be formed from (mineral oil)-in-(water)-in-(mineral oil) double emulsions. Figure 3.8 plots the DEP force in the $z$ direction as a function of the eccentricity. The outer shell radius is kept constant at 2 mm while the inner droplet radius is increased from 1.6 to 1.7 to 1.8 mm. The dielectric constant of the mineral oil is 2.2 while the dielectric constant of the water is 78.

![Figure 3.8: DEP force exerted on a (mineral oil)-in-(water)-in-(mineral oil) double emulsion as a function of the eccentricity. The radius of the inner droplet is changed; a larger radius results in a stronger force. The physical limit on eccentricity is that the inner droplet must remain fully enveloped by the shell fluid.](image)

The DEP force acting on the innermost droplet is $\sim 10^3$ greater than for the fluorobenzene case, which indicates a faster centering response to the electric field. The electric force is also larger when the shell layer is thin. This is evidenced by the $\sim 3$-fold increase in the centering force when the radius of the inner droplet is increased from 1.6 to 1.8 mm ($\zeta=1$).
Drag and buoyancy forces act on the inner droplet. The continuity equation in the $z$ direction relates those forces to the DEP force:

$$F_{\text{DEP, } Z} + F_{\text{drag}} + \frac{4\pi}{3} (\rho_3 - \rho_2)R_{\text{inner}}^3 g = m_{\text{eff}} \delta z$$

(3.34)

where

$$m_{\text{eff}} = \frac{4\pi}{3} (\rho_3 + 0.5\rho_2)R_{\text{inner}}^3.$$  

(3.35)

g is the gravitational constant, $m_{\text{eff}}$ is the effective mass of the inner droplet, and $\delta z$ is displacement in the $z$ direction. If the velocity of the inner droplet is low, the effective mass term can be omitted. Density-matching the fluids also makes the buoyancy term negligible to give:

$$F_{\text{DEP}} + F_{\text{drag}} \approx 0.$$  

(3.36)

The time taken to center the inner droplet mainly depends on the magnitudes of the electrical and drag forces. A strong DEP force or a small drag force decreases the centering time. The drag force can be reduced by using a shell fluid with a low viscosity.

### 3.5 Conclusion

It has been established that the water and oil droplets required to form the emulsions can be dispensed using electrowetting and dielectrophoresis forces. However, the voltage requirements will be higher when dielectrophoresis is used because the fluid is part of the circuit. In terms of electrically centering the emulsion, the dielectric constant of the fluid surrounding the innermost droplet must be high to result in a large dielectrophoresis force. Adding solvents such as dimethylacetamide to oil will allow water-in-oil emulsions to be centered, which is important for polystyrene and divinylbenzene chemistries.
Chapter 4: Requirements to form and center double emulsions

Introduction

Using dielectrophoresis to center a double emulsion places several constraints on the fluids used. The electrical, chemical, and physical properties of the emulsion need to be adjusted to achieve a quick centering response. The chemicals used in forming shells must also be added, which complicates the effort to satisfy the constraints. This chapter is divided into the following sections: requirements to electrically center the emulsion; requirements to transform the emulsion into a capsule shell; schemes to produce emulsions that meet the centering requirements; Gibbs free energy calculations to predict the effect of adding surfactant; and solubility studies on the surfactant.

4.1 Centering requirements

One requirement to electrically center a double emulsion is that the dielectric constant of the shell fluid must be greater than that of the surrounding fluid ($\kappa_2 > \kappa_1$) [Fig. 4.1]. To date, only oil-in-DMA-in-oil and oil-in-water-in-oil emulsions have been electrically centered. Bei demonstrated centering and curing of tri(propylene glycol) diacrylate shells using DMA as the shell fluid; Randall electically centered and cured poly(ethylene glycol) diacrylate shells with water as the shell fluid. These emulsions were centered because the dielectric constants of DMA and water are high relative to oil.
A second requirement for centering the emulsion is that the electrical conductivity of the shell fluid must be low enough for the electric field to permeate the emulsion. If the conductivity is too high, electrostatic shielding due to Maxwell-Wagner interfacial polarization diminishes the DEP centering force acting on the innermost droplet. The conductivity tends to increase when shell-forming chemicals or ionic species are added. For example, the shell fluid for making resorcinol formaldehyde shells has a conductivity of $2.2 \times 10^{-2}$ S/m due to the sodium bicarbonate and benzoic acid added. Note that the conductivity of DI water is $\sim 1 \times 10^{-4}$ S/m. Shielding effects are circumvented by using an operating frequency higher than the critical frequency ($f_{\text{crit, DEP}}$).

$$ f \gg f_{\text{crit, DEP}} \approx \frac{\sigma_2 d}{2\pi(\kappa_3 \varepsilon_0 R_{\text{outer}} + \kappa_2 \varepsilon_0 d)} $$

where $\varepsilon_0 = 8.854 \times 10^{-12}$ Fm$^{-1}$, $\sigma_2$ is the conductivity of the shell fluid, $d$ is shell thickness, $R_{\text{outer}}$ is the radius of the shell, and $d \ll R_{\text{outer}}$. When the operating frequency greatly exceeds $f_{\text{crit, DEP}}$, free charges cannot accumulate at the liquid-liquid interface and shielding is avoided. Reducing the shell thickness also lowers the critical frequency.
A third requirement to achieve centering is to density-match the fluids to within 0.1%. The specified density difference minimizes buoyancy effects. However, it is difficult to identify fluids that meet such stringent density requirements. To increase the density of oil, heavy non-polar additives such as HFE-7100, dichloromethane, or tetrachloroethane are added.\textsuperscript{31} One problem is that many non-polar solvents are volatile. With time the solvents diffuse out of the oil, decreasing its density. Moreover, gas bubbles have been observed to form in the fluid surrounding the emulsion when HFE-7100 is used, due to its low boiling point.\textsuperscript{31} Efforts to increase the density of the oil with solid compounds such as adamantane or 1-bromoadamantane are hampered by their limited solubility in oil.\textsuperscript{34}

Improved centering has been shown when a density gradient in the suspending fluid was used (Fig. 4.2), where the emulsion was situated between the heavier and lighter layers ($\rho_{1\ TOP} > \rho_3 \approx \rho_2 \approx \rho_{1\ M} > \rho_{1\ TOP}$).\textsuperscript{31} This was for a (silicone oil)-in-(DMA)-in (silicone oil) double emulsion. The density gradient distorts the emulsion into an oblate spheroid which counteracts the elongation effect of the applied electric field, resulting in improved sphericity.\textsuperscript{18} However, assembling a density gradient in a lab-on-chip process will be difficult and an alternative method is needed to suspend the emulsion.
A fourth requirement for centering the emulsion is that the liquid-liquid interfacial tension (IFT) must be greater than 15 mN/m. The high IFT reduces the elongation caused by the electric field. One issue is that the surfactant used to stabilize the emulsion lowers the IFT. This means that the lowest possible concentration of surfactant should be used to maintain a relatively high IFT in applications involving large droplets. Experimental evidence suggests that adding styrene-butadiene-styrene or polyacrylic acid actually increases the IFT.

4.2 Photo-initiated curing of the shell

Forming capsule shells with the assistance of electric fields requires switching from thermal curing to photo-initiated curing. Thermal curing is not compatible with electric-field centering because the densities of the different fluids have different temperature coefficients. Forming polymer shells using photo-initiation will require further work: for example, the intensity and duration of the ultraviolet (UV) light needs to be optimized. Earlier efforts using UV intensities of 90 to 100 mW/cm² resulted in vertically-elongated DMA-based shells that ruptured due to heating effects. The temperature effect could have been due to Joule heating of the fluids or from chemical reactions in the shell fluid. Bei found that lowering the UV intensity to 20-30 mW/cm² resulted in intact shells that met sphericity requirements. However, some of the shells were only partially-cured. This was presumably due to non-uniform UV exposure. In order to produce shells with consistent quality, the photo-polymerization process needs to be better controlled.
4.3 Schemes to form foam and fully-dense shells

Emulsion droplets with the appropriate shell-forming chemicals can be centered using electric fields by identifying fluid combinations that allow for a quick centering response from the emulsion. In this section, schemes are proposed to form foam and fully-dense shells. The chemical reactions involved in forming the shells are discussed.

Foam shells

One scheme to make resorcinol-formaldehyde (RF) shells would require dispensing aqueous droplets from three reservoirs and combining them into one volume: one droplet contains resorcinol, one droplet contains formaldehyde, and the third droplet contains photoinitiator and surfactant. The RF solution would then be transported to an oil droplet, where the RF droplet encapsulates the oil to form an oil-in-water emulsion. Adding another oil droplet would then form the oil-in-water-in-oil emulsion.

Once the emulsion is centered using dielectrophoresis, it is irradiated with UV light. The photoinitiator aids the resorcinol and formaldehyde in forming hydroxyl methyl resorcinol derivatives (HMTDs) [Eqn. 4.2]$.^{39}$ The HMTDs undergo condensation polymerization (Eqn. 4.3) to form colloid-sized hydroxyl methyl aggregates, which cross-link to form a foam shell (Eqn. 4.4).$^{40,41,42,43}$

\[
\text{C}_6\text{H}_6\text{O}_2 + 2 \text{CH}_2\text{O} \xrightarrow{\text{photoinitiator}} \text{Hydroxy methyl resorcinol derivative (HMTD)} \quad (4.2)
\]
HMTD + HMTD $\overset{\text{photoinitiator}}{\longrightarrow}$ Hydroxy methyl aggregates + H$_2$O \hfill (4.3)

(condensation polymerization of HMTD)

Hydroxy methyl aggregates $\overset{\text{photoinitiator}}{\longrightarrow}$ Cross-linked hydrogel + CH$_2$O \hfill (4.4)
This proposed chemistry replaces the acid/base catalysts from the traditional RF recipe with a photoinitiator.\textsuperscript{31} A photoinitiator reduces the electrical conductivity of the shell fluid, presumably allowing a faster centering.\textsuperscript{39}

**Fully-dense shells**

Producing polystyrene shells would involve dispensing and combining three droplets: one with water, one with styrene and photoinitiator, and one that is immiscible with styrene. The styrene-based droplet encapsulates the water phase, which is then enveloped by the third droplet.

The styrene droplet must be mixed with a fluid that has a higher dielectric constant for the double emulsion to electrically center.\textsuperscript{17a} In addition, a photoinitiator such as phenylbis (2,4,6-tri-methylbenzoyl) phosphine oxide (PPO) must be added to the styrene to initiate free radical polymerization.\textsuperscript{38,44,45,46}

After the DE is formed and electrically centered, the emulsion is exposed to UV light to separate the photoinitiator into PPO radicals (Eqn. 4.5).\textsuperscript{47} Each radical reacts with the styrene monomer to produce a styrene-photoinitiator radical (Eqn 4.6). The styrene-photoinitiator radical reacts with additional styrene to form a polystyrene chain (Eqn. 4.7), which is the basis of a polystyrene shell.

\[
PPO \xrightarrow{hv} 2 \text{PPO derived radicals} \tag{4.5}
\]

(photolysis of PPO with light)
The exact composition of the styrene-based liquid will require some adjustment. A high photoinitiator / styrene content presumably allows for a faster polymerization process. However, a high concentration of the dielectric-raising fluid in the styrene droplet is needed to center the double emulsion. The presence of such fluid may also change the structure of the polystyrene shell.
4.4 Energy considerations for forming stable emulsions

Forming an oil-in-water emulsion often requires adding a surfactant. This section discusses the role of surfactant in forming the emulsion when mineral oil is brought into contact with water containing surfactant Silwet L-77. By adding enough surfactant to the emulsion, it is possible to change the emulsion’s configuration from a water-in-oil (W/O) to an oil-in-water (O/W) emulsion.

A Gibbs free energy analysis can be used to predict the emulsion that is energetically favored as a function of surfactant concentration. The configuration with the lowest Gibbs free energy (GE) is the most likely to form:

\[
GE = A_{L2V} * Y_{L2V} + A_{L1L2} * Y_{L1L2} + A_{L2S} * Y_{L2S}
\]

(4.8)

where \( A_{L2V} \), \( A_{L1L2} \), \( A_{L2S} \) are the surface areas of the liquid/vapor, liquid/liquid, and liquid/solid interfaces; \( Y_{L2V} \), \( Y_{L1L2} \), \( Y_{L2S} \) are their respective interfacial energies. The subscript ‘2’ refers to the shell fluid, ‘1’ refers to the inner fluid.

Determining the free energy of the emulsion requires deriving equations for its interfacial areas. Equations have been derived for the emulsion in a variety of environments: in air, on a single substrate, and sandwiched between two substrates. In addition, the interfacial surface energy values were determined using contact angle and liquid-vapor / liquid-liquid interfacial measurements. The free energy of the emulsion was then calculated for the cases of W/O and O/W emulsions.
**Interfacial areas for an emulsion suspended in air**

An emulsion formed in air has two interfacial areas: the outer (liquid-vapor, \(A_{LV}\)) and inner (liquid-liquid, \(A_{LL}\)) area.

\[
A_{LV} = 4\pi R_2^2 = 4\pi \left(\frac{3V_{12}}{4\pi}\right)^{2/3} \\
A_{LL} = 4\pi \left(\frac{3V_1}{4\pi}\right)^{2/3} 
\]

where \(R_2\) is the radius of the emulsion, \(V_{12}\) is the total emulsion volume, and \(V_1\) is the inner droplet volume. Equations 4.9 and 4.10 are based on the assumption that an emulsion suspended in air adopts a spherical shape to minimize the surface area.

**Interfacial areas for an emulsion resting on a Teflon-coated substrate**

The interfacial areas for an emulsion resting on a single substrate (Fig. 4.3) are approximated by:

\[
A_{LV} = 2\pi R_2^2 (1 - \cos \theta_2) \\
A_{LL} = 2\pi R_1^2 (1 - \cos \theta_1) + \pi R_1^2 (\sin \theta_1)^2 \\
A_{LS} = 2\pi R_2^2 (\sin \theta_2)^2 
\]

where

\[
R_1^2 = \left(\frac{3V}{4\pi}\right)^{2/3} (2 - 3 \cos \theta + (\cos \theta)^3)^{-2/3}. 
\]

\(A_{LS}\) is the surface area that the liquid contacts the substrate. The radii of curvature, \(R_1\) and \(R_2\), are calculated by plugging in the volume of the inner droplet or the emulsion into Eqn. 4.14.

Simplifying assumptions are used in deriving these interfacial areas: the inner droplet has a contact angle that is equivalent to the case at a solid/liquid/air interface; and a thin film of fluid (2) resides underneath the inner droplet.\(^{49}\)
Interfacial areas for an emulsion bounded by two Teflon-coated substrates

For the case of an emulsion bound by two substrates (Fig 4.4), the interfacial areas are estimated using new assumptions: the interfacial surface areas for the shell fluid (2) reflect the total volume of the emulsion; the inner droplet (1) has a contact angle as if on a solid surface surrounded by air; and the inner droplet has a height approximating the spacing between substrates.

If the water phase has $\theta<90^\circ$, define $\theta^* = \frac{\pi}{2} - \theta$ and $r = \frac{h}{\cos \theta}$.

The surface area at the liquid-solid interface is:

$$A_{LS} = 2\pi R_2^2$$  \hspace{1cm} (4.15)

where $R_2$ is the radius of curvature for the emulsion seen from a top-view perspective (Fig. 4.5b). The factor of 2 accounts for the circular profile of the droplet on the two substrates. The surface area for the liquid-vapor interface is:
\[ A_{LV} = (2\pi R_2)(2 * r_2 * \theta_2^*). \]  

(4.16)

The first term corresponds to the circumference of the emulsion in contact with the substrates, where the radius of curvature \( R_2 \) is the same at the top and bottom substrates. The second term is the length of the air-liquid interface between the two substrates at a given point. Using the equation for \( r \) gives:

\[ A_{LV} = 4\pi R_2 \frac{h}{\cos \theta_2} * \theta_2^* \pi \frac{180}{180}. \]  

(4.17)

\( R_2 \) can be derived from the following equation for the emulsion volume.

\[ V_{12} = 2\pi R_2^2 h - P_2 r_2^2 \left( \frac{\pi}{180} 2\theta_2^* - \sin 2\theta_2^* \right) \text{ where } P_2 = 2\pi R_2 \]  

(4.18)

The first term is a cylindrical volume with radius \( R_2 \) while the second term is a doughnut-shaped volume. The bracketed multiplier of the second term represents the overestimated area at a given point for the emulsion. Multiplying that area by the solid-liquid perimeter for the emulsion \( (P_2) \) gives the volume that must be subtracted from the cylindrical volume. Thus,

\[ V_{12} = 2\pi h R_2^2 - \frac{\pi h^2 R_2}{(\cos \theta_2)^2} \left( \frac{\pi}{180} 2\theta_2^* - \sin 2\theta_2^* \right). \]  

(4.19)

The surface area at the liquid-liquid interface is:

\[ A_{LL} = 2\pi R_1^2 + 4\pi R_1 r_1 \theta_1^*, \]  

(4.20)

which simplifies to:

\[ A_{LL} = 2\pi R_1^2 + 4\pi R_1 h \theta_1^*/\cos \theta_1. \]  

(4.21)

\( R_1 \) can be derived from the following equation for the inner droplet volume.

\[ V_1 = 2\pi R_1^2 h - P_1 r_1^2 \left( \frac{\pi}{180} 2\theta_1^* - \sin 2\theta_1^* \right) \text{ where } P_1 = 2\pi R_1 \]  

(4.22)

This simplifies to:

\[ V_1 = 2\pi h R_1^2 - \frac{\pi h^2 R_1}{(\cos \theta_1)^2} \left( \frac{\pi}{180} 2\theta_1^* - \sin 2\theta_1^* \right). \]  

(4.23)
In the case the water phase has $\theta > 90^\circ$, define $\theta^* = \theta - \pi/2$ and $r = -h/\cos \theta$. If the water envelops the oil phase (Fig. 4.5a), Eqns. 4.15, 4.21 (for $A_{LS}, A_{LL}$), and 4.23 (for $V_1$) are valid. The liquid-vapor surface area is given by:

$$A_{LV} = 4\pi R_2 r_2 \theta^*_2 = 4\pi R_2 \theta^*_2 (-h/\cos \theta_2).$$

(4.24)

$R_2$ can be derived from following equation for the emulsion volume.

$$V_{12} = 2\pi h R_2^2 + R_2 \left[ \frac{\pi h^2}{(\cos \theta_2)^2} \right] \left[ \left( \frac{2\pi \theta^*_2}{180} - \sin 2\theta^*_2 \right) - 4\pi \frac{h^2}{\cos \theta_2} (1 - \cos \theta^*_2) \right]$$

(4.25)

Figure 4.5: Side view of an oil-water emulsion where the contact angle of the water exceeds $90^\circ$. (a) Water envelops the oil. (b) Oil envelops the water.

