On-Chip Double Emulsion Droplet Assembly Using Electrowetting-
on-Dielectric and Dielectrophoresis

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Curriculum Vitae

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Abstract

Target fabrication is a major bottleneck in the development of inertial confinement fusion as an energy source. Current bulk processing methods for laser target fabrication suffer from low yield. This thesis reports experimental results on the application of microfluidics to form double emulsion (DE) droplets used for fabrication of cryogenic foam targets. This microfluidic assembly-line automates the production process to achieve droplet-by-droplet processing so that each DE droplet meets the specifications. Because it is electrically controlled, this scheme provides excellent flexibility and scalability.

The voltage controllable electrowetting-on-dielectric (EWOD) and dielectrophoresis (DEP) effects make it possible to manipulate both conductive and dielectric droplets simultaneously on a microfluidic chip. We present a simple model to calculate the electric actuation forces using lumped parameter electromechanics. This model, identifying the frequency-dependent relationship between EWOD and DEP, can be used to predict the operational conditions to actuate particular liquids.

We demonstrate that aqueous and nonaqueous liquid droplets can be dispensed from on-chip reservoirs by EWOD and DEP actuations, respectively. Dispensed droplet volume reproducibility is tested over a range of operational parameters, including applied voltage, cutting electrode length, and the effect of connecting traces. By optimizing the operating conditions, we obtain a reproducibility of $\pm 3.0\%$, which is adequate for the laser target fabrication according to our sensitivity analysis.

DEP based manipulation of oil usually requires much higher voltages than water actuation. We introduce a new method of actuating oil droplets in water medium that exploits negative DEP to reduce oil actuation voltages. Theoretical modeling and experimental demonstrations for this scheme are presented. Microfluidic operations of transporting, splitting, merging, and dispensing of oil droplets are achieved at a voltage level of ~ 100 V.

After dispensing water and oil droplets, these droplets have to be combined to form DE droplets. We develop a Gibbs free energy model to test the likelihood of DE formation and present experimental results showing the formation of both water-in-oil and oil-in-water DE droplets in parallel-plate structure. In addition, we also investigate the form of DE droplets in open structures. The requirements to eject a droplet from a closed section are determined by force analysis. Corresponding experimental tests are done to demonstrate droplet movements from closed to an open section. While the ejection of water droplet is easily achieved by EWOD actuation, an oleophobic surface must be used to eject an oil droplet. We investigated two types of oleophobic surfaces- electrospun fiber mats and re-entrant Si structures, and used the latter one to achieve oil ejection movement.

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List of Abbreviations and Symbols

AC	alternating current
CAH	contact angle hysteresis
CCD	charge coupled device
CF ₃	trifluoromethyl group
CMC	critical micelle concentration
CO ₂	carbon dioxide
CV	coefficient of variation
CVD	chemical vapor deposition
D	deuterium
DC	direct current
DE	double emulsion
DEP	dielectrophoresis
DI	deionized
DT	deuterium-tritium
EW	electrowetting
EWOD	electrowetting-on-dielectric
ICF	Inertial Confinement Fusion
IFE	Inertial Fusion Energy
IPA	isopropanol alcohol
ITO	indium tin oxide

LLE	Laboratory for Laser Energetics
LLNL	Lawrence Livermore National Laboratory
LoC	Lab-on-a-Chip
O/W/A	oil-in-water-in-air
PCB	printed circuit board
PECVD	plasma enhanced chemical vapor deposition
PMMA	poly(methyl methacrylate)
POSS	polyhedral oligomeric silsesquioxane
RF	resorcinol and formaldehyde
RIE	reactive ion etching
SEM	scanning electron microscope
SiO ₂	silicon dioxide
SOG	spin-on-glass
T	tritium
TECE	carbon tetrachloride
W/O/A	water-in-oil-in-air
<i>A</i>	geometric factor for semicircular shape
<i>C</i>	capacitance
<i>D</i>	gap between top and bottom plates
<i>F</i>	electromechanical force acting on liquid droplet
<i>F</i> _{DEP}	dielectrophoretic force
<i>K</i>	complete elliptic integral of the first kind

L	electrode length
L'	electrode length for single plate scheme
P	pressure in a liquid
R_f	ratio of the roughened surface to the smooth surface in Wenzel model
S_B	base area of droplet
S_L	lateral surface area of droplet
U	voltage potential
V	voltage
V_{rms}	root mean square voltage
V_1	volume of the inner oil droplet of the double emulsion droplet
V_2	volume of the outer water droplet of the double emulsion droplet
W	lateral spacing of silicon dioxide cap patterns
Z	impedance
a	electrode size
c	speed of light
d	shell thickness of the double emulsion droplet
d'	thickness of the Teflon layer
f	frequency of applied voltage
f_c	critical frequency

f_{SL}	solid-liquid contact fraction in Cassie-Baxter model
g	lateral spacing between two coplanar electrodes
$g=9.81\text{m/s}^2$	gravitational field strength
g_L	conductance of liquid droplet
j	square root of minus one
k_d	dielectric constant of dielectric layer
k_{eff}	effective dielectric constant
k_L	dielectric constant of liquid
k_{oil}	dielectric constant of oil
k_t	dielectric constant of Teflon-AF
n	neutron
t	thickness of the dielectric layer
w	electrode width
w'	electrode width for single plate scheme
x	length of the liquid filled region
ΔG	Gibbs energy change
$\theta(V), \theta(0)$	contact angle with and without applied voltage
ϵ_0	vacuum permittivity
ϵ_r	dielectric constant
γ	surface tension
ρ	density of liquid
ρ_{SL}	surface charge density

σ_L conductivity of liquid

ν viscosity

ω angular frequency

Foreword

The author performed all experimental procedures in this thesis unless specified below:

Chapter 8, Section 8.3: The electrospinning experiments in this section were performed with assistance of Rui Xu, Professor James C. M. Li's student, in the lab of Professor Li.

Chapter 8, Figure 8.9: The fluorodecyl POSS material shown in this figure was produced by Raymond Campos, ERC, Inc., CA.