If the oil envelops the water phase (Fig. 4.5b), Eqns. 4.15, 4.16, and 4.19 ($A_{LS}, A_{LV}, V_{12}$) are still valid. The liquid-liquid surface area is now given by:

$$A_{LL} = 4\pi R_1 r_1 \theta^*_1 + 2\pi R_1^2.$$  

(4.26)

$R_1$ can be derived from the following equation for the inner droplet volume.

$$V_1 = 2\pi h R_1^2 + R_1 \left[ \frac{\pi h^2}{(\cos \theta_1)^2} \right] \left[ \left( \frac{2\pi \theta^*_1}{180} - \sin 2\theta^*_1 \right) - 4\pi \frac{h^2}{\cos \theta_1} (1 - \cos \theta^*_1) \right].$$

(4.27)

**Interfacial surface energies and contact angles**

The interfacial surface energies needed to calculate the free energy of the emulsion were measured using the Du Nouy ring method$^{50}$ and contact angle goniometry. The liquid-vapor interfacial energy was measured for water with a surfactant concentration up to 10x the critical micelle concentration (CMC). Mineral oil ($\gamma_{LV} = 29.6$
mJ/m², \( \gamma_{LS} = 8.6 \text{ mJ/m}^2, \theta_{eq} = 71.5° \) was layered on top of the water when the liquid-liquid interfacial energy was measured. The solid-liquid interfacial energy was calculated using Young’s equation.\(^{51}\) Contact angles were measured for 2 \( \mu \text{L} \) droplets of oil or water on a Teflon®-coated surface surrounded by air.

Increasing the surfactant concentration in the water from 0 to 10x the CMC limit decreased both the surface energy at each interface and the contact angle of the water (Figs. 4.6-4.7). The most significant decrease occurred below the CMC limit. These data are used to calculate the Gibbs free energy of an emulsion in the following section.

Figure 4.6: Surface energy at each interface of the Silwet-water solution as a function of the surfactant concentration in the water.
Free energy calculations

The total free energy of the emulsion is calculated from Eqn. 4.8 using the applicable equations for surface area and experimental interfacial energy values. In the following sections, the emulsion is assumed to contain 21 µL of mineral oil and 12.5 µL of water, values chosen to reflect the volume of a four-mm-diameter RF emulsion. The surfactant concentration in the water is varied from 0 to 10x the CMC limit. The free energy is calculated for a W/O emulsion and an O/W emulsion to determine which configuration is energetically favorable. This is done in a variety of environments: suspended in air; on a single substrate; or between two substrates. The surfactant concentration in the water is varied from 0 to 10x the CMC limit.

Figure 4.8 shows the total free energy versus Silwet concentration for an emulsion formed in air, that is, with no substrates. The two curves correspond to a W/O and an O/W emulsion. The curve with the lower free energy corresponds to the emulsion expected to form at each surfactant concentration. A W/O emulsion should form when the surfactant concentration in the water is less than 0.25x the CMC limit. The emulsion
transitions from a W/O to an O/W emulsion at ~0.3x the CMC limit. At higher surfactant concentrations, O/W emulsions should form.

![Graph](image)

**Figure 4.8** Free energy of an oil-water emulsion (~21:12.5 µL) surrounded by air. The two curves represent the cases that oil envelops the water and vice versa.

Emulsions resting on a single Teflon®-coated substrate (Fig. 4.9) should adapt a W/O configuration when the surfactant concentration is less than 0.45x the CMC limit. Having a surfactant concentration greater than 0.5x the CMC limit should result in O/W emulsions being formed. Compared with the case for a spherical emulsion (Fig 4.8) the total free energy increases by a factor of $10^3$ due to the liquid’s interaction with the substrate.
Figure 4.9: Free energy of an oil-water emulsion (~21:12.5 µL) on a single substrate. The two curves represent the cases that oil envelops the water and vice versa.

An emulsion between two Teflon®-coated substrates spaced 90-µm apart (Fig. 4.10) is predicted to transition from a W/O to an O/W configuration at ~1.7x the CMC limit. The increase in the surfactant concentration is attributed to the total free energy increasing at least five-fold, compared with the case of only one substrate. The second substrate flattens the emulsion into a pancake shape, which increases the solid-liquid contribution to the free energy. This results in more surfactant being required to lower the surface energy of the water below that of the mineral oil.
Effect of plate spacing on forming O/W emulsions

The effect of plate spacing on forming O/W emulsions is shown in Fig. 4.11. The surfactant concentration at which a W/O emulsion should transition to an O/W emulsion decreases from 1.7x to 0.6x the CMC limit when the plate spacing increases from 90 to 630 µm. This decrease is attributed to the emulsion becoming more spherical. Interestingly, the surfactant concentration that is required to form O/W emulsions at a 630-µm plate spacing is similar to the case with only one Teflon® substrate (Fig. 4.9).
Effect of the volume fraction of oil to water on forming O/W emulsions

The volume fraction of oil to water in the emulsion has a large impact on forming O/W emulsions. As the volume fraction increases from 0.1 to 0.8 for plates spaced at 90 µm, the surfactant concentration that is needed to form O/W emulsions should increase from 0.1x to 7x the CMC limit. This is attributed to a smaller volume of water requiring more surfactant to keep its surface energy low when in contact with an oil droplet.

The free energies are calculated assuming the emulsification process does not affect the interfacial energy at the liquid/vapor interface. However, Silwet L-77 is soluble in both liquids and will diffuse from the water into the oil. As a result, the calculations...
are applicable only when the emulsion is first formed. A solubility study on the surfactant is discussed in the next section.

4.5 Surfactant diffusion across liquid interfaces

Forming mineral oil-water emulsions will result in surfactant diffusing into the oil. To quantify the amount of surfactant that should remain in the water, the partition coefficient ($K_p$) was calculated (Eqn. 4.28). This coefficient provides an indication of the surfactant solubility ($S$) at equilibrium as a function of the relative concentration ($C$) in mineral oil and in water.$^{53,54,55}$

$$K_p = S_{oil}/S_{water} = C_{oil}/C_{water} = \frac{V_{water}}{V_{oil}} \left( \frac{C_{water\ initial}-C_{water}}{C_{water}} \right)$$ (4.28)

$V_{water}$ and $V_{oil}$ are the volume of water and oil, respectively. $C_{water\ initial}$ and $C_{water}$ are the concentrations of the surfactant in the water initially and at time ‘t’, respectively.

Using 33.5mL of mineral oil and 20.0 mL of water, the surface tension of the water was measured with the DuNoy Ring method prior to layering oil on top of the water (Fig. 4.13a), then 5 minutes after the oil was added (Fig. 4.13b), and then again 24 hours later (Fig. 4.13c). The initial surfactant concentration in the water was 1x the CMC. Syringes were immersed into the aqueous phase prior to adding the oil to extract liquid at the designated time. This extraction method prevented oil from mixing with the drawn-out sample of water.
Fig 4.13: Side-view schematic of a vessel that contains (a) water and surfactant, (b) oil layered on-top of the water-surfactant mixture, and (c) oil layered on-top of the water-surfactant mixture twenty four hours later.

Five minutes after adding the oil (Table 4.1) the surface tension of the water had increased slightly from 21 to 21.3 mN/m, but twenty four hours later the surface tension had increased to 34.3 mN/m. The surface tension corresponded to a surfactant concentration of 0.2x the CMC. Applying Eqn. 4.28, $K_p \approx 3.2$. This indicates that at equilibrium the surfactant concentration in the oil was ~3x greater than in the water.

The partition coefficient predicts that a majority of the surfactant in a mineral oil-water emulsion should diffuse into the oil. This suggests that more surfactant will be required to form an O/W emulsion than predicted in section 4.4. In addition, the time to reach equilibrium will presumably be much shorter than 24 hours for the oil-water emulsion as the liquid-liquid surface area to volume ratio is high.

<table>
<thead>
<tr>
<th>State</th>
<th>$Y_{LV}$ (mN/m)</th>
<th>Surfactant concentration (xCMC)</th>
<th>$K_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncombined</td>
<td>21</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>t=5 minutes</td>
<td>21.3</td>
<td>~0.9</td>
<td>-</td>
</tr>
<tr>
<td>t=24 hours</td>
<td>34.3</td>
<td>0.2</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Table 4.1: Surface tension of a water sample extracted from the water-mineral oil system at different time intervals. The surface tension value is used to determine the surfactant concentration in the water at a given time, which helps to determine the partition coefficient.
Chapter 5: Experimental setup

Introduction

Dispensing water and oil droplets in an electric-field based microfluidic device is made possible by selectively powering and depowering the electrodes. This chapter begins by discussing the electrode patterns used to dispense and transport the droplets. The effect of electrode size on the droplet volume is also discussed. This is followed by a discussion of the fabrication process used to make the device, the fluids dispensed, and the circuitry used to apply the voltage signals.

5.1 Electrode designs

The structures used for dispensing droplets consist of three or four electrodes (Figs. 5.1a-5.1b) depending on the application: a large U-shaped electrode that functions as a reservoir; a rectangular “cutting” electrode where the column of liquid is pinched-off to form a droplet; an optional heater trace used to form the droplet for surfactant-containing fluids; and a square “droplet” electrode where the droplet forms and is subsequently moved. The length of the cutting electrode is usually ~two times longer (2L) than the droplet electrode.

![Diagram](image)

Figure 5.1: Top view of an electrode design for dispensing droplets. (a) 3-electrode design (b) 3-electrode design with a heater trace. Note that the cutting electrode is bisected by the heater.
A variant on the design in Fig. 5.1b has a narrower cutting electrode to make the droplet volumes more consistent (see Chapter 6).

The droplet electrode ranged in size from 0.4 to 6-mm square, while the spacing between the patterned surface and the top ground electrode ranged from 30 to 270 μm to meet different volume specifications. For example, OMEGA-size water-in-oil emulsions require water and oil volumes of 315 nL and 18.2 nL, respectively. These volumes are achievable using droplet electrodes that are 0.4-mm and 2-mm square, respectively with a 30-μm plate spacing. Two droplets of oil and two droplets of water can be combined to meet the volume specifications (see Chapter 8).

NIF-size emulsions require ~10 μL droplets. This volume is achievable using 6-mm square electrodes with a plate spacing of either 180 μm or 270 μm. A 6-mm square electrode with a 180-μm plate spacing accommodates 6.5 μL of fluid, but viscous oil droplets produced on those electrodes are ~10 μL because the droplet overfills the droplet electrode. This point is discussed later. The amount of overfill depends on the viscosity, surface tension, and contents of the fluid.

Both square and rectangular electrodes were used to transport droplets. The square electrodes were discussed in Chapter 3. Rectangular electrodes (Fig. 5.2) were made wider and shorter in the direction of movement for reasons to be discussed in Chapter 8.
5.2 Device fabrication

Electrode designs were formed on the lower of two plates using lithographic etching. The plates were spaced 30-µm to upwards of 5-mm apart. The lower plate consisted of a glass substrate coated with a 100-nm thick layer of evaporated aluminum. The substrate was initially rinsed with acetone, isopropyl alcohol (IPA), and water, and then soft-baked at 130°C for several minutes to remove residual water. A P-20 solution consisting of 20 vol% hexamethyldisilazane (HMDS) and 80 vol% propylene glycol methyl ether acetate (PMA) was spin-coated onto the substrate to enhance adhesion (Table 5.1). The spin coater was made by Reynolds Tech.

<table>
<thead>
<tr>
<th>Step (P-20)</th>
<th>Spin speed (rpm)</th>
<th>Time (s)</th>
<th>Softbake time (s)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2100</td>
<td>30</td>
<td>60</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 5.1: Spin-coat parameters for P-20 (20 vol% Hexamethyldisilazane [HMDS], 80 vol% Propylene glycol methyl ether acetate [PMA])
A positive photoresist, S1813, was spin-coated on the primed surface (Table 5.2). It was important to bake the photoresist film for no more than 30 s because additional drying resulted in slow or incomplete etching when the electrode pattern was later developed. This is attributed to the drying process for HMDS not removing all of the PMA. With enough time, ammonia and PMA rise from the underlying HMDS film and partially crosslink the photoresist film. From experience, a faster spin speed for the S1813 improves the etching rate of the aluminum but causes the edge profile of the electrodes to be rougher.

<table>
<thead>
<tr>
<th>Step (S1813)</th>
<th>Spin speed (rpm)</th>
<th>Time (s)</th>
<th>Softbake time (s)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>3 (or 5*)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>2100</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>2300</td>
<td>60</td>
<td>30</td>
<td>130</td>
</tr>
</tbody>
</table>

Table 5.2: Spin-coat parameters for S1813. 5 s is used in the first step if the substrate is large. The intermediate spin step (2) is meant to curb the overshoot (rpm) of the spin-coater when it ramps to high speeds.

The photoresist film on the aluminum-coated substrate was covered with a 1:1 lithographic mask (made by Fineline Imaging) and irradiated with UV light to selectively imprint an electrode pattern: A 60s exposure in a mask aligner (OAI Hybralign Series 200) was used to ensure the UV light fully exposed the resist layer. The imprinted substrate was wet-etched for ~8 minutes with MF 319 to remove the unwanted photoresist and metal. The remaining metal on the substrate formed the electrode pattern. Acetone, isopropyl alcohol, and water were then used to clean the substrate of remaining photoresist and HMDS.

The bottom substrate was dried for several minutes at 130°C and then spin-coated with a 0.3-µm spin-on-glass (SOG) suspension layer and a 0.9-µm Teflon® layer (Tables 5.3, 5.4). The top substrate consisted of an indium-tin-oxide (ITO)–coated glass slide.
spin-coated with a 0.9-µm Teflon® layer; the ITO coating served as the ground electrode (Table 5.4). Before spin-coating, the substrate was scrubbed with a 1 wt% Alconox solution and soaked in 99.9% pure methylene chloride for 10 minutes. After fabricating the two electrode surfaces, spacers were placed between them to provide the desired height gap.

<table>
<thead>
<tr>
<th>Step (SOG)</th>
<th>Spin speed (rpm)</th>
<th>Time (s)</th>
<th>Softbake time (s)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1900</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>2100</td>
<td>40</td>
<td>180</td>
<td>200</td>
</tr>
</tbody>
</table>

Table 5.3: Spin-coat parameters for spin-on-glass fluid.

<table>
<thead>
<tr>
<th>Step (Teflon)</th>
<th>Spin speed (rpm)</th>
<th>Time (s)</th>
<th>Softbake time (s)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1600 (or 1500)</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>1800 (or 1700)</td>
<td>30</td>
<td>900</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 5.4: Spin-coat parameters for Teflon®. The first set of spin conditions are used for an aluminized glass substrate. The second set of conditions (in parentheses) is used for the ITO substrate.

5.3 Fluids used in these devices

The aqueous liquids used in this work were made by diluting the following additives in deionized water (18.2 MΩ-cm): surfactant Silwet L-77, which is a non-ionic trisiloxane surfactant suspended in solvent, polyvinyl alcohol (PVA), polyacrylic acid (PAA), and acetonitrile. Silwet L-77 was used as received from Momentive. The range of Silwet concentrations was 0.005, 0.01, 0.025, 0.05 wt%. The critical micelle concentration (CMC) in water is ~0.01 wt%, so the concentrations translate to 0.5x, 1x, 2.5x, and 5x the CMC limit. Surfactant solutions were used within two days to minimize degradation of the surfactant.
Acetonitrile was used as received from VWR Scientific.\textsuperscript{64} 2.5 wt% PVA solutions were prepared by chilling the water and adding PVA (88% hydrolyzed, MW 25,000 g/mol) slowly while stirring with a mixing bar. The solution was then heated and stirred at 90°C for ~2 hours. 0.1 wt% PAA solutions were made at room temperature by adding PAA (MW 1,250,000 g/mol) to water and stirring for several hours. PVA and PAA were used as received from Sigma Aldrich.\textsuperscript{65}

Fluids such as mineral oil\textsuperscript{65}, silicone oil\textsuperscript{65,66}, styrene\textsuperscript{65}, butanol\textsuperscript{65}, decane\textsuperscript{67}, dimethylacetamide\textsuperscript{67}, and Miglyol 812\textsuperscript{68} were used as received from Sigma Aldrich, Gelest, Alfa Aesar, and Peter Cremer. In addition, the styrene droplets in Chapter 10 had moderate amounts of phenylbis (2,4,6-tri-methylbenzoyl) phosphine oxide (PPO) and polystyrene (MW 123,000 g/mol). The PPO was from Sigma Aldrich and the polystyrene was from Pressure Chemical.\textsuperscript{65,69}

5.4 Electronic circuitry

Activation/de-activation of the electrodes was accomplished using a set of relay switches that were controlled from a desk-top computer. The setup is shown in Fig. 5.3. A Labview program was interfaced with a data acquisition (DAQ) module connected to a set of printed circuit boards (PCBs) that were connected to the electrodes. The DAQ module (NI USB-6509) was supplemented with a 12V\textsubscript{dc} external power supply in order to drive the digital signals coming from the DAQ device. Two signal generators (Stanford DS345) were connected to two power amplifiers (Krohn-Hite7602 or Fluke 7602) that connected to the PCBs. The signal generators produced voltages up to 3.5 V\textsubscript{rms} at frequencies of 0 to 30.2 MHz. The voltage amplitudes were increased by the power amplifiers (PA); the Krohn-Hite amplifier produced voltages up to 180 V\textsubscript{rms} at
frequencies of 10 Hz to 10 kHz. Meanwhile, the Fluke amplifier had a fixed 100x gain and a maximum output of 1100 V_{rms} at 0 to 100 kHz. A dc voltage source producing up to 32 V was also connected to the PCBs.