Chapter 1 Introduction

Meeting the growing energy demand while reducing carbon emissions is an urgent global challenge. Among the few alternatives for the large scale environmentally responsible production of electric power, fusion energy has many potential advantages, including abundant fuel in nature, no carbon dioxide or other emissions, and intrinsic safety. [1-4]

Fusion powers active stars. The fusion reaction of two nuclei with masses lower than iron releases energy [1]. The energy released in most fusion reactions is much larger than in chemical reactions because the binding energy that holds nucleus together is far greater than the energy that holds electrons in orbit. For example, fusion of deuterium with tritium creating helium-4, freeing a neutron, releases 17.59 MeV of energy [2]. This amount is consistent with the loss of mass Δm , that is, $E = \Delta mc^2$. See Figure 1.1. The extremely high energy output of the fusion reaction means that the fuel mass requirement for a fusion reactor is very low. In order to sustain annual production of 1 GW of electricity, one would need 100 km² of solar panels or

Fig. 1.1 Fusion reaction between deuterium and tritium. The reaction produces one helium-4 and one neutron and releases 17.6 MeV of energy at the same time.

2.7 megatons of coal, while on the other hand a fusion reactor would consume only 100 kg of deuterium and 150 kg of tritium.

The drawback of fusion is that the reaction is very difficult to achieve. It takes considerable energy to force nuclei to fuse. Atomic nuclei are held together by the residual strong force, which only acts between adjacent nucleons, while the positively charged protons in the nucleus repel each other electrostatically. As a consequence of these two forces, initiation of the fusion reaction requires very high temperature and density, as well as very small energy lost per unit time during the confinement. The conditions needed for a fusion reactor to reach ignition are defined by the Lawson Criterion, which is the triple product of density, temperature, and energy confinement time. For the deuterium-tritium fusion reaction, the physical value of Lawson Criterion is as high as 3×10^{21} keV s/m³. [5]

In support of the National Inertial Confinement Fusion (ICF) program, fusion research is being conducted at the Laboratory for Laser Energetics (LLE) at University of Rochester and at the Lawrence Livermore National Laboratory (LLNL) in Livermore, California. In the ignition experiments, laser beams or other drivers implode cryogenic targets filled with hydrogen isotopes to create the conditions necessary for fusion reactions. These targets are typically a few millimeters in diameter and must be fabricated to exacting requirements on the target diameter, wall thickness, and the inner and outer surface concentricity. During implosion, the slightest imperfections in the target's surfaces are greatly amplified and compromise fusion performance.

Producing these targets is a complex, delicate process. Laser targets are typically fabricated by polymerizing double emulsion (DE) shells and then voiding the inner fluids. Current preparation of DE droplets for target fabrication is done using a triple-nozzle droplet generator. [6,7] Two concentric nozzles are inserted into a tube where there is a flow of an exterior oil phase. An interior oil phase droplet is surrounded by a water phase shell, and they are pinched off at the tips of the two concentric nozzles by the exterior oil flow to form oil-in-water-in-oil DE droplets in the tube. The DE droplets are then delivered to a heated beaker for thermal initiated polymerization of the shell. After polymerization is complete, the water and organic solvent are exchanged with a mutually miscible solvent (typically isopropanol); this solvent is then exchanged with liquid carbon dioxide (CO_2). Dry foam shells are obtained by removing the CO_2 as a supercritical fluid. This preparation method produces quality targets for fusion experiments, but the overall yield of usable targets is quite low and the target size is severely constricted by the device dimensions. In this work, we propose a droplet-based microfluidic DE assembly-line for automated production of foam shells for laser targets. With our new method, individual water and oil droplets are generated from on-chip dispensers, and then combined directly to form DEs. The DE droplets are then transported to an electric-field induced centering device [8-10] for further processing.

Droplet based microfluidic devices manipulate liquids as individual droplets on a substrate. Because of their reconfigurability, flexibility, and scalability, droplet-based microfluidic devices [11-19,28-62,68-75] promise to overcome some of the

drawbacks of continuous flow systems – such as complexity, non-reconfigurability (application- specific). Several droplet actuation methods have been developed for droplet translocation, including electrostatic [13,14], thermocapillary [15,16], electrowetting [12,18,19,28-47,68-75], dielectrophoresis (DEP) [48-62,76], and surface acoustic wave transport [17]. Of these, electrowetting provides a flexible method to actively manipulate conductive liquid droplets and DEP is useful for manipulating electrically-insulating dielectric droplets. Thus, a microfluidic platform for target fabrication can be realized by integrating DEP with electrowetting to manipulate droplets with a wide range of conductivities and dielectric properties.

As sketched in Figure 1.2, the droplet-based microfluidic DE assembly-line works as follows: aqueous and non-aqueous droplets with precisely controlled volumes are dispensed respectively from two reservoirs on a microfluidic chip. The dispensed droplets are transported along the electrode array by EWOD and DEP actuation. To deliver the subsequently formed DE droplets to an electric-field induced centering device for centering and polymerization processes, both the aqueous and non-aqueous droplet are first delivered from closed section to an open section of the device, and then brought together. The closed section and open section are respectively the parallel-plate structure and single-plate structures as shown in Figure 1.2. Once the droplets come into contact, spontaneous emulsification combines them into an oil-in-water or water-in-oil DE droplet. Finally, the DE droplet is moved away for further centering process or other applications. Our on-chip DE assembly line has the advantages of excellent flexibility and scalability, plus the capability of

manipulating a wide variety of liquids. Challenges involved in this scheme include:

- EWOD and/or DEP based droplet dispensing with good reproducibility
- Droplet transport and movement from closed section to open section
- On-chip double emulsion formation

Fig. 1.2 Overall process for on-chip double emulsion formation. (a) Aqueous (water) and non-aqueous (oil) liquids preloaded in reservoirs. (b) Water and oil droplets dispensed by EWOD and DEP actuation, respectively. (c) The dispensed droplets are transported to open sections. (d) The water and oil droplets are combined into DE droplet at open section.

In this thesis, we present theoretical developments and experimental studies for the droplet-based microfluidic DE assembly-line. The thesis is organized as follows. Chapter 2 presents the background and motivation for this study, including an introduction of current DE preparation method and a comparison to our new scheme. Chapter 3 is devoted to EWOD and DEP actuation mechanisms. In Chapter 4 we discuss the droplet dispensability and dispensing reproducibility, which is the basis for droplet formation and droplet volume control. Chapter 5 is devoted to an introduction of a low-voltage oil droplet transport method in water medium. In Chapter 6 we provide theoretical predictions and experimental study of DE formation. Chapter 7 and 8 deal with droplet movement from closed section to open section. For oils, oleophobic surfaces are used to achieve closed to open section movement. Finally, Chapter 9 concludes this work and suggests directions for future research.