![Diagram of equipment](image)

Figure 5.3: Schematic of the equipment used to conduct experiments.

The voltages transmitted to the electrodes were controlled by the Labview program by means of solid-state relays mounted on the PCBs. These relays were switched between an open and closed position to transmit voltages on command. After configuring the relays, the voltage signals were transmitted from the PCBs to the pogo pins to the electrodes on the lower substrate. A ground line was attached to the ITO-coated glass substrate to complete the circuit.

There were three types of electrical connections in the PCBs. As shown in Fig. 5.4, the first type determined whether a high or low ac voltage was selected for that PCB; a signal from the DAQ module closed one relay switch to connect one voltage signal to the “HV select out” line while opening the other relay switch. The experimental
configuration used 4 PCBs, so it was possible to send 4 ac voltage signals to different electrodes simultaneously.

Figure 5.4: Circuitry schematic for switching between high and low ac voltage signals.
The remaining two electrical connections connected to the electrode pattern; both were rated to handle voltages up to 1000 $V_{\text{rms}}$. One type of connector (Fig. 5.5) determined whether the selected ac voltage was transmitted to an electrode or if the electrode was grounded with a pull-down resistor. One DAQ signal was required to open or close the relay switch in the connector.

![Circuit diagram](image)

Figure 5.5: Circuitry schematic for switching between an ac signal and ground.

The other type of electrical connection (Fig. 5.6) allowed for switching between ac voltage, dc voltage, and ground. Three DAQ signals were required to use the connector: (1) one controlled a relay to switch between dc and ac voltage, (2) one controlled a relay to switch between ac/dc voltage or ground, (3) one controlled a relay to connect (or not) to the electrodes on the bottom substrate. Two of these connectors were connected to one heater trace to operate it.
Figure 5.6: Circuitry schematic for choosing an ac or dc signal, ground, or float.
Chapter 6: Dispensing and transporting water droplets

6.1 Introduction

The process to dispense a water droplet using EWOD becomes complicated when the chemicals needed to form a double emulsion are added. This chapter discusses the conditions and electrode patterns necessary to dispense water, surfactant-containing water, and acetonitrile-containing water droplets of different sizes. The mechanisms involved in dispensing and transporting the droplets are discussed.

The main challenge to dispensing a water droplet is forming and rupturing the fluid membrane. This membrane is formed by pinning fluid at the droplet electrode using the EWOD force and then retracting the fluid on the cutting electrode back to the reservoir electrode (Fig. 6.1). This causes the menisci on the unpowered cutting electrode to converge and form a membrane. The ability to rupture the membrane and separate a droplet is related to the contents of the fluid, the surface tension, and the viscosity.

Figure 6.1: Schematic (top view) showing the electrode design that is used to dispense droplets. Fluid on the droplet electrode is attached to the reservoir fluid by a thin membrane. Black regions are the reservoir electrode, the cutting electrode, and two droplet electrodes. The circular blue (shaded) regions are the fluid.
6.2 Dispensing water droplets

Pure water droplets were rapidly dispensed using 75 $V_{\text{rms}}$ at 100 Hz on 2-mm square electrodes with a 90-µm spacing between the top and bottom substrates. Fluid was first pulled to the perimeter of the reservoir electrode (Fig. 6.2a) and then pulled from the reservoir electrode to the droplet electrode using the EWOD force (Figs. 6.2b-6.2c). Powering the reservoir and droplet electrodes and depowering the cutting electrode resulted in the two liquid menisci converging on the cutting electrode (Fig. 6.2d). The menisci formed a membrane that ruptured 0.1 s later, forming the water droplet on the droplet electrode (Fig. 6.2e).

![Figure 6.2](image)

Figure 6.2: Top view of a pure water droplet dispensed using 75 $V_{\text{rms}}$, 100 Hz. (a) Fluid was centered on the powered reservoir electrode. (b) Cutting electrode was powered, reservoir electrode was depowered, and fluid covered the cutting electrode. (c) Droplet electrode was powered, cutting electrode was depowered, and fluid covered the droplet electrode. (d) Reservoir electrode was powered, drawing fluid to the reservoir electrode. This action ruptured (e) the liquid membrane connecting the droplet and the reservoir fluid, forming a droplet.

6.2.1 Dispensing surfactant-containing water droplets

Adding surfactant Silwet L-77 to the water affected the ability to dispense droplets. This section discusses the trends observed when dispensing droplets with a surfactant concentration of 0.5 to 1x the CMC limit using 75 $V_{\text{rms}}$ at 10 kHz.
Figure 6.3 shows a 0.5x CMC-water droplet dispensed from a reservoir of fluid using 75 V\textsubscript{rms}. One interesting phenomenon was that the fluid advancing onto the cutting electrode came from the region of the reservoir closest to the cutting electrode (Fig. 6.3b). This response differed from the case for pure water (Fig. 6.2), where the fluid at the reservoir moved towards the cutting electrode as a single unit. The behavior with the surfactant-water solution is attributed to surfactant molecules pinning the liquid to the perimeter of the reservoir electrode, impeding the response of the liquid to the electric force.\cite{70}

The voltage application sequence to dispense the droplet was the same as described previously (Figs. 6.3c-6.3f). However, the membrane persisted for ~2.5 s before rupturing. This is attributed to the stabilizing effect of surfactant. At 0.5x the CMC limit, the air-liquid interfaces of the membrane are partially saturated with surfactant and retracting fluid to the reservoir electrode forces these surfactant molecules into close proximity. The repulsive interaction between these molecules helps to stabilize the membrane.

![Diagram of droplet dispensing process](image)

**Figure. 6.3:** Surfactant-water droplet dispensed at 0.5x the CMC limit (0.005-wt% Silwet) using 75 V\textsubscript{rms}, 10 kHz: (a) Cutting electrode was powered, the reservoir electrode was depowered, and fluid covered the cutting electrode. (b) Droplet electrode was powered, cutting electrode was depowered, and fluid covered the droplet electrode. (c) Reservoir electrode was powered drawing fluid to the reservoir electrode. (d) Fluid continued to flow to the powered reservoir electrode and the membrane grew in length. (e) The
membrane extended onto the reservoir electrode. (f) The membrane connecting the droplet and the reservoir fluid ruptured after 2.5 s.

Increasing the surfactant concentration to the CMC limit stabilized the membrane further (Fig. 6.4) as observed by the membrane not rupturing once fluid is fully retracted from the cutting electrode. This behavior is attributed to the surfactant molecules fully saturating the liquid-air interfaces and stabilizing the membrane. Note that the stabilized membrane still allowed fluid to flow from the droplet back into the reservoir as evidenced by the decreasing size of the droplet (Figs. 6.4c-6.4f).

Figure 6.4: Surfactant-water droplet dispensed at the CMC limit (0.01-wt\% Silwet) using 75 \( V_{\text{rms}} \), 10 kHz: (a) Cutting electrode was powered, reservoir electrode was depowered, and fluid covered the cutting electrode. (b) Droplet electrode was powered, cutting electrode was depowered, and fluid covered the droplet electrode. (c) Reservoir electrode was powered drawing fluid to the reservoir electrode. (d) Fluid continued to flow to the powered reservoir electrode and the membrane continued to grow in length. (e) The membrane persisted as fluid continued to retract onto the reservoir electrode. (f) After 200 s the membrane became thinner but a droplet did not form.

**Membrane profile**

The side-view profile of the membrane is believed to change from a thick cross-section to a thin cross-section as fluid on the cutting electrode is removed (Fig. 6.5). Surfactant molecules stabilize the membrane to create a “soap-bubble-like” film that may be only nanometers thick. It is likely that a thin film of fluid also extends to the edges of
the cutting electrode because the liquid-Teflon surface energy (6.8 mJ/m$^2$) is lower than the Teflon-air surface energy (18 mJ/m$^2$).

![Diagram](image)

Figure 6.5: Side view of a surfactant-water solution on the cutting electrode (a) before retracting the fluid onto the reservoir (b) after retracting onto the reservoir.

6.2.2 Voltage-dependency for dispensing surfactant-containing water droplets

On 2-mm square electrodes

Water droplets with a surfactant concentration up to 5x the CMC limit were formed on 2-mm square electrodes with a 90-μm spacing between plates by increasing the voltage from 75 to 150 V$_{\text{rms}}$. Figure 6.6 shows pure water and 0.5x CMC-water droplets dispensed at those voltages. The volume of the droplet increased as the applied voltage increased.

As the surfactant concentration was increased to the CMC limit, droplets only formed when the voltage was increased to 125 V$_{\text{rms}}$. At 2.5x and 5x the CMC limit, 150 V$_{\text{rms}}$ was required to form droplets. Furthermore, at these surfactant concentrations, droplets were one-half smaller. The smaller volume was attributed to the longer survival of the membrane before it ruptured that allowed more fluid to flow from the droplet to the reservoir.
Figure 6.6: Effect of the voltage and surfactant concentration on the volume of the dispensed droplet using 2 mm-square electrodes and a 90-μm plate spacing. The volumes increased as the voltage was increased from 75 to 150 Vrms, for solutions with surfactant concentrations up to 0.5x the CMC limit. Droplets containing 1x and 2.5 to 5x the CMC limit were dispensed only when using voltages of 125 Vrms and 150 Vrms, or higher, respectively.

**On 6-mm square electrodes**

To test the feasibility of dispensing larger droplets, experiments were performed using 6-mm square electrodes with a 270-μm plate spacing (Fig. 6.7). No droplets could be formed using 75 Vrms for two reasons: the pure water solution could not be transported from one electrode to the next; and while the surfactant-water solutions could be moved between electrodes, the fluid membrane would not rupture. Increasing the voltage to 100 Vrms allowed droplets with a surfactant concentration up to 1x the CMC limit to be produced. Increasing the voltage further to 125 Vrms allowed droplets containing 5x the CMC limit to be produced. It was not possible to form droplets with a surfactant concentration of 2.5x the CMC limit, possibly due to the concentration-based Marangoni effect. This is discussed later. At 150 Vrms, droplets were produced at all concentrations.
While water droplets with a surfactant concentration up to 5x the CMC limit can be dispensed using 150 V\textsubscript{rms}, there are several reasons why the dispensing process is impractical: the time needed to rupture the membrane is long and inconsistent, which increases the variability in the droplet’s volume; and the electrode surfaces foul and degrade quickly.

![Diagram](image)

**Figure 6.7.** Effect of the voltage and surfactant concentration on the volume of the dispensed droplet using 6 mm-square electrodes and a 270-µm plate spacing. The volumes increased as the voltage was increased from 75 to 150 V\textsubscript{rms}, for solutions with surfactant concentrations up to 0.5x the CMC limit. Droplets containing 1x the CMC limit were dispensed using voltages of 100 V\textsubscript{rms} or higher. Droplets containing 2.5x and 5x the CMC limit were dispensed only when using voltages of 150 V\textsubscript{rms} and 125 V\textsubscript{rms}, or higher, respectively.

**6.2.3 Effect of using high voltage to dispense surfactant-containing water droplets**

**Surfactant adsorption on electrode surfaces**

One problem with using high voltages is that the electrode surfaces foul quickly. For example, dispensing a 2.5x CMC droplet using 150 V\textsubscript{rms} resulted in white residue appearing at the edges of the cutting and reservoir electrodes (Fig. 6.8).
This residue is believed to be surfactant molecules adhering to the substrates, possibly having been polarized by the electric field. The residue forms a thin film on each substrate, pins the liquid contact line, and inhibits motion. Furthermore, the amount of surfactant on the Teflon® coating increases with the number of operations until the device is unusable. This behavior is similar to what is observed in protein-containing liquids manipulated at EWOD frequencies where applying voltage causes the protein molecules to plate onto the Teflon® substrates.

**Dielectric breakdown**

Another problem with using higher voltages is that the dielectric coatings in the device fail after dispensing 1 to 2 droplets. Evidence of the dielectric breakdown included gas bubbles produced by electrolysis, holes in the aluminum electrodes, and delaminated regions of the Teflon® coating on the ITO-coated slide. There are several explanations for the device failure: the dielectric coatings were too thin to handle the voltage and/or there were surface defects in the dielectric material. Lowering the voltage to less than 100 V_{rms} reduces the damage to the dielectric coatings. However, droplets cannot be dispensed when the surfactant concentration is high.
6.3 Mechanisms for forming and rupturing a membrane

6.3.1 Forming the membrane

As discussed in section 6.2, droplets are dispensed when the membrane forms and ruptures. This involves shrinking a column of liquid to form a membrane as shown in Fig. 6.9. The ability to do this is related to static pressure differences between the fluid on the reservoir and cutting electrodes (regions 1 and 2, respectively).

Figure 6.9: Top-view schematic of the fluid (a) prior to and (b) after retracting the fluid to the reservoir electrode. The radii of curvature seen from a top view are defined.

The static pressures arise from the Laplace equation:\textsuperscript{74,75}

\[
P_1 = P_{\text{air}} + \gamma_{LV} \left( \frac{1}{R_1} + \frac{1}{r_1} \right) \quad (6.1)
\]

\[
P_2 = P_{\text{air}} + \gamma_{LV} \left( \frac{1}{R_2} + \frac{1}{r_2} \right) \quad (6.2)
\]

where R and r are the radii of curvature of the air-liquid interface as viewed from the top and side views, respectively. R\textsubscript{1} is positive, but R\textsubscript{2} can either be infinite or negative. Cho et. al. derived an equation based on these static pressures, which details the role of substrate geometry (R\textsubscript{1}, Z) and voltage in dispensing a droplet:\textsuperscript{76}

\[
\frac{R_1}{R_2} = 1 - \frac{R_1}{Z} (\cos \theta_1 - \cos \theta_2) < 0 \quad (6.3)
\]
where $Z$ is the spacing between the top and bottom plates.

The fluid at the cutting electrode only transitions from a thick liquid column to a membrane when the expression in Eqn. 6.3 is negative. This occurs when the reservoir electrode is large, the spacing between plates is small, or the contact angle of the fluid in region 1 is smaller than it is in region 2. The latter is accomplished by applying voltage to the reservoir electrode while grounding the cutting electrode. After the liquid column collapses, the membrane may rupture to pinch off a droplet.

**6.3.2 Stability and rupture of the membrane**

**Marangoni effect**

The membrane ruptured rapidly for pure water but ruptured slowly or even persisted when surfactant was present. This difference in behavior is attributed to the Marangoni effect that produces a pressure that counteracts the capillary pressure for surfactant-water films. At surfactant concentrations up to the CMC, fluid redistributes along the air-liquid interface in response to gradients in the surface tension.\(^{77,78,79}\) The resulting flow stabilizes the film.

Consider Fig. 6.10. Once the surfactant-laden membrane forms, it subsequently flattens into a film (Fig. 6.10b). It is proposed that further outflow of fluid back to the reservoir electrode causes the film to curve inwards along a region of the surface (Fig. 6.10c). As the curved section forms and the surface area increases, there is a concomitant decrease in the number of surfactant molecules per unit area. This temporarily increases the surface tension along the curved section, causing fluid to flow to the curved section from the neighboring sections. The redistribution of fluid allows the membrane to
contract along the cutting electrode, stabilizing the membrane rather than rupturing it (Fig. 6.10d).

Figure 6.10: Schematic showing how the liquid film evolves during the dispensing of a droplet [a–d] of a low-surface-tension fluid that contains a surfactant: (a) Fluid is transported from the cutting electrode to the reservoir and droplet electrodes. (b) The opposing liquid/vapor surfaces join to form a flattened film. (c) Further fluid flow to both powered electrodes induces a localized thinned region within the film. Fluid flows from neighboring sections to the thinned region (curved arrows) to restore the thinned section to its former thickness. (d) Flow is towards the reservoir as the droplet is pinned at the electrode. The thinned region moves toward the reservoir electrode and the membrane becomes thinner as fluid is retracted. [e,f] If the fluid has a high-surface-tension and little or no surfactant: (e) Fluid flow to the powered electrodes induces a localized thinned region within the film; however, minimal or no restorative flow occurs. (f) The thinned section of the film ruptures and the droplet separates from the reservoir fluid.

The Marangoni effect is diminished for fluids with surfactant concentrations well below the CMC limit and does not occur in pure fluids, leading to membranes that
quickly rupture. Films with surfactant concentrations greater than the CMC limit have very small surface tension gradients along the liquid-air surface because the excess surfactant present in the bulk diffuses to the surface when the film curves inwards. While this might suggest that films with a surfactant concentration above the CMC should rupture easily, they are actually very stable due to the large number of surfactant molecules that increase the pressure within the film.

**Apparent film pressure**

As the film thins to less than 100 nm, there is more to consider than the static pressure differences and Marangoni convection. Figure 6.11 defines an “apparent pressure” within the film ($P'_f$) that can be defined as the sum of the static liquid pressure ($P_{\text{liquid}}$), the disjoining pressure ($\Pi$), and the hydrodynamic pressure ($P_{\text{hyd}}$).

![Figure 6.11: Schematic showing the pressure within a thin liquid film and in the adjacent liquid regions; the film pressure equals the sum of the disjoining pressure, the hydrodynamic pressure, and the static pressure of the adjacent liquid region on the cutting electrode.](image)

The pressure difference ($\Delta P$) between the liquid film and the surrounding air ($P_{\text{air}}$) must be negative for the film to rupture.\cite{77} $\Delta P$ can also be defined as:\cite{80,81}
\[ \Delta P = P_c - (\Pi + P_{hyd}), \text{where } P_c = P_{air} - P_{liquid} = Y_{LV} \left( \frac{1}{R} + \frac{1}{r} \right). \quad (6.4) \]

If \( \Delta P = 0 \), there is no driving force for the film to thin and a metastable film forms.\(^82\) This is sometimes the case with surfactant-water solutions as adding surfactant increases the molecular-electrostatic repulsive force.\(^77,83,84\) More specifically, the surfactant concentration must be high enough for the film to be stable.

**Disjoining pressure**

The disjoining pressure term from Eqn. 6.4 combines the theories of Derjaguin, Landau, Verwey, and Overbeek\(^80\) with theory that describes structural interactions. This pressure accounts for the Van der Waals (\( \Pi_{VDW} \)), electrostatic (\( \Pi_{elec} \)), and structural (\( \Pi_{structural} \)) intermolecular forces acting between the surfaces of the liquid film. The magnitude depends on the film thickness (\( h \)):\(^77,80,85,83\)

\[ \Pi(h) = \Pi_{VDW} + \Pi_{elec} + \Pi_{structural} \quad (6.5) \]

where the Van der Waals pressure component is negative and the electrostatic and structural terms are generally positive.\(^85\) The signs of the electrostatic and structural terms depend on the solute concentration in the film: solute includes surfactant and salt.

The electrostatic term is a result of the electrical double layer (EDL) forces acting between the two air-liquid interfaces.\(^80\) The term is large when the air-liquid interfaces are saturated with surfactant, unless there is also a high concentration of salt ions in solution. The salt ions reduce the Debye length, which reduces the range of the EDL forces.

The structural term arises from molecules layering between the two air-liquid interfaces as the film drains. At concentrations above the CMC limit, the term also
accounts for the organizing of micelles into ordered structures.\textsuperscript{77,85,83,86,87} At higher surfactant concentrations, the micelles reorganize into liposomes or bilayers that increase the film’s stability.\textsuperscript{88}

**Hydrodynamic pressure**

The hydrodynamic pressure term is related to the fluid’s viscosity (\(\eta\)) and the fluid’s velocity in the direction of drainage (\(V_x\)). Consider the simplified Navier-Stokes equation:\textsuperscript{80}

\[
\frac{\partial P_{\text{hyd}}}{\partial x} = \eta \frac{\partial}{\partial r} \left( \frac{\partial V_x}{\partial r} \right)
\]  

(6.6)

where \(r\) and \(x\) are cylindrical coordinates and \(r\) is perpendicular to the flow direction. The \(\partial V_x/\partial r\) term is strongly affected by the “mobility” of the fluid at the film’s air-liquid surface. Air-liquid interfaces that do not contain solute particles are considered fully-mobile. This situation corresponds to a pure slip boundary condition that allows plug flow and the hydrodynamic pressure approaches zero because the fluid’s velocity marginally varies with height (\(r\)).

Interfaces are considered fully-immobile when there is no flow at the surface. This occurs when the Marangoni flow, caused by the gradient in surface tension, is large enough to counteract the drainage of fluid from the film at the air-liquid interface. This happens when surfactant molecules are present and corresponds to a no-slip boundary condition. In this case, the velocity gradient with height (\(\partial V_x/\partial r\)) is large and the hydrodynamic pressure is:

\[
P_{\text{hyd}} = \frac{3\eta R_0 V_x}{2r^2}
\]  

(6.7)

where a higher viscosity or a thicker film increases the hydrodynamic pressure.
The air-liquid surface of the membrane is likely semi / fully-immobile at the surfactant concentrations tested. It is rarely the case that films are free of contaminants or surfactants.\textsuperscript{89} In addition, the surface is only fully-immobile when the gradients in surface tension are sufficiently large.

### 6.4 Dispensing surfactant-containing water droplets with resistive heating

One method to dispense surfactant-containing water droplets at low ac voltages is to use a resister heater that is embedded in the electrode pattern. Heat emitted from the resistor ruptures the surfactant-stabilized membrane. In this work, the heater consists of a single trace of aluminum that bisects the cutting electrode (Fig. 6.12), and is activated by dc voltage. The heater power delivered to the membrane is approximated by $I^2R_N$ where

$$R_N = R_{meas} \frac{L_N}{w_N} \left( \frac{L_1}{w_1} + \frac{L_2}{w_2} + \cdots + \frac{L_N}{w_N} \right)^{-1}$$

and

$$I = \frac{V_{DC}}{R_{meas}}.$$  \hspace{1cm} (6.8)

$I$ is the current; $R_N$ is the resistance of the heater’s flat section that bisects the cutting electrode; $R_{meas}$ is the resistance of the entire heater; $L_N$ is the length of the flat section that bisects the cutting electrode; $L_1, L_2, \ldots$ are lengths of the heater trace adjacent to the flat section; $w_N$ and $w_1, w_2, \ldots$ are the widths of the flat section and the sections adjacent to it, respectively.

The use of a heater to dispense 1x CMC-water droplets was demonstrated using 75 V\textsubscript{rms} at 10 kHz on 2-mm square electrodes with a 90-\textmu m plate spacing. Nine microliters of fluid was first centered on the reservoir electrode and a portion was moved onto the droplet electrode. Fluid on the cutting electrode was then retracted to the reservoir electrode eight seconds prior to the t=0 s frame shown in Fig. 6.12a. At t=0 s,
30 V\textsubscript{DC} was applied to the heater. This resulted in \(~0.15\) W of heater power being applied to a section of the membrane, indicated with the red arrow. The membrane ruptured within 0.33s, forming a \(~0.49\) μL droplet (Fig. 6.12d).

![Figure 6.12](image)

Figure 6.12: Top view showing the fluid membrane for a 1x CMC solution being locally heated by a resistive strip (30V\textsubscript{DC}). The strip had a resistance of 306 Ω. [a-d] The electrode width was 2 mm and the plate spacing was 90 μm. The membrane ruptured after \(~0.33\) s to separate a \(~0.49\) μL droplet.

A \(~12.2\) μL droplet with a surfactant concentration at the CMC limit was also produced using 75 V\textsubscript{rms} at 10 kHz on 6-mm square electrodes with a 270-μm plate spacing (Fig. 6.13). This process required 30 V\textsubscript{DC} be applied across the heater to deliver \(~2.1\) W to the membrane. The membrane ruptured within 0.4 s of heating.
Figure 6.13: Top view showing the fluid membrane for a 1x CMC solution being locally heated by a resistive strip (30V_{DC} application). The strip had a resistance of 113 Ω. [a-d] The electrode width was 6 mm and the plate spacing was 270 µm. The membrane ruptured within 0.4 s to separate a ~12.2 µL droplet.

The destabilizing mechanism can be understood by increasing the camera magnification and recording the membrane as it ruptures at a video capture rate of 30 fps. An example of this is shown in Fig. 6.14, where 20 V_{DC} was applied to the heater to dispense water droplets containing surfactant at 0.5x, 1x, 2.5x, and 5x the CMC limit. The small circular dot in the first frame, indicated by the arrow, shows the location of the heater. Oscillations along the 0.5x CMC-water membrane became visible 0.4 s after heat was applied (Fig. 6.14a). The amplitude of the oscillations grew with time and the membrane ruptured 0.1 s later, forming a string of satellite droplets.

Increasing the surfactant concentration to the CMC extended the time before oscillations became visible to ~2.44 s (Fig. 6.14b). The need for longer heating times is attributed to the surfactant molecules at the air-liquid interfaces more effectively stabilizing the membrane. Increasing the surfactant concentration to 2.5x the CMC increased the required heating time to ~3.0 s (Fig. 6.14c). However, at 5x the CMC, the membrane ruptured after only ~1.33 s of heating (Fig. 6.14d). The shorter heating time is attributed to the concentration-based Marangoni effect being weakened. At the higher surfactant concentration, surfactant within the membrane diffuses readily to the air-liquid interface, which minimizes the gradients in surface tension.
(a) 0.5x CMC

(b) 1x CMC

(c) 2.5x CMC
Figure 6.14: Photograph sequences (top view) showing the breakup of a surfactant-water membrane heated from below using 20 V\textsubscript{DC}. The electrode width was 6 mm, and the plate spacing was 270 µm. Heat was applied at t=0 s. Images for (a) 0.5x CMC solution, (b) 1x CMC solution, (c) 2.5x CMC solution, (d) 5x CMC solution.

The heating time needed to rupture the membrane decreased to 0.3 s or less when the heater voltage was increased to 30 V\textsubscript{DC} for surfactant concentrations up to 5x the CMC limit (Fig. 6.15). The faster rupture time is attributed to large thermal gradients that develop within the membrane. The mechanism for this phenomenon is discussed later.

(a) 0.5x CMC
Figure 6.15: Photograph sequences (top view) showing the breakup of a surfactant-water membrane heated from below using 30 V\textsubscript{DC}. The electrode width was 6 mm, and the plate spacing was 270 µm. Heat was applied at t=0s. Images for (a) 0.5x CMC solution, (b) 1x CMC solution, (c) 2.5x CMC solution, (d) 5x CMC solution.
Figure 6.15 indicates that the membrane destabilizes with a wave-like instability that develops along the entire length of the membrane. The breakup pattern is unexpected because theory suggests that a liquid film on a non-uniformly heated substrate should simply rupture at the site of heating.\textsuperscript{90,91,92} It is probable that the top substrate helped to stabilize the membrane.\textsuperscript{76,93} This hypothesis is based on the observation that a long column of fluid between parallel plates is hydrodynamically stable.\textsuperscript{76} The two-plate structure stabilizes the fluid column when small perturbations are applied. However, the column destabilizes when a large volume of fluid flows out from it. By extension it is presumed that heating the membrane induces enough fluid displacement to destabilize the membrane along its entire length.

**Calculating the critical wavelength and measuring the unstable wavelength**

The breakup pattern observed in Fig. 6.15 indicates that the rupture process can be explained by wave fluctuations along the membrane’s air-liquid surface. The critical wavelength ($\lambda_{\text{crit}}$) required to destabilize the membrane is:

$$\lambda_{\text{crit}} = 2\pi \sqrt{\frac{\pi \gamma_{\text{LV}} H^4}{A}}$$

(6.10)

where $\pi$ is 3.1419, $\gamma_{\text{LV}}$ is the surface tension of the fluid, $H$ is the average thickness of the film, and $A$ is the Hamaker-van der Waals constant.

A 100 nm-thick membrane with a surfactant concentration at the CMC limit has a Hamaker constant of $\sim 3 \times 10^{-20}$ J and a surface tension of 21 mN/m, so that $\lambda_{\text{crit}} = 0.13$ mm.\textsuperscript{95} Once the wavelength at the membrane’s air-liquid surface exceeds the critical value, the membrane destabilizes.\textsuperscript{94}
**Experimental measurement**

The wavelength that destabilized the membrane was estimated by measuring the distance between the centers of the satellite droplets (Fig. 6.15). These data are shown in Fig. 6.16 for surfactant concentrations ranging from 0.5 to 5x the CMC limit with either 20 $V_{\text{DC}}$ or 30 $V_{\text{DC}}$ applied across the heater.

![Figure 6.16: The measured wavelength that destabilized the membrane. The dc voltages used were 20V and 30V. The surfactant concentration ranged from 0.5 to 5x the CMC limit.](image)

The measured wavelengths shown in Fig. 6.16 are ~50% to 100% larger than the calculated critical wavelength. The wavelength was ~0.19 mm when the surfactant concentration was 0.5x the CMC limit. The wavelength increased to ~0.28 mm when the surfactant concentration was at the CMC or higher. The difference in wavelengths is attributed to the increased stability of the membrane at the higher surfactant concentrations.

**Effect of heater power on the heating time**

Figure 6.17 shows that the heater power had a large impact on the heating time that was needed to rupture the membrane. The heating time decreased from ~90 s to ~4 s
when the dc voltage was increased from 10V to 20V, equivalent to a power increase from ~0.02 W to 0.07 W. The heating time decreased further to ~0.4 s or less when 30V was applied, equivalent to a heater power of ~0.15 W.

Figure 6.17: Length of time that heat was applied to the membrane to rupture it. The electrode width was 2 mm and the plate spacing was 90 µm. The error bars were calculated by determining the average heating time and finding the values that represented one standard deviation.

Figure 6.18 shows that the heating times were short when 6-mm square electrodes with a 270-µm plate spacing were used. Under those conditions 20 or 30 V$_{DC}$ was applied to the heater: ~0.95 W and 2.1 W of heater power, respectively. These heater powers were necessary given the large size of the membrane. Using 0.95 W caused the membrane to rupture after 0.6 to 2.4 s. Increasing the heater power to 2.1W decreased the heating times to ~0.3 s or less. The short times were presumably related to large thermal gradients that developed near the heater.
Figure 6.18: Length of time that heat was applied to the membrane to rupture it. The electrode width was 6 mm and the plate spacing was 270 µm. The error bars were calculated by determining the average heating time and finding the values that represented one standard deviation.

**Effect of heater power on the droplet’s volume**

Applying different heater powers had a wide-ranging effect on the droplet volume. See Fig. 6.19. The droplet volumes were often smaller when 0.02 W was applied. At this heater power, the time needed to rupture the membrane was long, which allowed the droplet volume to decrease. When the heater power was increased to 0.07 W or 0.15 W, the droplet volumes were larger. This is attributed to the heating times being too short to allow a significant amount of fluid to drain out from the forming droplet back into the reservoir.
Figure 6.19: Droplet volumes formed with a range of heater powers (0.02 W to 0.15 W) applied to the membrane. The electrode width was 2 mm and the plate spacing was 90 µm. The error bars were calculated by determining the average droplet volume and finding the values that represented one standard deviation.

Heating the membrane at a rate of 0.95 W or 2.1 W had little effect on the droplet volume when 6-mm square electrodes with a 270-µm plate spacing were used, as shown in Fig. 6.20. Instead, differences in the droplet volume were closely related to the surfactant concentration. The droplet volume at 0.5x the CMC limit was the largest, likely due to Marangoni effects that increased the fluid volume on the droplet electrode during the initial dispensing steps.

Figure 6.20: Droplet volumes formed with a range of heater powers (0.95 W to 2.1 W) applied to the membrane. The electrode width was 6 mm and the plate spacing was 270 µm. The error bars were
calculated by determining the average droplet volume and finding the values that represented one standard deviation.

**Effect of heater power on the time needed to dispense a droplet**

The time required to dispense a droplet varied significantly with the heater power when 2-mm square electrodes were used. For example, applying a heater power of 0.02 W resulted in dispensing times of 4.6, 2.0, and 1.6 minutes for the 1x, 2.5x, and 5x CMC solutions, respectively. These long times were a result of the long time needed to rupture the membrane. Note that the reported dispensing times are estimates.

Increasing the heater power to 0.07 W decreased the dispensing times to 0.3, 0.3, and 0.4 minutes for the 1x, 2.5x, and 5x CMC solutions, respectively. The shorter dispensing times were a result of the membrane rupturing within seconds versus minutes. However, increasing the heater power to 0.15 W had little effect on the dispensing times: 0.2, 0.3, and 0.4 minutes for the same surfactant concentrations. The dispensing times were similar using the two heater powers because the heating times were short.

The dispensing time was consistently ~0.8 minutes when the electrode size was increased to 6 mm-square, irrespective of the heater power. This was a result of the long time needed to move the fluid on the large electrodes.
6.4.1 Mechanisms for rupturing the membrane using the heater

The time that the membrane must be heated is related to the applied heater power. Increasing the heater power decreases the time that the membrane must be heated from minutes to seconds to fractions of a second. Three mechanisms are proposed to explain why the membrane ruptures at the different timescales. In all of these mechanisms, heating the base of the membrane introduces a transient and evolving temperature gradient along the length and height of the membrane. Regions nearest to the heater trace develop a pressure gradient that drives fluid away from the heater to the colder regions along the length of the membrane and towards the top electrode (Fig. 6.21).

Figure 6.21: Profile of a fluid membrane heated from below. (a) An isometric view and (b) a side view.

Mechanism 1: Rapid fluid transport when the heating time is short

The thermally-induced pressure gradient that develops near the heater is presumed to be the force that ruptures the membrane in less than a second. A large gradient
increases the flow rate through the midsection of the membrane, causing the midsection to rapidly thin. When the distance between the two air-liquid interfaces becomes small enough, the membrane ruptures at the midsection. The energy released by this rupture induces a wave-like instability along the length of the membrane, making the membrane appear to rupture almost simultaneously.

**Mechanism 2: Benard-Marangoni instability when the heating time is longer**

An unsteady-state form of Benard-Marangoni convection presumably causes the membrane to rupture after several seconds of heating. Circular flow patterns develop due to the gradients in surface tension at the membrane’s air-liquid surface. The thermally-induced flow at the air-liquid surface pulls fluid from within the membrane to the surface, resulting in a flow pattern.\(^{96,97}\) It is proposed that eddies, versus hexagonal rolls, form along the length and height of the membrane as fluid flows away from the heater. Eddies will form within the membrane because the fluid’s velocity at the air-liquid surface is lower than inside the membrane. This is a result of the surfactant molecules at the air-liquid interface partially immobilizing the surface, creating a no-slip boundary condition.

The membrane will destabilize when eddies increase the wavelength of the surface waves above that of the critical wavelength. Eddies should develop when the Marangoni number (Ma) exceeds 174: \(^{98}\)

\[
Ma = \left| \frac{\partial \gamma}{\partial T} \right| \frac{Z\Delta T \rho C_p}{\mu k} \tag{6.11}
\]

where \(\gamma\) is the surface tension, \(\Delta T\) is the temperature difference between the membrane’s top and bottom surfaces, \(\rho\) is the fluid’s density, \(C_p\) is the fluid’s specific heat capacity, \(\mu\) is the fluid’s viscosity, and \(k\) is the fluid’s thermal conductivity.
The temperature difference required to induce the instability can be calculated using Eqn. 6.11. For \( \frac{\partial \Upsilon}{\partial T} = -0.12 \, \text{mN/m*K}, \rho = 1000 \, \text{kg/m}^3, \, C_p = 4183 \, \text{J/kg*K}, \, \mu = 0.00089 \, \text{Pa*s}, \) and \( k=0.6 \, \text{W/m*K}, \) an instability develops when the membrane’s temperature near the top substrate is ~2° or ~0.7° lower than near the bottom substrate for plate spacings of 90 µm and 270 µm, respectively. The temperature differences should be obtainable using the resistive heater.