Chapter 2 Background and motivation

In inertial fusion, the reaction is ignited by illuminating and compressing a target containing deuterium (D) and tritium (T) with intense laser or ion beams as drivers. For successful fusion ignition, the laser targets must meet certain stringent requirements. We will discuss these restrictions in more details in section 2.1. The conventional batch-processing method reviewed in section 2.2 is capable of producing laser targets with ignition requirements. However, its low yield remains a problem for the mass production needs of a fusion power plant. We put forward a novel microfluidic scheme for assembling DE droplets for target fabrication. With automated electric control, this scheme provides a possible solution for on-demand production of laser targets. The advantages of the microfluidic scheme will be further discussed in section 2.3.

2.1 Requirements on double emulsion droplet uniformity for laser target fabrication

A concentric fusion target is composed of a spherical capsule containing a solid cryogenic shell of DT ice layer, which is over-coated with an outer ablator layer and surrounds a low-density DT gas bubble. When the target capsules are illuminated by laser beams, the outer ablator layer is rapidly heated and driven away from the capsule. The resulting shock wave compresses the DT ice layer to achieve very high pressure in the central DT gas region. Then, the laser illumination ceases, and the DT

fuel shell begins to decelerate, but still compressing the core and converting the kinetic energy to thermal energy which heats the core to be a “hot spot”. Once the core material reaches 20 times the density of lead and a temperature of 100,000,000°C, a “spark” is generated at the “hot spot” to initiate the thermonuclear burn wave, propagating through the compressed DT fuel in a few tens of picoseconds and leading to significant energy gain. [20,21]

The fabrication of cryogenic laser targets usually starts with the formation of low-density foam shells of high spherical symmetry. These foam shells are typically formed from DE droplets. A concentric DE droplet structure is shown in Figure 2.1. Targets are typically a few millimeters in diameter and their shell thickness are on the order of hundreds of microns. Given the complex nature of the fusion reaction, stringent requirements are imposed on the sphericity and wall thickness uniformity of the targets. [22,23] The symmetry requirements are achieved by proper process control during polymerization, and the wall thickness uniformity is maintained by controlling volumes of inner oil phase and outer water phase of DE droplet.

Fig. 2.1 The concentric DE droplet for foam shell formation for target fabrication.

The relationship between wall thickness and DE water and oil volumes can be understood through the following sensitivity analysis. The volumes of the inner oil phase and outer water phase of the DE droplet are represented by V_1 and V_2 , respectively.

$$V_1 = \frac{4\pi}{3} R_1^3$$

$$V_1 + V_2 = \frac{4\pi}{3} R_2^3$$

The shell thickness is

$$d = R_2 - R_1$$

Thus d can be written

$$d = \frac{\left(\frac{3}{\pi}\right)^{1/3} \cdot (V_1 + V_2)^{1/3}}{2^{2/3}} - \frac{\left(\frac{3}{\pi}\right)^{1/3} \cdot V_1^{1/3}}{2^{2/3}} \quad (2-1)$$

By taking partial derivatives of equation (2-1), we obtain an expression for the uncertainty of d in terms of the uncertainties of V_1 and V_2 :

$$\Delta d = \left| \Delta V_1 \cdot \left(\frac{1}{6^{2/3} \pi^{1/3} (V_1 + V_2)^{2/3}} - \frac{1}{6^{2/3} \pi^{1/3} V_1^{2/3}} \right) \right| + \left| \Delta V_2 \cdot \frac{1}{6^{2/3} \pi^{1/3} (V_1 + V_2)^{2/3}} \right| \quad (2-2)$$

The specified diameters of an IFE target are: $2R_2=4\pm0.2$ mm, $d=289\pm20$ μm . Thus $V_1=20.98$ mm³, and $V_2=12.53$ mm³. By substituting these values into equation (2-2), we can determine wall thickness variation ($\Delta d/d$) in terms of water and oil volume variations ($\Delta V/V$). Refer to Figure 2.2. Different values for wall thickness variation ($\Delta d/d$) are represented by straight lines in the ($\Delta V_1/V_1$) vs. ($\Delta V_2/V_2$) chart. All these lines have the same slope. The shaded triangular area denotes the space where the target specification on wall thickness variation is satisfied, i.e., $\Delta d/d < 20/289 = 6.92\%$. For example, if the oil volume variation ($\Delta V_1/V_1$) is 5%, and water volume

variation ($\Delta V_2/V_2$) is 4%, the corresponding point indicated by a star in Figure 2.2 locates within the shaded area. Thus, for this set of uncertainty values of the volumes ($\Delta V_1/V_1$) and ($\Delta V_2/V_2$), the wall thickness condition is met.

Fig. 2.2 Sensitivity analysis of shell wall thickness for IFE target. The wall thickness variation is related to drop volume variations by equation (2-2). The shaded area denotes the space where the target specification on wall thickness variation is satisfied.

The red line in Figure 2.2 represents the special case where the uncertainties of water and oil phase volumes are identical, while the blue line represents the case where the relative volume variations of water and oil phases are the same. Under this latter condition, $(\Delta V_1/V_1) = (\Delta V_2/V_2)$ must be smaller than 5% to meet the laser target requirement.

Ultimate success of the IFE program requires a target fabrication scheme that can

rapidly produce targets meeting these rigid dimensional and symmetry requirements. Fusion-power system studies indicate that the energy released per target implosion could range between hundreds of megajoules and several gigajoules. The corresponding repetition rates then must be in the range from several per second to about once every ten seconds for a 1-GW(e) power plant. [4] Therefore, between 100,000 and 500,000 targets per day will have to be made at a fraction of a dollar per target [4,24] to produce economically useful power. To avoid the need for a huge inventory of Tritium, these targets must be produced and then consumed continuously.

2.2 Conventional methods for forming uniform double emulsion droplets

In target fabrication, production of the foam shells used to hold the DT ice layer is the first step. At present, DE droplets for foam shell formation are produced using a triple-nozzle droplet generator. [6,7] The system is shown schematically in Figure 2.3. The inner-most nozzle contains an interior oil phase, the middle concentric nozzle flows an aqueous phase, and the outer tube has an exterior oil phase. When the three liquid phase flow rates are properly adjusted, an interior oil droplet is first enveloped by an aqueous shell, which is then pinched off at the tip of the interior nozzles by the exterior oil flow to form oil-in-water-in-oil DE droplets continuously within the tube.