Consider the time that heat is localized in the membrane when in contact with a 100 nm x 2 mm piece of glass. Heat in the membrane is only localized for ~0.1 ms before it transfers to the glass, assuming the thermal diffusivity of glass is \( 5.6 \times 10^{-7} \, \text{m}^2/\text{s}. \) The short time indicates that heat should be rapidly transferred through the membrane to the top substrate, which helps to regulate the membrane’s temperature near that region. The temperature regulation would presumably allow for the required temperature difference to develop in the membrane.

**Mechanism 3: Random temperature fluctuations when the heating time is long**

According to this hypothesis, temperature fluctuations at the membrane’s air-liquid surface cause the membrane to rupture after minutes of heating. Heating the membrane increases the evaporation rate of the fluid, which increases the rate that heat transfers from the membrane to the air. The heat transfer presumably induces temperature variations in the membrane’s surface waves. The membrane ruptures when the surface waves become unstable.
6.5 High aspect-ratio electrodes

In an effort to better control the volume of droplets dispensed on 6-mm square electrodes, the width of the cutting electrode was reduced from 6 mm to 1.5 mm. The purpose was to reduce the fluid volume on the cutting electrode that was attached to the forming droplet, which is known as the droplet’s “tail”.

Water droplets with a surfactant concentration of 2.5x the CMC limit were dispensed using 100 V_{rms} at 10 kHz and ~2.1 W of heater power (Fig. 6.22). The dispensed droplets were 13.1 ± 0.53 μL (average volume ± one standard deviation).

Contrary to expectations, reducing the width of the cutting electrode did not improve the consistency of the droplet volume. The variability (σ) in the volume was ~4.0%. This was 2.1% greater than when a 6-mm-wide cutting electrode was used in Fig. 6.20. The higher variability was related to the higher voltage required to dispense the droplet using the narrower cutting electrode. As mentioned in section 6.2.3, higher voltages increase the amount of surfactant that adsorbs on the substrates. The adsorbed
surfactant alters the size of the droplet tail as multiple droplets are dispensed, resulting in inconsistent droplet volumes.

**6.6 Dispensing water droplets with an emulsion stabilizer or a density additive**

In an effort to dispense water droplets with the chemicals needed to electrically center an emulsion, water was mixed with polyvinyl alcohol, polyacrylic acid, or acetonitrile. The purpose of adding PVA or PAA is to increase the stability of the emulsion. Meanwhile, adding acetonitrile lowers the density of the water to match that of oil, which should help in forming density-matched emulsions.

**Dispensing water droplets containing polyvinyl alcohol or polyacrylic acid**

Surfactant-water droplets containing polyvinyl alcohol or polyacrylic acid were dispensed using 75 V_{rms} and ~0.15 W of heater power. The following sections describe the effect of ac frequency on the ability to dispense droplets.

*Water droplets containing PVA and Silwet L-77*

Water droplets containing 1 wt% PVA and 0.05 wt % Silwet L-77 were dispensed at frequencies of 50 kHz and 100 kHz. The frequencies were chosen because the fluid responded rapidly to the electric field. Using 50 kHz allowed a droplet to be dispensed within 43 s (Fig. 6.23). Increasing the frequency to 100 kHz decreased the dispensing time to ~16 s. The lower dispensing time at 100 kHz is attributed to the larger electric force acting on the fluid.
Figure 6.23: Process to dispense a PVA-water droplet using 75 V$_{\text{rms}}$ at 50 kHz on 2-mm square electrodes with a 180 μm plate spacing. A resistive heater was embedded in the electrode pattern. Fluid was: (a) centered on the reservoir electrode, (b) moved onto the droplet electrode, (c) retracted to the reservoir electrode. (d) ~0.15 W of heater power was applied to the membrane, which (e) ruptured after ~4.3 s. The droplet volume was ~0.87 μL.

Water droplets containing PAA and Silwet L-77

A water droplet containing 0.01 wt% PAA and 0.05 wt% Silwet L-77 was dispensed using a frequency of 30 kHz. This frequency was chosen because the fluid responded quickly to the electric field. After the initial dispensing steps, it took ~0.9 s of heating to rupture the membrane (Fig. 6.24e). The entire dispensing process took ~40 s.

Solutions containing higher PAA concentrations such as 0.05 wt% could not be dispensed at frequencies ranging from 30 to 100 kHz. At these frequencies, the liquid appeared to be pinned on the electrode surfaces. The fluid pinning is likely a result of the Silwet molecules being unable to prevent the PAA molecules from adsorbing on the electrode surfaces.
Figure 6.24: Process to dispense a PAA-water droplet using 75 $V_{rms}$ at 30 kHz on 2-mm square electrodes with a 180 μm plate spacing. A resistive heater was embedded in the electrode pattern. Fluid was: (a) centered on the reservoir electrode, (b) moved onto the droplet electrode, (c) retracted to the reservoir electrode. (d) ~0.15 W of heater power was applied to the membrane, which (e) ruptured after ~0.90 s. The droplet volume was ~0.79 μL.

**Dispensing acetonitrile-containing water droplets**

Water droplets containing 28 wt% acetonitrile were dispensed without the need for a resistive heater using 60 $V_{rms}$ at 100 Hz (Fig. 6.25). It took an estimated 5.3 s to dispense a 0.22 μL droplet.

The operating conditions used to dispense the acetonitrile-containing water droplets were similar to those used on pure water. This is attributed to several factors: the low viscosity of acetonitrile (μ~0.34 cP); and its high dielectric constant (κ~38). Blending acetonitrile with water lowers the fluid’s viscosity, which makes the fluid easier to move. Moreover, the dielectric constant of the water-acetonitrile solution is high, which results in a large EWOD force. One observation from dispensing the water-acetonitrile droplets was that the fluid began to pin to the edges of the reservoir electrode after 2 to 3 droplets were formed (Fig. 6.25b), possibly because acetonitrile molecules adsorbed on the electrode surfaces under the action of the electric field.
Figure 6.25: Process for dispensing a water-acetonitrile droplet on 2-mm square electrodes with a 90-µm spacing between the top and bottom substrates. The voltage applied was 60 V$_{\text{rms}}$ at 100 Hz. Fluid first was centered on the reservoir electrode (a) and then drawn onto the droplet electrode (b-c). Fluid was pinned at the droplet electrode and a droplet formed when the liquid on the cutting electrode was retracted to the reservoir electrode (d-e). The droplet volume was 0.22 ± 0.02 µL.

6.7 Transporting water droplets

Once a water droplet is dispensed, it must be transported from the dispensing site to an oil droplet. This section discusses the effect of surfactant on the ability to transport the water droplet from one electrode to the next.

To study the transport of droplets on a 6-mm square electrode pattern, 12.5 µL water droplets were moved back-and-forth between two electrodes using 75 V$_{\text{rms}}$ or 100 V$_{\text{rms}}$. The surfactant concentration in the water was varied from 0 to 5x the CMC limit. One electrode was powered for 6 s while the other was grounded. The grounded electrode was then activated while the other one was de-energized for 6 s. The results of these tests are shown in Fig. 6.26, which details the time that a droplet was successfully transported back-and-forth between the electrodes.
Figure 6.26: Water droplets containing surfactant at 0 to 5x the CMC limit were transported back-and-forth between two 6-mm square electrodes using 75 or 100 V\textsubscript{rms}. The spacing between plates was 270 µm. One electrode was activated for 6 s while the other was unpowered. The time that the droplet successfully moved from one electrode to the next is presented.

Pure water droplets were moved successfully back-and-forth between two electrodes for one hour using 75 V\textsubscript{rms} or 100 V\textsubscript{rms} at 100 Hz. A 0.5x CMC surfactant-water droplet was also moved between the two electrodes for one hour using 75 V\textsubscript{rms} at 10 kHz. Using 100 V\textsubscript{rms}, on the other hand, caused the droplet to pin on the electrode surfaces after ~6 minutes.

Increasing the surfactant concentration to 5x the CMC limit caused the droplet to pin more rapidly still: 2 minutes using 75 V\textsubscript{rms}, and 0.2 minutes using 100 V\textsubscript{rms}. The short transport time using 100 V\textsubscript{rms} suggests the voltage should be limited to extend the usability of the electrode patterns.

The transport tests show that adding surfactant diminishes the ability to transport water droplets. The electrode surfaces become fouled as surfactant molecules adsorb on
the surfaces. For this reason, the surfactant concentration in a water droplet should be as low as possible when forming emulsion droplets.

6.8 Conclusion

Pure water, surfactant-containing water, and acetonitrile-containing water droplets were dispensed using the EWOD force. Dispensing the surfactant-containing water droplets, however, was more difficult due to a persistent membrane of fluid that formed between the nascent droplet and the reservoir of fluid. It is proposed that the membrane’s persistence is related to Marangoni convection, as well as the disjoining pressure within the membrane. One solution to rupture the membrane is to heat it using a resistive element embedded in the electrode pattern. It is proposed that the heat destabilizes the membrane by inducing pressure gradients, Benard-Marangoni instability, and evaporation. The mechanism by which the membrane destabilizes depends strongly on the heater power.
Chapter 7: Dispensing and transporting oil droplets

7.1 Introduction

Dispensing and transporting oil droplets is another requirement for forming emulsions. This task is complicated by the fact that each oil has distinct electrical and physical properties. This chapter discusses the conditions required to dispense the oil droplets, the times required, the consistency of the droplet sizes, and the ability to move the droplets. Pure oil and butanol-containing styrene droplets were dispensed.

7.2 Dispensing pure oil droplets

Controlling the volume of an oil droplet requires changing the size of the electrodes and/or the spacing between the top and bottom substrates. The following sections describe the effect of these variables when droplets of decane, mineral oil, and Miglyol 812 are dispensed. The time needed to produce a droplet and the variability in the droplet volume are also covered. The conditions used to dispense the droplets are reported in Table 7.1.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Electrode width (mm)</th>
<th>Spacing (µm)</th>
<th>Voltage ($V_{\text{rms}}$)</th>
<th>Dielectric constant</th>
<th>Viscosity (cP)</th>
<th>Droplet volume (µL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decane</td>
<td>2</td>
<td>90</td>
<td>460</td>
<td>2</td>
<td>0.92</td>
<td>0.53 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>90</td>
<td>460</td>
<td>2</td>
<td>0.92</td>
<td>5.41 ± 0.75</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>180</td>
<td>460</td>
<td>2</td>
<td>0.92</td>
<td>9.16 ± 1.0</td>
</tr>
<tr>
<td>Mineral oil</td>
<td>2</td>
<td>90</td>
<td>672</td>
<td>2.2</td>
<td>26.6</td>
<td>0.70 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>90</td>
<td>672</td>
<td>2.2</td>
<td>26.6</td>
<td>4.98 ± 0.69</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>180</td>
<td>672</td>
<td>2.2</td>
<td>26.6</td>
<td>10.5 ± 0.71</td>
</tr>
<tr>
<td>Miglyol 812*</td>
<td>6</td>
<td>180</td>
<td>672</td>
<td>3.8</td>
<td>30</td>
<td>10.8 ± 0.54</td>
</tr>
</tbody>
</table>

Table 7.1: Conditions for dispensing droplets of decane, mineral oil, and Miglyol 812. The droplet volume is reported as average volume ± one standard deviation.

*Reference 75
Decane

For decane droplets, the process was fastest using small electrodes and small plate spacings. The process took an estimated 5.3 s using 2-mm square electrodes with a 90-µm plate spacing (Fig. 7.1). There are several reasons for the dispensing time being low: the small electrode size ensures the stiction and viscous drag forces are small; and the small plate spacing ensures a large DEP force acts on the fluid.

![Figure 7.1: Process for forming decane droplets using 460 Vrms at 100 Hz on 2-mm square electrodes with a 90-µm plate spacing.](image)

The dispensing time increased to ~15.7 s when 6-mm square electrodes were used. The longer time was a result of using the larger electrodes. The increased contact area between the substrates and the droplet increased the viscous drag force acting on the fluid nine-fold, which slowed the dispensing.

The dispensing time increased to ~33 s when a 180-µm plate spacing was used, because the DEP force was reduced by ~50% as a result of the larger plate spacing.
**Volume variability**

The volume of the droplets was most consistent using 2-mm square electrodes with a 90-µm plate spacing. Under those conditions, the variability was 8.1%. The variability increased to 14% and 11% for droplets dispensed on 6-mm square electrodes with 90 and 180-µm plate spacings, respectively. The higher variability obtained with 6-mm square electrodes is attributed to the large volume of fluid remaining in the tail of the droplet after the membrane forms. These tails are shown in Figs. 7.2a and 7.2b, indicated by the red arrows, for plate spacings of 90 µm and 180 µm, respectively.

Figure 7.2: Photos showing a large volume of fluid on the cutting electrode that is attached to a forming decane droplet. The electrodes were 6-mm square. The plate spacing was: (a) 90 µm, (b) 180 µm.

**Mineral oil**

The dispensing time for a mineral oil droplet was longer than for a decane droplet, apparently because of the higher viscosity of the mineral oil. For example, dispensing a mineral oil droplet took ~35 s using 2-mm square electrodes with a 90-µm plate spacing.

The dispensing time increased to ~20 minutes using 6-mm square electrodes (Fig. 7.3). It took ~10 minutes to position the fluid on the reservoir electrode and draw a
portion of the fluid onto the droplet electrode. The reason for this was a membrane that formed between the cutting and droplet electrodes that restricted flow onto the droplet electrode (Fig. 7.3a). A further ~10 minutes was needed to rupture the membrane once the fluid at the cutting electrode had retracted to the reservoir (Figs. 7.3c-7.3e).

![Figure 7.3](image)

Figure 7.3: Process for forming mineral oil droplets using 672 V_{rms} at 100 Hz on 6-mm square electrodes with a 90-µm plate spacing.

The dispensing time decreased to 8 minutes when the plate spacing was increased to 180 µm. This was related to the uninhibited movement of fluid onto the droplet electrode and the membrane rupturing in ~3.5 minutes (Fig. 7.4). The shorter rupture time was in spite of the electric force being halved by the increase in plate spacing. The larger spacing changed the membrane’s shape to more closely resemble a fluid jet in air that more easily destabilizes.76

Forming mineral oil droplets on 6-mm square electrodes is not a viable option given the long dispensing times; the majority of the time is spent moving the fluid from the reservoir to the droplet electrode. The time can be reduced by either decreasing the length of the electrodes or using a fluid that has a higher dielectric constant.
Volume variability

The lowest variability in the droplet volume was achieved using 2-mm square electrodes with a 90-µm plate spacing. Under those conditions, the variability was 1.7%. The variability increased to 14% and 6.8% for droplets dispensed on 6 mm-square electrodes with plate spacings of 90 µm and 180 µm, respectively. There are two reasons for the higher variability with 6-mm square electrodes: the long time required to rupture the membrane; and the large fluid volume on the cutting electrode that is connected to the forming droplet.

Miglyol 812

Miglyol 812 droplets, a blend of coconut oil, palm oil, and glycerin, were dispensed more quickly than mineral oil droplets. While Miglyol 812 is more viscous, it has a higher dielectric constant. Miglyol 812 droplets were dispensed in ~136 s using 6-mm square electrodes with a 180-µm plate spacing (Fig. 7.5). The faster dispensing time is attributed to the larger DEP force.
Figure 7.5: Process for dispensing droplets of Miglyol 812 using 672 V\textsubscript{rms} at 100 Hz. The electrode width was 6 mm and the plate spacing was 180 µm.

The variability in the droplet volume was 5%, lower than for decane and mineral oil droplets dispensed on the same-sized electrodes. Two factors may explain this result: the large DEP force that expedites the process to rupture the membrane; and the higher viscosity that slightly delays the membrane from rupturing. The latter factor reduces the volume of fluid on the cutting electrode before the membrane ruptures, which in turn reduces the variability in the amount of liquid that retracts onto the droplet electrode.

**Benefits of dispensing smaller droplets**

The dispensing experiments with decane and mineral oil reveal two benefits to dispensing smaller droplets versus larger ones. One benefit is shorter dispensing times. Droplets were dispensed at least three to fourteen-fold faster on 2-mm square electrodes than on 6-mm square electrodes. The second benefit is better control over the droplet volume: the variability in the droplet volume was at least 3% lower using 2-mm square electrodes.
7.2.1 Using heat to dispense mineral oil droplets

To reduce the time required to dispense a mineral oil droplet, a resistive heater embedded in the electrode design was used. Droplets were dispensed using 672 V\textsubscript{rms} at 100 Hz on 2-mm square electrodes with a 90-\textmu m plate spacing. In the final dispensing step, heat was applied to the membrane. Table 7.2 lists the heater power used to destabilize the membrane, the required heating time, and the time the membrane persisted. These results are compared with the case of using no heater.

<table>
<thead>
<tr>
<th>Heater power (W)</th>
<th>Heating time (s)</th>
<th>Total rupture time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>3.4</td>
<td>5.2</td>
</tr>
<tr>
<td>0.07</td>
<td>0.42</td>
<td>2.1</td>
</tr>
<tr>
<td>0.15</td>
<td>0.09</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 7.2: Heater power delivered to the membrane, heating time needed, and the time the membrane existed. The electrode width was 2 mm, and the plate spacing was 90 \textmu m. The droplet volume was 0.73 \textmu L when the different heater powers were applied.

The total time taken to rupture the membrane decreased from 23 s to 5.2 s to 1.0 s when the heater power was increased from 0 W to 0.02 W and then to 0.15 W. Heating served two purposes: creating a temperature gradient; and decreasing the fluid’s viscosity. Both of these effects increase the fluid flow out of the membrane, thereby reducing the time needed to rupture it.

The tests on mineral oil indicate that using a resistive heater reduces the dispensing time by ~66%. These results suggest that the heater should also be used when the electrode size is large or when the DEP force is diminished at large plate spacing.
7.3 Dispensing butanol-containing styrene droplets

To meet the DEP centering requirements for water-in-oil emulsions, styrene was mixed with butanol at a weight ratio of 60 wt% to 40 wt%. This ratio was chosen to match the density of the water-acetonitrile solution (section 6.6). Styrene-butanol droplets of volume ~20 nL are needed for making 8-μm thick polystyrene shells for OMEGA. Two methods to achieve droplets of this size are presented.

One method involved dispensing three 7.6 nL styrene-butanol droplets in succession and then combining them using 133 V_{rms} at 0.9 kHz (Fig. 7.6). One droplet was dispensed and moved up the electrode pattern before the next droplet was formed. The entire process took ~2.3 s.

The second approach was to dispense and combine two 10.6 nL droplets, where two electrodes were used as the cutting electrode. These droplets were more easily dispensed due to the larger distance between the forming droplet and the reservoir, which increased the pressure difference between the air and the membrane; though, the larger distance also increased the variability in the droplet volume.
7.4 Transporting oil droplets

Once an oil droplet is dispensed, it must be transported along an array of electrodes. The velocity of the moving droplet depends on the viscosity of the fluid as well as the applied voltage. The following sections discuss the trends observed when decane and mineral oil droplets were transported on electrodes of different sizes with different plate spacings (Table 7.3).
Factors affecting the velocity of a decane droplet (460 V<sub>rms</sub> at 100 Hz)

The trend observed when moving decane droplets was that their velocity decreased as the electrode size and plate spacing were increased. The velocity of the decane droplet decreased from 4.7 to 3.1 mm/s after the electrode width was increased from 2 to 6 mm at 90-μm plate spacing. This is attributed to two factors: larger stiction forces; and larger viscous drag forces.

The droplet’s velocity decreased to 1.4 mm/s when the plate spacing was increased to 180 μm. The lower velocity is related to the DEP force being smaller with the larger plate spacing.

The velocity of the decane droplet was also limited by the maximum voltage sustainable by the device’s dielectric coatings. Voltages larger than 460 V<sub>rms</sub> caused rapid breakdown of the dielectric coatings when the plate spacing was 90 μm.
Factors affecting the velocity of a mineral oil droplet (672 V\text{rms} at 100 Hz)

The velocity of the mineral oil droplet also decreased as the electrode size and plate spacing were increased. The reasons behind this trend are the same as explained in the last section; however, the velocity of the mineral oil droplet was consistently below 1 mm/s, presumably due to the high viscosity of the fluid. The velocity was 0.9 mm/s when the droplet was moved on 2-mm square electrodes with a 90-\text{µm} plate spacing. The velocity decreased to 0.5 mm/s and 0.2 mm/s using 6 mm-square electrodes with 90 \text{µm} and 180-\text{µm} plate spacings, respectively.

7.5 Conclusion

Oil droplets ranging in size from 8 nL to 11 \text{µL} were dispensed in an effort to form volumes appropriate for making capsule shells. It was found that smaller droplets formed on 2-mm square electrodes were dispensed at least three times faster than for larger droplets formed on 6-mm square electrodes. In addition, the droplet size was found to be more consistent using smaller electrodes. These results indicate that 10 \text{µL} oil droplets should not be dispensed on large electrodes. One alternative is to combine several smaller droplets to form a larger droplet.
Chapter 8: Forming and transporting emulsions

8.1 Introduction

Forming emulsion droplets that accommodate the shell-forming chemistries used in OMEGA and NIF experiments requires using both electrowetting-on-dielectric and dielectrophoresis forces. This chapter discusses methods to dispense and transport emulsion droplets of varying size. Performing these actions required coordinating the voltages and frequencies applied to the microfluidic device. It was found that water-in-oil emulsions form more readily than oil-in-water emulsions.

8.2 Forming water-in-oil emulsions

Water-in-decane emulsions

Water-in-oil emulsions are the basis for making polystyrene shells. As a first step to form OMEGA-size polystyrene shells, a water-in-decane emulsion was produced (Fig. 8.1) using 0.4 and 2-mm square electrodes with a 30-µm plate spacing. Decane was chosen as a model for styrene because of its similar viscosity and dielectric constant values.

First, a ~0.18 µL decane droplet was deposited on the smaller reservoir electrode (Fig. 8.1a) using the DEP force. Three ~9.2 nL droplets were dispensed from the reservoir and combined (Figs. 8.1b-8.1c). Two ~180 nL water droplets were then dispensed from the water reservoir and combined (Figs. 8.1c-8.1e) using the EWOD force. The water droplet was then transported to the decane droplet (Fig. 8.1f), where the decane enveloped the water to form a water-in-oil emulsion. The entire process took ~1.2
minutes, though the time can be reduced by decreasing the time that voltage is applied to the electrodes.

Figure 8.1: Top view showing a water-in-decane emulsion formed from two reservoirs of fluid. Decane was moved using 424 Vrms at 100 Hz, while water was moved using 88 Vrms at 100 Hz. (a) Decane was centered onto its reservoir electrode. (b) A decane droplet rested at the end of the 0.4-mm square electrode pattern while a second droplet was dispensed. (c) Three decane droplets were combined to form a single volume while a water droplet was in the process of being dispensed. (d) A second water droplet was being dispensed while the first droplet resided on another section of the electrode pattern. (e) The two water droplets were combined. (f) The water and decane droplets formed a water-in-oil emulsion upon contact. On average, each decane droplet was 10 ± 0.8 nL while water droplets were 180 ± 7.4 nL.

The water-in-decane emulsion was then transported on an array of 2-mm square electrodes using the EWOD force. Two electrodes were simultaneously powered for 2 s to move the water component of the emulsion (Fig. 8.2b). The low voltage had little effect on the decane, which was dragged along with the water. The process involved
applying voltage to the electrode ahead of the emulsion while keeping the front electrode with water on it activated, and deactivating the electrode at the trailing end of the emulsion (Figs 8.2b-8.2d).

Figure 8.2: Top view showing a water-in-decane emulsion being transported along an electrode pattern using 88 Vrms at 100 Hz. (a) All electrodes were grounded. (b) The first two electrodes were powered, which pulled the emulsion onto those electrodes. (c) The emulsion moved along the electrode pattern by activating two electrodes at a time. (d) The emulsion reached the top of the electrode pattern.

(Water-acetonitrile)-in-(styrene-butanol) emulsions

The next step in making polystyrene shells was to use styrene as the oil component of the water-in-oil emulsion. To meet the DEP centering requirements, the dielectric constant of the styrene solution needed to be higher than that of mineral oil; and the fluids needed to be precisely density matched. These requirements were met by mixing styrene with isobutanol at a ratio of 39 wt% to 61 wt%. Sudan IV dye, ~0.1 wt%, was added to the styrene solution to increase the contrast of the fluid. Water was mixed with acetonitrile at a ratio of 72 wt% to 28 wt% to match the density of the styrene
solution. The individual properties of acetonitrile, butanol, and styrene are reported in Table 8.1.

The process to form the (water-acetonitrile)-in-(styrene-butanol) emulsion was similar to that in Fig. 8.1. Using an identical electrode pattern, five styrene-butanol droplets were dispensed and combined to form a ~50 nL droplet (Figs. 8.3a-8.3b). A ~0.3 µL water-acetonitrile droplet was then dispensed and transported to the styrene droplet, where the styrene enveloped the water to form a water-in-styrene emulsion (Figs. 8.3c-f). The entire process took ~1.8 minutes.

Figure 8.3: Top view showing the formation of a (water-acetonitrile)-in-(styrene-butanol) emulsion from two reservoirs of fluid. The styrene-butanol solution was moved using 133 V_{rms} at 900 Hz, while the water-acetonitrile solution was moved using 75 V_{rms} at 100 Hz. (a) One droplet of styrene-butanol rested on a 2-mm square electrode while another was dispensed. (b) Five styrene-butanol droplets rested on the 2 mm-square electrode pattern while the water-acetonitrile solution was centered on its reservoir electrode. (c) The water solution was moved onto the droplet electrode. (d) A water-acetonitrile droplet was dispensed.
(e) The water droplet was transported. (f) The combined water and styrene-based droplets formed a water-in-styrene emulsion upon contact.

Forming the emulsion took special planning as both fluids react strongly to the same voltage. First, the styrene-butanol droplet was positioned to partially fill a 2-mm square electrode. The water-acetonitrile droplet was then transported onto the electrode next to the styrene-based droplet, where the water spread until it spontaneously contacted the styrene. Using this approach is necessary to prevent water and styrene droplets from moving onto a single powered electrode, which causes the styrene droplet to disperse into tiny globules in the water-based solution.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>ρ (g/mL)</th>
<th>γ_{LV} (mN/m)</th>
<th>μ (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>0.786</td>
<td>29.3</td>
<td>0.39</td>
</tr>
<tr>
<td>Butanol</td>
<td>0.81</td>
<td>24.2</td>
<td>2.95</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.906</td>
<td>32.1</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Table 8.1: Chemical properties of acetonitrile, butanol, and styrene.64,65,102,103,104

**Large water-in-oil emulsions**

Larger water-in-oil emulsions, in the range of 20 μL, will be required to form NIF targets.105 However, the movement of those emulsions is impeded by the larger frictional drag and pinning forces. Transporting the emulsion becomes difficult if the oil volume is large or the oil viscosity is high. The effect of having a large oil volume is shown in Fig. 8.4, where an emulsion consisting of 12.5 μL of water in an equal volume of silicone oil was moved on an array of 6 mm-square electrodes with a 180-μm plate spacing. Attempts to move the emulsion over four electrodes caused it to split into two volumes with most of the silicone oil left behind (Fig. 8.4d). This behavior is attributed to the large
drag/pinning forces acting on the oil. Options to increase the cohesiveness of the emulsion include reducing the oil volume or increasing the spacing between the top and bottom substrates.\textsuperscript{26}

Figure 8.4: Top view showing a water-in-silicone oil emulsion being transported along an array of 6-mm square electrodes using 75 V\textsubscript{rms} at 100 Hz. The spacing between plates was 180 μm. The volume of water and oil were 12.5 μL each. (a) The water droplet was centered on the powered electrode. (b) The emulsion advanced. (c) A membrane formed in the silicone oil as the water droplet advanced. (d) The membrane ruptured and a silicone oil droplet was pinched off, which reduced the oil volume surrounding the water droplet.

It was found that reducing the oil volume to 3 μL keeps the emulsion intact as it moves forward (Fig. 8.5). The silicone oil initially lagged behind the water (Fig. 8.5b), but within ~6 s the oil was dragged forward due to surface tension (Figs. 8.5c-8.5d).
Figure 8.5: Top view showing a water-in-silicone oil emulsion transported along an array of 6-mm square electrodes with a 180μm plate spacing. The volume of water was 12 μL while the volume of oil was 3 μL. (a) Emulsion on an unpowered electrode. (b-d) The emulsion advanced onto the powered electrodes.

The effect of high viscosity oil is shown in Fig. 8.6, where an emulsion containing 12 μL of water and 4 μL of mineral oil was transported. The water-in-oil emulsion proved difficult to transport: as the emulsion was moved across two electrodes (Figs. 8.6b-8.6c), the mineral oil lagged behind. The large viscous drag force acting on the emulsion also prevented it from completely filling the powered electrode in Fig. 8.6c, a requirement for the emulsion to advance further. This situation can be remedied by reducing the oil volume.

Figure 8.6: Top view showing a water-in-mineral oil emulsion transported along an array of 6-mm square electrodes with a 180 μm plate spacing. The volume of water was 12 μL while the volume of oil was 4 μL. (a) Emulsion on an unpowered electrode. (b-c) The emulsion advanced to the powered electrode but with the mineral oil lagging behind. As a result, the emulsion could not completely fill the powered electrode in c.
8.3 Forming water-styrene-mineral oil emulsions

After demonstrating that water-in-oil emulsions could be formed (Fig. 8.3), the next step was to form a density-matched double emulsion. One test to form a stable DE involved placing water-acetonitrile, styrene-butanol, and mineral oil droplets onto a 2-mm square electrode array (Fig. 8.7a). The top and bottom substrates were aligned with a 1.5° wedge, while the bottom substrate was inclined 1.3° above the horizontal.

The double emulsion was formed in a two-step process. The water-acetonitrile and styrene-butanol droplets were combined (Fig. 8.7b) to form a water-in-styrene emulsion. The emulsion was then transported to the mineral oil droplet, where the mineral oil enveloped the emulsion to form a water-in-styrene-in-mineral oil emulsion in ~0.57s (Fig 8.7c). The water-based droplet centered itself in the mineral oil droplet after an additional 0.7 s (Fig 8.7d) but the styrene-based droplet became difficult to distinguish from the oil, partly because the fluids have similar refractive indices.

One disturbing observation was that white particulates appeared in the mineral oil ~3s after the fluids were combined (Fig. 8.7e). Within 52 s (Fig. 8.7f) a single, turbid solution appeared to envelop the water droplet. While it may appear that the double emulsion destabilized, the DE presumably remained intact, as styrene and butanol are insoluble in mineral oil.\(^{106}\) The fluids likely redistributed in the emulsion depending on their relative densities, turning the solution cloudy. Further testing of the styrene-butanol solution is presented in Chapter 10.
Figure 8.7: Top view showing the formation of a water-styrene-mineral oil double emulsion. (a) 20 μL of mineral oil, 4 μL of styrene-butanol, and 8 μL of water-acetonitrile were placed on the bottom substrate with the top substrate angled ~1.5° relative to the bottom substrate. The arrow indicates larger spacing. The bottom substrate was also tilted above the horizontal by ~1.3° in the direction of the mineral oil droplet. (b) The styrene and water-based droplets were combined using 120 V_{rms} at 100 Hz. The emulsion was then transported towards the mineral oil. (c) The mineral oil enveloped the water-in-styrene emulsion. (d) The water-based droplet moved to the center of the mineral oil, but the outline of the styrene droplet became indistinguishable from the oil. (e) White particulates formed within the mineral oil and (f) a cloudy solution appeared to envelop the water droplet.

8.4 Forming oil-in-water emulsions

The first step in making resorcinol-formaldehyde shells is to demonstrate that oil-in-water emulsions can be formed. This section discusses methods for forming and transporting mineral oil-in-water emulsions. For these experiments, the Silwet concentration in the water was 5x the CMC limit.
Initial tests with oil-in-water emulsions combined a ~0.4 μL mineral oil droplet with a 0.4 μL surfactant-containing water droplet on 2 mm-square electrodes with a 90-μm plate spacing (Fig. 8.8a). The water-based droplet was dispensed and then transported to the oil droplet that had been pipetted in place beforehand. The water engulfed the oil within ~8 s.

Transporting the emulsion on the electrode array proved difficult because the oil portion of the emulsion barely moved when the electrodes were actuated (Fig. 8.8). Advancing the water droplet onto the powered 3rd electrode from the top (Fig. 8.8c) resulted in a surfactant-stabilized membrane forming on the 2nd electrode while the oil portion of the emulsion barely moved. The situation remained the same after thirty seconds (Fig. 8.8d). The oil droplet also did not move after the water droplet was moved onto the 4th electrode. The problem in moving the oil is attributed to several factors: (i) viscous drag forces that inhibited the trailing end of the emulsion from moving forward; (ii) pinning forces that pinned the trailing end of the emulsion; (iii) and an interfacial tension between liquids of 7 mN/m that allowed the membrane to form.

Figure 8.8: Top view showing a mineral oil-in-water emulsion being made and transported on 2-mm square electrodes with a 90-μm plate spacing. (a) A surfactant-water droplet was dispensed using 75 V_{rms} at 10 kHz and 0.15 W of heater power, while a mineral oil droplet was centered on the top electrode using 672 V_{rms} at 100 Hz. (b) After combining the fluids, the second electrode from the top was activated to center the
water phase over it. (c) The water portion of the emulsion advanced to the third electrode while the trailing end of the emulsion had barely moved after 10 s. (d) After 30 s, the trailing end of the emulsion was in the same position. (e) The water droplet advanced onto the 4th electrode, which extended the length of the membrane.

One method that improved transport was increasing the plate spacing to 180 µm (Fig. 8.9). Moving the emulsion onto a powered electrode resulted in the trailing end of the emulsion flowing forward over the course of ~20 s. This improvement was a result of two factors: the frictional drag force was reduced at the 180-µm plate spacing; and the surface tension in the water filament surrounding the oil was sufficiently high to drag the oil. A problem with this method is that mineral oil droplets cannot be dispensed on 2-mm square electrodes with a 180-µm plate spacing. The DEP force is too weak. An alternative method to form and transport the oil-in-water emulsion is discussed in the next section.

Figure 8.9: Top view showing the transport of a mineral oil-in-water emulsion on 2-mm square electrodes with a 180-µm plate spacing. (a) The 2nd electrode (from the top) was energized and occupied by the water portion of the emulsion. (b-e) The 3rd electrode was energized and occupied by the water droplet, forming a membrane between it and the oil droplet. (f-k) Surface tension in the water filament surrounding the oil moved the oil onto the 2nd electrode. (l) The emulsion was transported to the 4th electrode.
An improved electrode design to form oil-in-water emulsions

A mineral oil-in-water emulsion was dispensed and transported on a single electrode design using 2-mm square electrodes with a 90-µm plate spacing (Fig. 8.10). Forming the emulsion involved dispensing a ~0.62 µL mineral oil droplet (Figs. 8.10a-8.10c) and transporting it to a given electrode (Fig. 8.10d). A ~0.54 µL surfactant-water droplet was then dispensed and transported to the oil droplet to form an oil-in-water emulsion (Fig. 8.10h). The entire process took ~2.4 minutes.

About 60% of the time needed to form the emulsion was spent dispensing and transporting the mineral oil droplet. This problem is attributed to the high viscosity of the fluid. Meanwhile, dispensing and transporting the water droplet took ~30% of the total time. Transporting the water droplet was slowed due to the trailing end of the droplet lagging behind. The remaining 10% of the time was used for the water droplet to engulf the oil droplet.
Transporting the emulsion on the array of 2-mm square electrodes required moving the water droplet back-and-forth between two electrodes before advancing it onto the new electrode (Fig. 8.11). As shown in Fig. 8.11a, the emulsion initially resided on
the two electrodes at the bottom of the electrode array. Activating the second electrode from the bottom generated a EWOD force to pull the water onto it. The water then moved onto the third electrode when it was activated for 4s with the 2nd electrode grounded, leaving half of the emulsion and most of the oil behind (Fig. 8.11b). Surface tension then drew the oil along with the bulk water phase so that a thin layer of water encompassed the oil.