The stream of DE droplets flows down the delivery tube into a gently stirred, heated beaker filled with more of the exterior phase oil. Agitation of the shells is necessary to maintain drop sphericity. Agglomeration and coalescence of the shells is

reduced by the addition of SPAN 80 surfactant to the exterior oil phase. Approximately 200–300 shells are created per batch, of which one-third to two-thirds may finally become usable foam shells. [6,25]

Fig. 2.3 Schematic diagram of the triple-orifice droplet generator. This diagram is adapted from [6].

The aqueous phase of the DE droplets contains a mixture of resorcinol and formaldehyde (RF). These chemicals react at elevated temperature in the beaker to form a crosslinked aerogel. Gradually the aerogel turns into a stiff interconnected polymer structure. After polymerization, surviving shells are soaked in IPA to dissolve excess exterior oil phase and to replace the water solvating the gel and the oil inside the shell. This exchange step must be repeated many times with fresh IPA to replace

water and oil completely before IPA is exchanged with liquid CO₂. Dry foam shells result by removal of the CO₂ in a supercritical drying process.

In the DE droplet formation process, the densities of the inner droplet and the shell phase must be carefully matched to eliminate buoyancy effects, which would otherwise lead to non-uniform shell wall thickness or even DE droplet instability. The density of the exterior oil phase is also carefully adjusted to be slightly less than that of the DE drops to help keep them suspended during the gentle agitation. It has been found that liquid oils with higher viscosity retard water transport out of the shell, [6] so mineral oil with viscosity of 35 cP is used as the interior and exterior oil phases. Density matching is achieved by mixing mineral oil with about 40 wt % carbon tetrachloride (TECE), which has a high density and comparably low water solubility. For the exterior oil phase, pure mineral oil is used as the stripping phase in the tube, but the container into which the DE drops flow for gelation contains a mixture of mineral oil, carbon tetrachloride and surfactant.

While this process generates remarkably monodisperse DE droplets, there are serious problems with it as a target fabrication system for an IFE power plant. First, the yield of usable targets is low. The only process parameter to control target concentricity is density matching. Because of the difficulty in maintaining the densities within the prescribed range, only one-third to two-thirds of the targets survive the polymerization. Second, DE droplet size is constricted by the device dimensions and cannot be adjusted by flow control. Basically, the diameter of the shell is determined by the diameter of the delivery tube. The wall thickness of the

shell is determined by the ratio of the interior oil phase and RF solution flow rates. For example, one reported droplet generator [6] is limited to making shells with dimensions in the range from 1.6 to 2.3 mm in diameter and from 100 to 200 μm in wall thickness. To produce targets with diameters outside this range, a new droplet generator must be used and new process parameters must be established.

2.3 Droplet based microfluidic scheme for the formation of uniform double emulsion droplets

In this work, we investigate an on-chip DE assembly line to form DE droplets upon demand for laser target fabrication. According to this scheme shown in Figure 1.2, aqueous droplets containing polymer precursors and non-aqueous immiscible droplets are dispensed respectively from different on-chip reservoirs, then transported to a location where they are combined to form DE droplets. The DE droplets thus formed can then be transported to another location on the substrate for centering and other processing.

In this scheme, all droplet manipulations are done by electric-field actuation. Such an approach offers several advantages over the triple-nozzle generator. (i) The current production process by triple-orifice generator requires labor-intensive, batch-based manufacture and selection procedures to obtain acceptable targets. The on-chip assembly line endeavors to miniaturize and automate these processes effectively to achieve droplet-by-droplet controllability so that each DE droplet meets the specifications. Direct computer-based control of each process step helps to

achieve maximum operational flexibility. (ii) As discussed in section 2.2, there are limitations on the sizes of foam shells produced by the triple-orifice generator. On the other hand, the on-chip DE droplets formation scheme is highly scalable. As a droplet-based system, large droplets can be easily obtained by combining several smaller dispensed droplets. Thus droplets of basically any size that is a multiple of the dispensed droplet volume can be formed. Furthermore, the corresponding water-to-oil volume ratio can be changed conveniently. (iii) The on-chip assembly line is capable of manipulating a wide variety of liquids, and can form both oil-in-water and water-in-oil emulsions. In the case of RF targets, polymerization occurs in the aqueous medium and an oil-in-water-in-oil system is needed to create RF aerogel shells. In some other targets, such as methacrylate foam shells, [26,27] a water-in-oil-in-water system will be needed for target fabrication. DE droplets of a wide variety of types and materials can be formed using the same chip architecture with our scheme. This capability may save a lot of manufacturing and set-up effort compared with triple-nozzle systems. (iv) In our scheme, the DE droplets are formed into symmetric shells using electric-field mediated centering. [8-10] This method for DE droplet centering achieves very good control over droplets concentricity. (v) This scheme enjoys the advantages recognized for droplet-based microfluidic systems, including ease of cleaning, ability to control many droplets independently, 100% reagent utilization, and better energy efficiency.

As noted above, the DE droplet assembly line concept provides a possible solution to meet the target fabrication requirements for IFE power plant. Such

research is important for achieving a low-cost, high-output source of laser targets for future fusion-reactor operations. In the rest of the thesis, the feasibility of this scheme will be discussed, including both theoretical developments and experimental studies. We start the discussion with the electromechanical actuation mechanisms for droplet manipulation as to be presented in Chapter 3.

Chapter 3 Electromechanics of electrically-actuated microfluidics

The actuation mechanisms used in the DE droplet assembly line for fabrication of cryogenic foam targets are electrowetting-on-dielectric (EWOD) and dielectrophoresis (DEP). Both EWOD and DEP mimic the capillary force on liquids but provide great flexibility with voltage control. To enlist these forces, we use two types of microfluidic devices. The first is a parallel-plate device consisting of two parallel substrates with the droplet sandwiched between them. A cross section of such a device is shown in Figure 3.1. The bottom substrate consists of a patterned array of individually addressable electrodes, and the top substrate is coated with a transparent indium tin oxide (ITO) layer as a continuous ground electrode. The bottom substrate is coated with a dielectric layer, and both the top and bottom surfaces are covered with a thin hydrophobic film to decrease the surface wettability.

Fig. 3.1 Cross-section of a parallel-plate (closed) device to manipulate oil and water droplets by DEP and EWOD, respectively.

The second device is an open, single-plate structure with coplanar electrodes and the droplet resting on top of the substrate. As shown in the top and side views of Figure 3.2, the substrate consists of two arrays of electrodes – the electrodes on one side are all grounded and the electrodes in the other array are individually addressable. This substrate is also coated with a dielectric layer and a hydrophobic film.

Fig. 3.2 Schematic of co-planar electrode configuration. Ground potential is connected to an array of electrodes parallel to actuation electrodes. Left: top view; Right: side view.

For the application in DE droplet formation, these two configurations are integrated on a single chip. As shown in Figure 1.2, the parallel-plate scheme is referred to as the closed section of the microfluidic device, and the single-plate scheme is referred to as the open section. The two sections are interconnected and this integrated device is capable of transferring droplets between the closed and open sections.

In both the open and closed sections, the droplets generally move toward activated electrodes. The driving mechanisms for conductive and dielectric droplets

are, however, not the same. Actuation of conductive droplets is mainly attributed to electrowetting (EW) [28-47,68-75], while dielectric droplet actuation is achieved by DEP [48-62]. In this chapter, we present the theoretical background of these electrical actuation mechanisms. The actuation force is derived using an electromechanical model.

3.1 Basics of electrowetting (EW) and dielectrophoresis (DEP)

Electrowetting (EW)

As shown in Figure 3.3, when a conductive droplet is placed on top of an electrode that has been covered by a thin dielectric layer, a voltage applied between the electrode and the droplet will result in a reduction in the solid/liquid contact angle. This phenomenon exemplifies the electrowetting effect. More generally, the term ‘electrowetting’ describes the electric forces exerted on conductive liquids at triple contact lines.

Electrowetting was first discovered by Gabriel Lippmann [28] in 1875 when he observed a change in the capillary rise of mercury in the presence of electric charge. He formulated a theory of the electro-capillary effect, and his equation is now called Lippmann’s law: $d\gamma_{SL}^{eff} = -\rho_{SL} dU$ where γ_{SL}^{eff} is the effective solid/liquid interfacial tension, ρ_{SL} is the surface charge density of the counter-ions, and U is the applied voltage potential.

The recent rapid development of EW-based microfluidic applications was initiated by Berge [29,30] in the early 1990s, who introduced a thin layer of

dielectrics between the conductive liquid and the metallic electrode to eliminate the problem of electrolysis. This scheme is the basis of the well-known electrowetting-on-dielectric (EWOD) effect. Berge combined Lippmann's law with Young's law to obtain a new equation relating the change in contact angle to the applied electric voltage. The result is named the Lippmann-Young equation:

$$\cos \theta(V) = \cos \theta(0) + \frac{\epsilon_0 \epsilon_r}{2t\gamma_{LG}} V^2 \quad (3-1)$$

where $\theta(V)$ and $\theta(0)$ indicate the contact angle with and without applied voltage, γ_{LG} indicate the liquid-gas interfacial tension, ϵ_0 denotes the permittivity of vacuum, ϵ_r the dielectric constant of the dielectric material, and t the thickness of the dielectric layer.

Fig. 3.3 Principle of electrowetting-on-dielectric (EWOD). (a) The droplet is initially at rest on a hydrophobic insulated electrode. (b) Application of voltage reduces the contact angle.

EW-based microfluidic devices to manipulate droplets were first demonstrated in 2000 [19]. The basic design of an EWOD actuator consisting of two parallel plates is found in Figure 3.1. Droplets sandwiched between parallel plates can be manipulated by selectively applying voltage to an array of electrodes (here on the bottom). In EWOD, the water itself serves as a moving, deformable electrode. To achieve the

capabilities needed for Lab-on-a-Chip (LoC) systems, a wide variety of fundamental fluid operations have been realized on EWOD devices, including droplet transport [19,31], dispensing [32-34], separation [32,34], coalescence [32], dilution [35], and others.

Dielectrophoresis (DEP)

Dielectrophoresis (DEP) is the force exerted on dielectrics when subjected to a non-uniform electric field [48-50]. As another extensively studied mechanism for droplet manipulation, DEP has the capability for moving insulating, polarizable media. For example, decane cannot be moved by EWOD [43], but can be moved by DEP [44].

The investigation of liquid DEP has a long history. More than one hundred years ago, Pellat demonstrated the rise against gravity of a dielectric liquid by applying a DC voltage between a pair of electrode plates dipped into a dish full of the dielectric liquid [48]. Early applications considered for DEP were in spacecraft, such as the management of liquid propellant in low gravity conditions [51].

More recently, similar to dielectric liquids, aqueous liquids were driven vertically by AC voltage between parallel electrode plates coated with dielectric layers [53,54]. The dielectric layer was used to prevent electrolysis, and high AC frequency was used to achieve liquid DEP. This experiment demonstrates that DEP and EWOD are related by frequency. Furthermore, aqueous liquid columns and nanoliter-sized droplets have been formed on open surfaces by DEP actuation using dielectric-coated co-planar

electrode designs [55-58].

In the field of LoC applications, a large variety of particles, including nucleic acids, proteins, cells, and nano-particles [50,59-62], have been successfully manipulated by DEP forces. For most DEP-based LoC devices, particles and liquid droplets [62] are suspended in fluid media, and the DEP force acts as a central force exerted on the whole particle. Recently, Fan [44] has reported the manipulation of dielectric droplets in a parallel-plate structure by DEP, including droplet transport, splitting, and recombination.

Strictly speaking, microfluidic devices based on DEP actuation of dielectric liquids do not require the use of a dielectric layer on the electrodes. Nevertheless, the dielectric layer is convenient to achieve a general microfluidic platform capable of performing both EWOD and DEP actuations. The dielectric layer slightly increases the required voltage for DEP actuation, but has no further influence.