The second and third electrodes were then simultaneously activated for 1 s (Fig. 8.11c), causing the water droplet to move back to the second electrode, which combined with surface tension forced the trailing end of the emulsion to advance to the 3rd electrode. The EWOD force then moved the water onto the third electrode for 4 s by deactivating the 2nd electrode (Fig 8.11d), causing the emulsion to move forward. Repeating the back-and-forth motion four times forced the emulsion to creep forward as a single unit (Figs. 8.11b-8.11i). The incremental progress between each cycle was noted by the white residue lines within the emulsion, which indicated the previous and current location of the oil-water interface during transport.

Moving the water droplet back-and-forth between electrodes allowed the emulsion to transport along the electrode pattern (Fig. 8.11k). However, the trailing end of the emulsion was eventually left behind (Fig. 8.11l) as viscous drag and pinning forces overcame the surface tension force pulling the emulsion forward. This indicates that the transport method is only suitable for moving emulsions a short distance. One possible solution is to use rectangular electrodes, which is discussed in the next section.
Figure 8.11: Top view showing the transport of a mineral oil-in-water emulsion along an electrode pattern. (a) The second electrode from the bottom was powered, which pulled the water droplet onto it. (b) The third electrode was activated, and the majority of the water flowed onto it. (c) The second and third electrodes were powered, which caused the bulk of the water to recombine with the emulsion. (d) The water droplet moved forward after the second electrode was grounded and the third electrode remained active. (e) The front end of the emulsion was pulled back when the second electrode was powered. (f) The water droplet was pulled forward after grounding the second electrode. (g) The emulsion pulled back after the second electrode was powered. (h) The emulsion moved forward after grounding the second electrode. (i) The emulsion moved forward after powering and then grounding the second electrode. (j) The emulsion was transported to the next electrodes. (k) The emulsion was transported across three electrodes. (l) The front of the emulsion reached the end of the electrode pattern, but the rest of the emulsion was left behind.

**Transporting large emulsions on rectangular electrodes**

To test the ability to move large emulsions, mineral oil-in-water emulsions were transported on 2.5 mm x 10 mm electrodes with a 180-µm spacing between plates (Fig
Transport was improved by moving the emulsion on the rectangular electrodes while cycling the water droplet back-and-forth as previously described.

The transport process was similar to that in Fig. 8.11 with a few exceptions. As the water droplet advanced onto the fourth electrode from the right, the trailing end of the emulsion started to move forward (Fig. 8.12b). Cycling the water droplet back and forth between the third and fourth electrodes resulted in the emulsion moving forward as a single unit (Figs. 8.12b-8.12f). The emulsion was then transported across three more electrodes using the same movement sequence (Figs. 8.12g-8.12l). Changing the aspect ratio of the electrodes allowed surface tension forces to more effectively pull the trailing end of the emulsion. The transport process may be improved further by increasing the aspect ratio of the electrodes, though doing so would increase the time needed to transport the emulsion.
Figure 8.12: Top view showing a mineral oil-in-water emulsion being transported using 75 V\textsubscript{rms} at 10 kHz across a rectangular electrode pattern. The electrodes were 2.5 mm x 10 mm, and the plate spacing was 180 µm. The emulsion had 6 µL of mineral oil and 6 µL of water. (a) The water droplet moved onto the powered electrode. (b) The water droplet advanced onto the electrode ahead of the emulsion. (c) The water droplet retracted after powering two electrodes at once. (d) The water droplet advanced after powering the fourth electrode from the right. (e) The water droplet moved backwards after powering the third electrode. (f) The water droplet advanced. (g) The water droplet moved onto the next electrode. (h) The water droplet retracted. (i) The water droplet advanced. (j) The water droplet advanced again. (k) The emulsion advanced to the next electrode. (l) The emulsion advanced to the final electrode.
8.5 Conclusion

Water-in-oil and oil-in-water emulsions meeting OMEGA and NIF requirements were dispensed and transported using DEP and EWOD forces. The time required to dispense the emulsions varied from about 1 to 2.5 minutes. Differences in the dispensing time are attributed to a few factors: the size of the droplets dispensed; the viscosity of the fluids; and the presence of a surfactant. In addition, it was found that transporting smaller water-in-oil emulsions (0.4 µL) was much easier than transporting larger emulsions (16 µL) due to smaller stiction and viscous drag forces. Transporting oil-in-water emulsions was difficult due to the presence of surfactant. However, the transport process was improved by using rectangular electrodes.
Chapter 9: Transporting a droplet from a narrow to wide plate spacing

9.1 Introduction

Once the initial emulsion and the encapsulating droplet are dispensed, the droplets must combined in a space suitable for dielectrophoresis centering. In a two-plate system, this requires transporting the droplets from a space with a narrow plate spacing to one with a wide plate spacing. This effort is complicated by capillary and pinning forces that resist the droplets from being transported.\textsuperscript{27,107} By itself, the electrical force is inadequate to overcome these forces.\textsuperscript{25} One solution is depicted in Fig. 9.1: incline the bottom surface so gravity helps to transport the droplets.\textsuperscript{108} This would allow the droplets to move to the wider spacing where they can be combined to form a double emulsion.

![Figure 9.1: Side-view schematic of a concept for making double emulsions. The oil-water emulsion and the encapsulating droplet are formed between narrowly-spaced plates and transported down inclined surfaces. The double emulsion forms when the encapsulating droplet envelops the emulsion.](image)

The first step in implementing the geometry of Fig. 9.1 is to demonstrate that single droplets can be transported from a narrow to wide plate spacing. This chapter begins with a discussion of the forces that act on the droplet as it moves between two diverging plates followed by a discussion of the conditions needed to transport oil and
surfactant-water droplets down an inclined surface. The forces acting on the droplet are calculated. Lastly, the conditions needed to transport pure water droplets on a horizontal surface are considered.

9.2 Forces acting on a droplet between diverging plates

Consider the net force ($F_{\text{net}}$) needed to move a droplet bounded by two diverging plates to a space with a wider plate separation. This force is approximated by the sum of the electrical ($F_{\text{elec}}$), gravitational ($F_{\text{grav}}$), capillary ($F_{\text{lap}}$), hysteresis ($F_{\text{st}}$), and frictional interaction ($F_{\text{fric}}$) forces.\textsuperscript{28,107-109,110} These contributions are:

\begin{align*}
F_{\text{elec}} &= \frac{V_{\text{rms}}^2}{2} \left( \frac{dC}{dx} \right) \quad (9.1) \\
F_{\text{grav}} &= V \rho g \sin \alpha_{\text{tilt}} \quad (9.2) \\
F_{\text{lap}} &= -D h_D \left[ P_{\text{front}} - P_{\text{back}} \right] = -D h_D \left[ -\frac{\gamma_{LV} \cos \left( \frac{\beta}{2} + \theta \right)}{(l_{\text{path}} + l_{\text{drop}}) \sin \left( \frac{\beta}{2} \right)} + \frac{\gamma_{LV} \cos \left( \frac{\beta}{2} - \theta \right)}{l_{\text{drop}} \sin \left( \frac{\beta}{2} \right)} \right] \quad (9.3) \\
F_{\text{st}} &= 2DY_{LV} \left( \cos \theta_{\text{rec}} - \cos \theta_{\text{adv}} \right) \quad (9.4) \\
F_{\text{fric}} &= -\mu_{\text{static}} V \rho g \cos \theta \quad (9.5)
\end{align*}

In the above, $C$ is capacitance, $x$ is horizontal distance, $V$ is the droplet volume, $\rho$ is the density, $g$ is the gravity constant, $\alpha_{\text{tilt}}$ is the angle the bottom substrate is tilted from horizontal, $P_{\text{front}}$ and $P_{\text{back}}$ are the pressures at the front and back sections of the droplet, $\beta$ is the separation angle between the top and bottom substrates, $D$ is the width of the droplet, $h_D$ is the plate spacing at which the droplet width is measured, $l_{\text{path}}$ is the distance from the point where the plate spacing would have been 0 mm to the back section of the droplet, $l_{\text{drop}}$ is the lengthwise diameter of the droplet, $\theta_{\text{rec}}$ and $\theta_{\text{adv}}$ are the receding and
advancing contact angles, and $\mu_{\text{static}}$ is the coefficient of static friction for a given liquid on the substrates.

The electrical and gravitational forces must dominate for the droplet to move to a wider plate spacing. One problem is that the electrical force decreases as the plate spacing increases, because the contact area between the droplet and the plates becomes smaller at larger plate spacing. On the other hand, the decrease in electrical force is offset by the gravitational force. The gravitational force in the direction of movement depends on the volume of the droplet and the tilt angle of the bottom substrate.

The capillary force ($F_{\text{lap}}$) causes low-surface-energy droplets to flow from regions with a wider plate spacing to one with a narrower plate spacing. Its magnitude depends on a few factors: the orientation of the diverging plates; the surface tension of the fluid; and the relative position of the droplet. Equation 9.3 is an approximation. It assumes the pressures at the front and back of the droplet act on a rectangular surface area ($D*h_D$) corresponding to the middle of the droplet.

The hysteresis force ($F_{\text{st}}$) accounts for the fluid pinning on the substrates. The droplet will only advance when the contact angles at the front and back of the droplet equal the advancing and receding contact angles, respectively. There is also a frictional interaction force due to molecular interactions between the substrates and the fluid. $F_{\text{fric}}$ is assumed to be negligible. Once the droplet is in motion, a frictional drag force ($F_{\text{drag}}$) also acts on the fluid (Eqn. 3.28).
9.3 Transporting μL-size mineral oil droplets

Increasing the plate spacing from 0.18 mm to 0.45 mm

The first test on mineral oil involved transporting a 6 μL droplet from a plate spacing of 0.18 mm to 0.45 mm using 672 V\textsubscript{rms} at 100 Hz (Fig. 9.2). The top and bottom plates were positioned to diverge at an angle of \(\sim 0.31^\circ\) while the bottom plate was inclined 45°. Initially, fluid was moved to the 0.18-μm plate spacing by pipetting the droplet onto a region of the bottom plate not covered by the top plate. This is just left of the vertical white line in Fig. 9.2. The droplet then rolled down until it reached the edge of the top plate. Capillary pressure then drew the droplet into the two-plate configuration.

The droplet was moved between the diverging plates by powering two electrodes at a time for 10 s. After the droplet had moved onto a set of electrodes, the electrode at the trailing end of the droplet was depowered while the electrode in front of the droplet was powered. This scheme allowed for control over the droplet’s movement.
Figure 9.2: Top view showing a 6 µL mineral oil droplet being transported down a 45° incline between two plates separating at an angle of ~0.31°, from a plate spacing of 0.18 mm to 0.45 mm. The applied voltage was 672 V\text{rms} at 100 Hz. Each electrode was 2.5 mm x 10 mm. The individual images (a-h) show the progression of the droplet as successive electrodes were energized.

As the droplet was transported from a plate spacing of 0.18 mm to 0.45 mm, it made a smaller and smaller contact area with the substrates. The droplet also became more rounded, allowing it to cover more than one electrode. The circular shape of the droplet helped to decrease the loss in electrical force due to the shrinking contact area with the electrodes.

The controlled droplet movement can be explained by calculating the forces acting on the droplet. The forces were graphed as a function of plate spacing (Fig. 9.3) by combining the force equations from section 9.2 with droplet dimensions and distance measurements taken from video images analyzed with ImageJ software. Calculations
reveal that the net force acting on the droplet was always positive after powering the electrode in front of the droplet. This is attributed to several factors: the large gravitational force; and the smaller pinning and capillary contributions at large plate spacing. The large gravitational force was instrumental in transporting the droplet because the force does not depend on plate spacing. Notably, at a 0.24-mm plate spacing, the magnitude of the gravitational force is larger than that of the net force. This indicates that the droplet would have stalled at that plate spacing without the assistance of gravity.

Figure 9.3: Forces acting on a 6 µL mineral oil droplet moving between two diverging plates. The bottom substrate had a 45° tilt. The applied voltage was 672 V_{rms} at 100 Hz. The net force (electrical, gravitational, pinning, and capillary) was calculated for plate separation distances ranging from ~0.2 to 0.42 mm.

**Increasing the plate spacing from 0.45 mm to 2.2 mm**

Transporting the mineral droplet from a plate spacing of 0.45 mm to 2.2 mm required changing the operating parameters. A 10 µL droplet of mineral oil was transported using the same electrode array with the top plate offset ~2.3° from the bottom plate (Fig. 9.4). The bottom plate was inclined at a 45° angle. The voltage was increased
to 755 V\textsubscript{rms} to partially compensate for the wider plate spacing. The electrodes were powered in the same manner as in Fig. 9.2 except that each set of electrodes was powered for 20 s.

The electric field was needed to move the mineral oil droplet to a space with a 1-mm plate spacing (Fig. 9.4b). However, control over the droplet was lost at that plate spacing. From that position gravity was sufficient by itself to overcome the pinning and capillary forces. This resulted in the droplet moving down the inclined surface with a velocity ranging from 0.7 to 4.2 mm/s (Figs. 9.4c-9.4h).^{26-27}

![Figure 9.4: Top view showing a 10 µL mineral oil droplet being transported down a 45° incline between two plates separating at an angle of \~2.3°, from a plate spacing of 0.45 mm to 2.2 mm. The electrical condition was 755 V\textsubscript{rms} at 100 Hz. The electric field was needed to move the droplet a portion of the distance (a-b), thereafter gravity took over as the capillary force decreased and the droplet rolled down the two-plate construction. (c-h).]
Using data gathered from Fig. 9.4, the forces acting on the droplet were calculated (Fig. 9.5). The transport system lost control of the droplet at the 1-mm plate spacing, because the electrical force became too weak to hold the fluid on the activated electrodes. The droplet then accelerated down the inclined surface because of the strong gravitational force, reduced pinning and capillary forces, and the weak frictional drag force.

![Figure 9.5: Forces acting on a 10 µL mineral oil droplet moving between two diverging plates. The bottom substrate had a 45° tilt. The applied voltage was 755 V_{rms} at 100 Hz. The net force (electrical, gravitational, pinning, capillary, and drag) was calculated for spacing ranging from ~0.8 to 1.9 mm.](image)

Better droplet control can be achieved by adjusting the tilt of the bottom surface. An alternative approach is to use coplanar electrodes on the bottom plate with the powered and grounded electrodes positioned side-by-side: the advantage of this configuration is that the electrical force does not depend on the spacing between the top and bottom plates.
9.4 Transporting µL-size surfactant-water droplets

Increasing the plate spacing from 0.18 mm to 0.45 mm

Similar experiments were performed with surfactant-containing water droplets. Figure 9.6 shows a 6 µL water droplet containing Silwet at 5x the CMC limit transported from a plate spacing of 0.18 mm to 0.45 mm spacing using 75 V\text{rms} at 10 kHz. This was accomplished by inclining the bottom substrate 45° while positioning the plates to diverge at an angle of ~0.31°. The droplet movement was controlled by powering the electrode ahead of the emulsion for 6 s. After the droplet was pulled onto the powered electrode, the electrode in front of droplet was powered, while the previous electrode was depowered.

Figure 9.6: Top view showing a 6 µL water droplet with a surfactant concentration of 5x the CMC limit being transported down a 45° incline between two plates separating at an angle of ~0.31°, from a plate spacing of 0.18 mm to 0.45 mm. The electrical condition was 75 V\text{rms} at 10 kHz. The contact area of the droplet with the substrates decreased with distance traveled. The droplet also became more rounded.
Using data taken from Fig. 9.6, the forces acting on the water droplet were calculated (Fig 9.7). Droplet movement was controllable because the electrical force dominated. Moreover, the electrical force was at least three-fold larger than the gravitational force. This prevented the droplet from moving down the inclined surface uncontrollably.

![Figure 9.7: Forces acting on a 6 µL water droplet with a surfactant concentration of 5x the CMC limit moving between two diverging plates. The bottom substrate was tilted 45°. The applied voltage was 75 V_rms at 10 kHz. The net force (electrical, gravitational, pinning, and capillary) was calculated for spacing ranging from ~0.2 to 0.43 mm.](image)

**Increasing the plate spacing from 0.45 mm to 2.2 mm**

A 10 µL surfactant-water droplet was then transported from a plate spacing of 0.45 mm to 2.18 mm (Fig. 9.8) using 75 V_rms at 10 kHz. The top plate was offset ~2.3° from the bottom plate while the bottom plate was inclined 45°. The sequence for powering the electrodes was the same as in Fig. 9.6.
As shown in Figs. 9.8a-9.8c, the structure maintained control of the droplet up to a plate spacing of 0.9 mm. However, at 1.2-mm plate spacing (Fig. 9.8d), the droplet moved down the inclined surface uncontrollably. Over the course of 8 s the velocity of the droplet increased from 2.1 to 8.2 mm/s (Figs. 9.8d-9.8i). This speed resulted in the droplet becoming increasingly elongated in the direction of motion.

Figure 9.8: Top view showing a 10 µL water droplet with a surfactant concentration of 5x the CMC limit being transported down a 45° incline between two plates separating at an angle of ~2.3°, from a plate spacing of 0.45 mm to 2.2 mm. The electrical condition was 75 Vrms at 10 kHz. The electric force controlled the droplet movement initially (a-c), but eventually (d-i) the droplet rolled beyond the activated electrodes. In those frames, the droplet velocity increased due to reduced Laplace pressure and pinning forces.

Using data from experiments such as that shown in Fig. 9.8, the forces acting on the water droplet were calculated (Fig. 9.9). According to these calculations, the droplet transport was controllable up to a plate spacing of 1 mm because the electrical force was large. At plate spacing larger than 1 mm, droplet control was lost.
Figure 9.9: Forces acting on a 10 µL water droplet with a surfactant concentration of 5x the CMC limit moving between two diverging plates. The bottom substrate was tilted 45°. The applied voltage was 75 V$_{\text{rms}}$ at 10 kHz. The net force (electrical, gravitational, pinning, capillary, and drag) was calculated for spacing ranging from ~0.6 to 2.1 mm. The electrical force only acted on the droplet for the first three data points.