3.2 Electromechanical model of EW and DEP

3.2.1 Derivation of the electromechanical model

When a droplet is placed in an electric field, there are two relevant effects involved in the electric actuation: changing the droplet's contact angle and inducing translational motion. Both effects can be understood by considering the forces exerted on the droplet by the electric field. There are two approaches to calculating the electromechanical forces acting on droplets- the Maxwell stress tensor method [53,63,64] and the method of lumped parameter electromechanics. [52,65] Of the two,

the lumped parameter electromechanics has an advantage of simplicity because it can avoid the difficulty of analyzing the geometry and details of liquid profiles.

Capacitive lumped parameter electromechanics represents electromechanical systems by discrete circuit components. The capacitive and resistive components are series and parallel connected and the nodes between them represent interfaces. A lumped parameter electromechanical model is valid under the electroquasistatic limit, where the electrical wavelength is much greater than the characteristic physical dimensions. [65] To calculate the electromechanical forces exerted on a droplet, the first step is to obtain an expression identifying the system capacitance.

Fig. 3.4 (a) Equivalent circuit model for the parallel-plate microfluidic device. (b) A simplified circuit for the model. The Teflon-AF layer on the top plate and the Teflon-AF / SOG layers on the bottom plate are grouped and represented by a capacitor.

Electromechanical force for the parallel-plate scheme

Figure 3.4 shows a parallel-plate microfluidic device and its equivalent circuit. In diagram (a), the left side represents the droplet filled region, and the right side is the medium region. Most of the experiments in this research are done in air medium,

which is modeled as pure capacitance. The droplet, which is slightly conductive, is modeled as a resistor and capacitor in parallel. The hydrophobic layer (Teflon-AF) on the top plate, and the hydrophobic (Teflon-AF) / dielectric (SOG) layers on the bottom plate are assumed to be perfect dielectrics represented by pure capacitors. For simplicity, the Teflon-AF layer on the top plate and the Teflon-AF / SOG layers on the bottom plate are grouped together as capacitor C_{cl} in the following calculation.

For the simplified circuit shown in Figure 3.4 (b), the capacitances and conductance of each element are:

$$C_L = \frac{\varepsilon_0 k_L x w}{D} \quad (3-2a)$$

$$g_L = \frac{\sigma_L x w}{D} \quad (3-2b)$$

$$C_M = \frac{\varepsilon_0 k_{air} x w}{D} \quad (3-2c)$$

$$C_{cl} = \frac{1}{\frac{1}{C_t} + \frac{1}{C_t} + \frac{1}{C_d}} \quad (3-2d)$$

$$C'_{cl} = \frac{1}{\frac{1}{C'_t} + \frac{1}{C'_t} + \frac{1}{C'_d}} \quad (3-2e)$$

$$\text{where } C_t = \frac{\varepsilon_0 k_t x w}{d'}, \quad C_d = \frac{\varepsilon_0 k_d x w}{d}, \quad C'_t = \frac{\varepsilon_0 k_t (L-x) w}{d'}, \quad C'_d = \frac{\varepsilon_0 k_d (L-x) w}{d}.$$

The device parameters and liquid properties used in the calculation are detailed in Table 3.1, and x is the length of liquid filled portion of the activated electrode. We evaluate the voltages across each circuit element using standard AC circuit methods. Let Z_1, Z_2 be the impedances of the liquid and the combined dielectric/hydrophobic layers for the liquid filled side, and Z_3, Z_4 be the impedance of air and the combined layers for the medium side.

$$Z_1 = \frac{1}{g_L + j\omega C_L}, \quad Z_2 = \frac{1}{j\omega C_{cl}}, \quad Z_3 = \frac{1}{j\omega C_M}, \quad Z_4 = \frac{1}{j\omega C'_{cl}} \quad (3-3)$$

From the voltage divider relation, the corresponding voltages defined in Figure 3.4 are:

$$V_1 = \frac{Z_1}{Z_1 + Z_2} V, \quad V_2 = \frac{Z_2}{Z_1 + Z_2} V, \quad V_3 = \frac{Z_3}{Z_3 + Z_4} V, \quad V_4 = \frac{Z_4}{Z_3 + Z_4} V \quad (3-4)$$

Table 3.1 List of symbols and constants used in the electromechanical force calculation.

Symbol	Meaning	Value
ϵ_0	Permittivity of free space	8.85×10^{-12} F/m
k_L	Dielectric constant of liquid	78 for water
k_t	Dielectric constant of Teflon-AF	1.93
k_d	Dielectric constant of SOG	4.5
σ_L	Conductivity of liquid	10^{-4} S/m for water
k_{oil}	Dielectric constant of oil	2.2 for mineral oil
f	Frequency of applied voltage	
ω	Angular frequency	$2\pi f$
x	Length of the liquid filled region	
w	Electrode width	1 mm
L	Electrode length	1 mm
D	Gap between top and bottom plates	90 μ m
d	Thickness of the SOG layer	0.5 μ m
d'	Thickness of the Teflon layer	1 μ m
g	Lateral spacing between two coplanar electrodes	40 μ m
w'	Electrode width for single plate scheme	280 μ m
L'	Electrode length for single plate scheme	280 μ m

The force calculation is done using the coenergy method based on the *principle of virtual work*, which states that the total work done by an external force acting on a body initially in equilibrium plus electrical energy input is equal to the internal energy

stored in the body at the new state. The force of electrical origin is equal to the derivative of stored energy with respect to the displacement.

In lumped parameter modeling of DEP and EWOD-based microfluidic systems, the assumption is made that the droplet moves without changing its shape. This assumption is a good one on the size scale of $\leq 10^2$ microns because surface tension dominates in controlling the liquid interfacial profile.

There are four capacitive energy terms recognized for the reduced circuit shown in Figure 3.4(b). The total energy U of the system is $U = \sum_{i=1}^4 \frac{1}{2} C_i V_i^2$. Thus, the total electromechanical force F acting on the liquid is $F = \frac{\partial U}{\partial x}$. Combining with equation (3-2) (3-3) and (3-4), we obtain:

$$|V_1| = \left| \frac{i\omega\epsilon_0 k_{eff} D}{i\omega\epsilon_0 (k_L (2d' + d) + k_{eff} D) + \sigma_L (2d' + d)} \right| V \quad (3-5a)$$

$$|V_2| = \left| \frac{i\omega\epsilon_0 k_L + \sigma_L}{i\omega\epsilon_0 (k_L + \frac{k_{eff} D}{2d' + d}) + \sigma_L} \right| V \quad (3-5b)$$

$$F = \frac{1}{2} \epsilon_0 w \left\{ \frac{k_L}{D} |V_1|^2 + \frac{k_{eff}}{(2d' + d)} |V_2|^2 - \frac{k_{eff} k_{air}}{k_{eff} D + k_{air} (2d' + d)} V^2 \right\} \quad (3-5c)$$

where k_{eff} is a convenient effective dielectric constant for the combined

dielectric/hydrophobic layers, $k_{eff} = \frac{k_t k_d (2d' + d)}{k_t d + 2k_d d'}$, and k_{air} is the dielectric constant

for air medium, $k_{air} = 1$.

Electromechanical force for the single plate scheme

In the single-plate scheme, the electric field between coplanar electrodes is more complex than for the parallel-plate scheme, where the electric field is mostly uniform.

To estimate the electromechanical force acting on the droplet in the single plate scheme, we use three approximations. (i) Given that the electrode width w' and the lateral spacing between two coplanar electrodes g are both much larger than the dielectric thickness d , the electric-field in the dielectric layer is approximately uniform; (ii) The electric-field lines in air between two coplanar electrodes are approximately semicircular [66]. One of these electric-field lines traces from the outer edge of one electrode to the outer edge of the other with a radius of $(2w'+g)/2$. Refer to Figure 3.5; (iii) With no applied voltage, the equilibrium contact angle of water on Teflon-AF is 115° . Under EWOD actuation, the contact angle reduces gradually with voltage to a saturation value of $\sim 70^\circ$. [34] Under DEP actuation, the electric field penetrates the liquid and shapes the surface profile, making it parallel to the semicircular electric-field lines. For both cases, one may expect a contact angle close to 90° made by the water droplet against substrate. Based on these points, it is reasonable to assume that the cross-section of liquid is uniform and semicircular.

With these three assumptions, we can model the single plate device by equivalent circuit shown in Figure 3.5. Once again the liquid is modeled as a resistor and capacitor in parallel, the hydrophobic (Teflon-AF) / dielectric (SOG) layers on the bottom substrate are combined and represented by a single capacitor, and the air is modeled as another capacitor. The expressions for the capacitances and conductance of each circuit element are:

$$C_{water} = \epsilon_0 k_L x A \quad (3-6a)$$

$$g_{water} = \sigma_L x A \quad (3-6b)$$

$$C_{air} = \varepsilon_0(L-x)A \quad (3-6c)$$

$$C_1 = \frac{1}{\frac{d'}{\varepsilon_0 k_t x w'} + \frac{d}{\varepsilon_0 k_d x w'}} \quad (3-6d)$$

$$C_2 = \frac{1}{\frac{d'}{\varepsilon_0 k_t (L-x) w'} + \frac{d}{\varepsilon_0 k_d (L-x) w'}} \quad (3-6e)$$

where x = the length of liquid filled portion of the activated electrode, the geometric factor $A = K(1-k^2)/2K(k^2)$, and K is the complete elliptic integral of the first kind with modulus $k = g/(2w'+g)$ [67].

Fig. 3.5 Semicircular electric-field distribution on the coplanar electrode structure and the corresponding circuit model. (a) The liquid filled region. (b) The air filled region.

With these conductances and capacitances, it is easy to find the impedances for the liquid, air, and the combined dielectric layers.

$$Z_{water} = \frac{1}{g_{water} + j\omega C_{water}}, \quad Z_1 = \frac{1}{j\omega C_1}, \quad Z_{air} = \frac{1}{j\omega C_{air}}, \quad Z_2 = \frac{1}{j\omega C_2} \quad (3-7)$$

The approximate voltage drops across the liquid, the air, and the dielectric layers are, respectively,

$$V_{water} = \frac{Z_{water}}{Z_{water} + 2Z_1} V, \quad V_1 = \frac{Z_1}{Z_{water} + 2Z_1} V, \quad V_{air} = \frac{Z_{air}}{Z_{air} + 2Z_2} V, \quad V_2 = \frac{Z_2}{Z_{air} + 2Z_2} V \quad (3-8)$$

There are six stored energy elements for the system, so the total energy inside the area of interest is $U = \sum_{i=1}^6 \frac{1}{2} C_i V_i^2$. The total electromechanical force F acting on the liquid is $F = \frac{\partial U}{\partial x}$.

Combing with equation (3-6) (3-7) and (3-8), we obtain:

$$|V_{water}| = \left| \frac{i\omega\epsilon_0 \frac{k'_{eff} w'}{(d' + d)}}{i\omega\epsilon_0 \left(\frac{k'_{eff} w'}{d + d'} + 2k_L A \right) + 2\sigma_L A} \right| V \quad (3-9a)$$

$$|V_1| = \left| \frac{i\omega\epsilon_0 k_L A + \sigma_L A}{i\omega\epsilon_0 \left(\frac{k'_{eff} w'}{d + d'} + 2k_L A \right) + 2\sigma_L A} \right| V \quad (3-9b)$$

$$F = \frac{1}{2} \epsilon_0 \{ k_L A |V_{water}|^2 + \frac{2k'_{eff} w'}{(d' + d)} |V_1|^2 - \frac{A k'_{eff} w'}{k'_{eff} w' + 2A(d' + d)} V^2 \} \quad (3-9c)$$

where k'_{eff} is the effective dielectric constant for the combined dielectric/hydrophobic

layers on the bottom substrate, $k'_{eff} = \frac{k_t k_d (d' + d)}{k_t d + k_d d'}$.

3.2.2 Discussion of the electromechanical model

Frequency-dependent nature

The electromechanical forces acting on a water droplet in both the parallel-plate

and single-plate schemes are calculated and plotted versus voltage frequency in Figure 3.6. Both forces show a clear frequency transition from the EWOD regime (low frequency) to the DEP regime (high frequency). This transition can be accounted for by defining a critical frequency f_c [52] above which a liquid transitions from conductive to dielectric behavior. Analysis of the liquid side circuit reveals a critical frequency

$$f_c = \frac{\mathcal{G}_{water}}{2\pi(C_{water} + C_{total})} \quad (3-10)$$

where C_{total} is the total capacitance of all dielectric/hydrophobic layers. $C_{total} = C_{cl}$ for

Fig. 3.6 The electromechanical forces acting on a 90 nL water droplet in both parallel-plate scheme and single-plate scheme. The parallel-plate scheme has a spacing of 90 μm between substrates and the electrode is 1 mm by 1 mm square. The single-plate scheme has square electrodes of 0.28 mm by 0.28 mm. All the applied AC voltages are set to be 100 Vrms.

the parallel-plate scheme, and $C_{\text{total}} = C_1/2$ for the single-plate scheme. Using the liquid properties and device geometries in Table 3.1, we calculate the critical frequencies for both parallel-plate scheme and single-plate scheme. The values are shown by the vertical lines in Figure 3.6.