9.5 Transporting water droplets on a horizontal surface

To determine if pure water droplets could be transported from a narrow to wide plate spacing, a 20 µL droplet was transported between two plates separated at an angle of ~5.5° using 75 V$_{\text{rms}}$ at 100 Hz (Fig. 9.10). The bottom substrate was horizontal. The electrodes were powered in the same manner as in Fig. 9.8.

The experimental setup was different from the other experiments. The droplet was pipetted onto the bottom plate before placing the top plate over it. The high surface energy of the water on the Teflon surface (53.2 mJ/m$^2$) caused the droplet to move to a space with a 1-mm plate spacing.

The droplet was transported over three electrodes (Figs. 9.10a-9.10d) to a space with a plate spacing of ~1.7 mm. The droplet then stalled on the electrode on its right side.
at a plate spacing of 1.9 mm. While the droplet did stall, the plate spacing was wide enough for dielectrophoresis centering.

![Image](image-url)

**Figure 9.10**: Top view showing a 20 µL water droplet being transported from a plate spacing of ~1 to 1.7 mm. The plates separated at an angle of ~5.5°, and the bottom substrate was horizontal. The electrical condition was 75 V rms at 100 Hz. In (a)-(d) the droplet became more rounded and had a smaller footprint on the substrates.

Forces acting on the droplet were calculated using Fig. 9.10. The droplet could not be transported past a plate spacing of 1.9 mm because the electrical force decreased as the plate spacing increased (Fig. 9.11). In addition, there was a large pinning force acting on the droplet.
The droplet stalled because the electrical force was inadequate. There are two solutions to this problem: increase the applied voltage or incline the bottom substrate to incorporate a gravitational force in the direction of motion. The latter option is more practical as high voltages cause the dielectric coatings to break down.

9.6 Conclusion

Low-surface-energy droplets were transported from a plate spacing of 0.18 mm to 2.2 mm using electrical and gravitational forces. It was found that using gravity is crucial in overcoming pinning and capillary forces. The droplet movement was controlled until the plate spacing reached ~1 mm. At this plate spacing, the droplet moved uncontrollably down the inclined surface. Better control over the droplet can be achieved by adjusting the position of the bottom plate. Pure water droplets were transported to a space suitable for DEP centering without tilting the bottom plate.
Chapter 10: Forming double emulsions

10.1 Introduction

To form capsule shells, the double emulsions need to have the appropriate electrical and physical properties for dielectrophoresis centering, as well as contain the shell-forming chemicals. In this chapter, emulsions were formed by pipetting µL-size droplets into an oil bath several millimeters deep. Inserting a styrene droplet into the bath formed an emulsion (Fig. 10.1a) and inserting oil into that droplet formed a double emulsion (Fig. 10.1b). The experiments were conducted in an aquarium-like setup to determine the feasibility of different fluid combinations for spherical droplets. Fluid densities were measured with a DMA 4500M unit (Anton Paar) at 20 °C, which has an accuracy of 0.00005 g/cc.

Figure 10.1: Process to form a double emulsion. (a) A styrene droplet is pipetted into the silicone oil, forming an emulsion. (b) A silicone oil droplet is pipetted into the styrene droplet to form a double emulsion.
This chapter discusses a process to form oil-styrene-oil double emulsions with the chemicals needed to form a polystyrene shell. The first step in this process is forming a stable styrene-in-oil emulsion. This is followed by developing chemical mixtures that will transform styrene into polystyrene. The last step is forming and centering an oil-styrene-oil double emulsion.

10.2 Forming stable styrene-in-oil emulsions

Styrene-butanol droplets in mineral oil

The first attempt to form a stable styrene-in-oil emulsion involved pipetting a styrene droplet containing 56.6 wt% butanol into a mineral oil bath (Fig. 10.2a). The solutions were density matched. Two seconds after the styrene solution was added to the mineral oil, the styrene droplet began to rise (Fig. 10.2b). The droplet then elongated vertically in the seconds that followed (Figs. 10.2d-10.2f). This was unexpected as the emulsion should have adopted a spherical shape to minimize the free energy.

The droplet elongation was presumably a result of the styrene and butanol separating, given their densities differ by 0.1 g/cc. As such, the butanol needs to be replaced with a fluid with a density closer to styrene.
Figure 10.2: Images of a 1 µL styrene-butanol droplet in mineral oil. The density of the styrene solution was 0.85725 g/cc, while the density of the mineral oil was 0.85665 g/cc. (a) The droplet was pipetted and (b-c) the droplet began to tilt upwards. (d-f) The droplet vertically elongated, presumably an effect of the differences in density between the styrene and butanol.

**Styrene-dimethylacetamide droplets in mineral oil**

As a replacement for the butanol, DMA was mixed with styrene at a ratio of 51.5 wt% to 48.5 wt%. DMA has a density similar to styrene, which suggests that it is a good replacement for butanol. DMA also has a high dielectric constant that will improve the response of the styrene-based fluid to an electric field. A stable emulsion formed when a styrene-DMA droplet was pipetted into a bath of mineral oil (Fig. 10.3). The droplet retained a spherical shape as it sank in the fluid (Figs. 10.3a-10.3b) though it deformed as it approached the bottom substrate (Fig. 10.3c). The sphericity of the styrene-DMA droplet indicates that the fluid combination is suitable for making emulsion droplets.
10.3 Photo-initiated polymerization of styrene

Proof-of-concept test

The next step in forming the double emulsion was to develop chemical mixtures that would photo-polymerize styrene into polystyrene. One mixture consisted of 37.6 wt% styrene, 7.4 wt% polystyrene, 45 wt% DMA, and 10 wt% PPO. The polystyrene was added to the solution because it reduces the polymerization time from about one hour to minutes.

A proof-of-concept test was conducted by placing a 3 µL droplet of the styrene mixture on a glass microscope slide. Before exposing the droplet to UV light, the droplet had a distinct yellow tint due to the PPO (Fig. 10.4a). Two minutes of exposure with a 1W UV light source (360 nm) caused the droplet to become clear (Fig. 10.4b). A solid plate-like material formed near the center of the droplet that was surrounded by a low viscosity fluid. The solid plate was presumably rich in polystyrene and the surrounding
liquid was presumably rich in DMA. This result is attributed to the DMA not polymerizing with the styrene, which forced the DMA from the middle of the droplet. The clear tint of the droplet indicates that the UV exposure was adequate to decompose the photoinitiator.\textsuperscript{47b}

Figure 10.4: A 3 $\mu$L styrene-polystyrene-DMA-PPO droplet was (a) pipetted onto a glass microscope slide, (b) exposed to UV light for two minutes. The droplet became clear and a solid plate formed in the center with a low viscosity fluid surrounding it.

**Polymerization of styrene-based droplets in a silicone oil blend**

Having developed a chemical mixture that can form polystyrene, the next step was to polymerize styrene droplets in oil. A series of polymerization tests were conducted to determine the effect of increasing the styrene and polystyrene contents. Matching the density of the styrene-polystyrene-DMA-PPO solution required replacing mineral oil with a silicone oil blend.

The first test involved pipetting a 2 $\mu$L droplet containing 37.6 wt\% styrene, 7.4 wt\% polystyrene, 45 wt\% DMA, and 10 wt\% PPO into silicone oil. One minute of UV exposure caused the styrene droplet to separate into two droplets, both of which rose in the silicone oil (Fig. 10.5b). The darker droplet had a diameter of 1.4 mm, which translated to a volume of 1.4 $\mu$L. The lighter droplet presumably consisted of DMA,
although some of the DMA remained entrapped in the darker droplet given the initial droplet had ~0.9 µL of DMA. The droplets rising in the silicone oil is attributed to the density of DMA being lower than that of the silicone oil. The darker droplet presumably rose because it was attached to the lighter droplet.

Figure 10.5: Images showing a 2 µL droplet containing 37.6 wt% styrene, 7.4 wt% polystyrene, 45 wt% DMA, and 10 wt% PPO being polymerized in silicone oil. The densities of the styrene solution and the silicone oil were 0.95870 g/cc and 0.95827 g/cc, respectively. (a) Prior to exposing the droplet to UV light, the droplet slowly sank. (b) The droplet was exposed to UV light for a minute, resulting in the droplet separating into two volumes. (c) Another minute of UV exposure caused the darker droplet to sink. (d-e) The droplet then approached the bottom surface and (f) after an additional minute of exposure the droplet wet the bottom surface.
Curing the styrene-based mixture for another minute (Fig. 10.5c) resulted in the darker droplet slowly sinking with time. This is attributed to the styrene polymerizing into polystyrene. The lighter droplet presumably rose to the top of the silicone oil. Over the course of three more minutes of UV curing, the droplet sank to the bottom surface and formed a hemisphere (Figs. 10.5d-10.5f). The shape of the droplet indicated that it had not formed a hard bead and was only partially polymerized.

To fully polymerize the polystyrene bead, it was left overnight in the silicone oil. It was then removed from the oil and air-dried for three days on a glass substrate. SEM images of the bead’s surface and interior (Figs. 10.6-10.8) revealed a porous-like material, presumably an effect of the DMA phase-separating as the polystyrene crosslinked. Micron-size craters were present along the surface of the bead (Fig. 10.6) and micron and sub-micron pores existed within the bead (Fig. 10.8).

The quality of the polystyrene material needs to be improved in order to be suitable for ICF experiments. There are several possible explanations for the large number of voids in the material: the high concentration of DMA; and the rate that styrene was polymerized into polystyrene.
Figure 10.6: SEM image of the surface of a dried polystyrene bead. Small craters exist along the surface.
Figure 10.7: SEM image of a cross-sectioned dried polystyrene bead. There are voids throughout the polystyrene material.
Effect of increasing the styrene content on the polymerization rate

To determine if a higher styrene content increases the polymerization rate of the styrene monomer, the mixture was modified to consist of 58.3 wt% styrene, 11.7 wt% polystyrene, 20 wt% DMA, and 10 wt% PPO. A 2 µL droplet of the styrene mixture was pipetted into a silicone oil bath where it slowly sank. Upon exposure to UV light for 1 minute (Fig. 10.9b), the droplet rose slightly with a plume at the top. The droplet became rapidly opaque, which indicates a more rapid polymerization process. The diameter of the droplet also decreased from 1.6 mm to 1.2 mm, equivalent to a 50% drop in volume.
Figure 10.9: Images showing a 2 µL droplet containing 58.3 wt% styrene, 11.7 wt% polystyrene, 20 wt% DMA, and 10 wt% PPO photo-polymerizing in silicone oil. The density of the styrene solution was 0.95590 g/cc, while the density of the silicone oil was 0.95577 g/cc. (a) Prior to exposing the droplet to UV light, the droplet slowly sank. (b) The droplet was exposed to UV light for one minute, which resulted in a plume forming at the top of the droplet. The droplet turned from clear to opaque. (c) Another minute of UV exposure caused the droplet to sink. (d-f) With three more minutes of UV curing the droplet diameter decreased. Material expelled from the droplet formed ribbon-like-strands in the silicone oil.

An additional minute of UV exposure (Fig. 10.9c) resulted in a column of fluid rising from the droplet. This continued even after five minutes of UV exposure (Figs. 10.9e-10.9f). The appearance of this liquid column indicates that the bead had not fully polymerized after 5 minutes of curing.
In a control test, DMA was removed from the styrene-based mixture. A 2 μL droplet containing 75 wt% styrene, 15 wt% polystyrene, and 10 wt% PPO was pipetted into a silicone oil bath. After a minute of UV exposure, the droplet had elongated vertically with liquid extruded from the top (Fig. 10.10b). An additional four minutes of UV exposure (Figs. 10.10c-10.10f) shrunk the droplet and caused it to either flatten or roll on its side.

The oblong shape of the styrene droplet after one minute of UV exposure indicates that the styrene polymerized quickly; however, the fast polymerization presumably pushed a large volume of the less-polymerized styrene from the center of the droplet into the silicone oil. Evidence for this is the large number of opaque ribbons surrounding the styrene droplet in Fig. 10.10f.
Figure 10.10: Images showing a 2 µL droplet containing 75 wt% styrene, 15 wt% polystyrene, and 10 wt% PPO photo-polymerizing in silicone oil. The density of the styrene solution was 0.95052 g/cc, while the density of the silicone oil was 0.95040 g/cc. (a) Prior to exposing the droplet to UV light, the droplet slowly sank. (b) The droplet was exposed to UV light for one minute, which resulted in a strand of liquid being extruded from the top of the droplet. (c) The droplet then tilted. With three more minutes of UV curing (d-f) the droplet appeared to have flattened or rolled on its side.

10.4 Using dielectrophoresis to form a concentric double emulsion

The next step was to use dielectrophoresis to form a concentric double emulsion. As shown in Fig. 10.11a, a (silicone oil)-(styrene-polystyrene-DMA-PPO)-(silicone oil) double emulsion was formed. The emulsion was bounded by top and bottom electrodes spaced 14 mm apart. The innermost droplet had a volume of 20 µL while the styrene-
based fluid had a volume of 5 µL with a composition of 37.6 wt% styrene, 7.4 wt% polystyrene, 45 wt% DMA, and 10 wt% PPO.

With 4 minutes of applying 840 V\textsubscript{rms} at 20 MHz between the top and bottom electrodes, the layers of the emulsion still did not become concentric (Figs. 10.11b-10.11e). This failure is attributed to the dielectrophoresis force being too weak to center the emulsion. The innermost droplet remained vertically off-centered as the emulsion sank in the silicone oil.

To improve the emulsion’s response to the electric field, there are a couple options: increase the DMA content; and increase the voltage applied. Previous work by Tucker-Schwartz et. al.\textsuperscript{19} showed that a DMA-diacrylate shell with 74 vol% DMA was electrically centered using a similar electric field strength. Presumably, a similar DMA content would help to electrically center a styrene-containing double emulsion. However, the DMA content must be adjusted to avoid decreasing the polymerization rate of the styrene. The voltage could be increased but the resulting electric field may cause the emulsion to elongate.

![Figure 10.11: Images showing a (silicone oil)-in-(styrene-polystyrene-DMA-PPO)-in-(silicone oil) double emulsion: (a) prior to applying voltage, (b) 1 minute after applying 840 V\textsubscript{rms} at 20 MHz, (c) 2 minutes later,](image-url)
(d) 3 minutes later, and (e) 4 minutes later. The density of the inner droplet was 0.95880 g/cc, the density of the styrene solution was 0.96856 g/cc, and the density of the surrounding oil was 0.95821 g/cc.

10.5 Conclusion

A double emulsion containing the appropriate chemistry to form a polystyrene shell was constructed using a series of steps. DMA was mixed with styrene because it has a similar density. Styrene droplets were also polymerized into polystyrene using UV light. However, after incorporating the shell chemistry into the double emulsion, the emulsion could not be electrically centered. To improve the emulsion’s centering response, the DMA content in the shell fluid should be increased.
Chapter 11 Conclusion and future work

11.1 Conclusion

Emulsion droplets were formed using electric fields as an initial step to making foam and fully-dense shells.

The first challenge was dispensing the droplets required to form the emulsions from reservoirs containing surfactant with water, water, and oil. Water droplets containing surfactant were dispensed using a low ac voltage (75 Vrms) by embedding a resistive heater into the electrode pattern and heating the membrane. The mechanisms involved in destabilizing the membrane are based on heat-induced pressure gradients and thermal Marangoni convection. Oil droplets were also dispensed, but smaller droplets were dispensed quicker than larger droplets. This is attributed to smaller pinning and drag forces acting on the fluid. To decrease the dispensing time, a large droplet should be constructed by combining multiple smaller droplets.

Microliter-size emulsions with a low surface energy were formed within 70 to 150 seconds. The formation time increased when the viscosity of the fluid was high or when multiple droplets were dispensed. The time will be reduced by decreasing the volume of the viscous fluids and/or by optimizing the electrode patterns to dispense fewer droplets.

Oil and surfactant-water droplets with a volume of 6 to 10 μL were transported to a separation distance that is suitable for forming capsule shells. This was achieved by inclining the bottom plate at 45° above the horizontal. This work demonstrated the importance of using gravity to assist the electrical force when pinning forces were large.

Emulsion droplets containing the chemicals required to form a polystyrene shell were formed in an oil bath. Chemical mixtures were developed to photo-polymerize the
styrene into polystyrene. A mixture containing 37.6 wt% styrene, 7.4 wt% polystyrene, 45 wt% dimethylacetamide, and 10 wt% photoinitiator was then used as the shell-making fluid in a double emulsion. However, the emulsion could not be centered using dielectrophoresis when 840 V$_{\text{rms}}$ at 20 MHz was applied. Centering can be achieved by increasing the dielectric constant of the shell fluid, but the chemistry must be tuned to not adversely affect the shell’s polymerization rate.

11.2 Future work

3D device to assemble double emulsions

The next step is building a three-dimensional device to produce double emulsions similar to that in Fig. 9.1. This will involve designing electrode patterns that incorporate the different electrodes used in this thesis. A major challenge will be fabricating the devices, given that most deposition and photolithography techniques are designed for two-dimensional substrates. One novel approach is to use flexible substrates. Assuming the required coatings can be applied to thin sheets of chemically-resistant polymer or glass, the sheets can be shaped into 3D structures. The fabrication process would benefit from the lightness of the device and would only be limited by the size of the fabrication tools. Another option is to interconnect different substrates to create a 3D channel structure. The challenge is transitioning the droplets from one substrate to another: the substrates must be joined sufficiently well to prevent low-surface-energy fluids from leaking out of the device or pinning in the gaps where the substrates meet.
**Electric-field centering and UV curing of double emulsions**

A second project involves centering a styrene-based double emulsion and transforming it into a polystyrene shell. This will involve formulating a styrene-based mixture that responds strongly to the electric field, polymerizes quickly, and forms a fully-dense material with minimal vacuoles and surface craters. Forming the shell will be challenging as double emulsions are fragile; the shells may rupture during the polymerization process due to surface stresses. This effort should be extended to resorcinol-formaldehyde shells.
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