When $f \ll f_c$, the liquid behaves as a pure conductor. All the voltage drops across the dielectric layers and under actuation, the liquid acts like a moving electrode. This is the so called EWOD regime. Substituting $V_1 = 0$, and $V_2 = V$ into equation (3-5c), and because $D \gg (2d' + d)$, the electromechanical force is simplified to

$$F \approx \frac{1}{2} \epsilon_0 w \frac{k_{\text{eff}}}{(2d' + d)} V^2 \quad (3-11)$$

This form of the EWOD force can also be derived from the contact angle models. [18,42]

When $f \gg f_c$, the liquid is purely insulating. Now, most of the voltage drop occurs across the liquid and the dielectrophoretic mechanism causes the droplet movement. This is the liquid DEP regime. Neglecting the resistor in the circuit of Figure 3.4(b), the voltages across the liquid and the dielectric/hydrophobic layers in equation (3-5) are simply

$$V_1 = \frac{k_{\text{eff}} D}{k_{\text{eff}} D + k_L (2d' + d)} V, \quad V_2 = \frac{k_L (2d' + d)}{k_{\text{eff}} D + k_L (2d' + d)} V \quad (3-12)$$

Using these results in the electromechanical force equation (3-5c), we obtain

$$F_{\text{DEP}} = \frac{\epsilon_0 k_{\text{eff}} w}{2} V^2 \left(\frac{k_L}{k_L (2d' + d) + k_{\text{eff}} D} - \frac{k_{\text{air}}}{k_{\text{air}} (2d' + d) + k_{\text{eff}} D} \right) \quad (3-13)$$

This equation expresses the DEP force acting on a liquid (either water or oil) in a parallel-plate geometry. Though obtained in air medium, this equation is also usable

for a liquid medium by replacing k_{air} with the dielectric constant of the medium.

Voltage distribution analysis

According to the previous discussion, the voltage drop across the liquid (V_1) and the dielectric layers (V_2) at EWOD regime are

$$V_1 = 0, \text{ and } V_2 = V \quad (3-14)$$

Comparing equations (3-12) and (3-14), it is clear that V_1 and V_2 are both frequency dependent. Using equation (3-5a) and (3-5b), the voltages V_1 and V_2 are plotted in Figure 3.7. At low frequencies, i.e., $f \ll f_c$, all the voltage drops across the dielectric layers. With the increase of frequency, more and more voltage drops across the liquid. Both V_1 and V_2 eventually approach the value shown in equation (3-12) at DEP frequencies.

Fig. 3.7 The frequency dependency of voltage drops across the liquid and the dielectric layers. The voltages are calculated based on equations (3-5a) (3-5b) and device parameters listed in Table 3.1.

The frequency dependency of voltages indicates that the performance of the dielectric layer may deteriorate at low frequencies due to electrical breakdown.

Influence of liquid properties

Equation (3-5) reveals the influence of the conductivity (σ_L) and the dielectric constant (k_L) of liquid upon the electromechanical force. When the liquid conductivity increases with k_L fixed, the electromechanical force curve shifts towards high frequencies, but the low and high frequency limits of EWOD and DEP remain unchanged. See Figure 3.8. This dependence can be understood from the force expressions (3-11) and (3-13) for the low and high frequency limits, which are independent of the conductivity. On the other hand, the critical frequency,

$$f_c = \frac{g_{water}}{2\pi(C_{water} + C_{total})} = \frac{\sigma_L}{2\pi\epsilon_0(k_L + k_{eff}) \frac{D}{2d' + d}}, \text{ is directly proportional to the liquid}$$

conductivity. Thus the main influence of liquid conductivity is its effect on f_c , the transition frequency between EWOD and DEP.

When the liquid dielectric constant increases, the electromechanical force is increased in DEP regime, while the EWOD force remains unchanged as shown in Figure 3.9. This is because the liquid behaves like a dielectric at DEP frequency, so the DEP force is strongly influenced by k_L . On the other hand, in EWOD regime, the liquid is a conductor, and its dielectric property has no effect on the EWOD force.

Fig. 3.8 The influence of liquid conductivity on frequency-dependent behavior of force. The electromechanical force is calculated based on equations (3-5c) for $k_L = 78$. The device parameters used in calculation are listed in Table 3.1.

Fig. 3.9 The influence of liquid dielectric constant on frequency-dependent behavior of force. The electromechanical force is calculated based on equations (3-5c) for $\sigma_L = 1 \cdot 10^{-4}$ S/m. The device parameters used in calculation are listed in Table 3.1.

3.3 Advantages of the electromechanical model

In EW theory, the phenomenon has been treated using either a thermodynamic approach or an energy minimization approach, as detailed in Mugele's review paper [18]. In both approaches, the Lippmann-Young equation (3-1), i.e., the dependency of the contact angle according to the applied voltage, is derived, and then the EWOD force is calculated based on the contact angle.

In the electromechanical model, the EWOD force is determined with no reference to the actual shape of the liquid meniscus, as can be noticed from the previous derivations. Using equation (3-11), and balancing the electric force and capillary force in the horizontal direction at the triple line, one can recover the Lippmann-Young equation. [42]

Compared with the contact angle model, the electromechanical model has several advantages in predicting the electrostatic force effects upon liquids. First, the electromechanical model easily accommodates the frequency dependency of the electrostatic force. Using the proper mechanical variable for each capacitive and resistive element, the electromechanical model predicts both the liquid's conductive behavior at low frequencies and its dielectric behavior at high frequencies, and the transition between low and high frequency limits. The contact angle model cannot achieve such a general predictive result.

The second advantage is that the derivation used in the electromechanical model requires no information about contact angle or liquid profile because the electromechanical force does not depend on the shape of the liquid meniscus. This

result solves the problem in contact angle model that the contact angle cannot be reduced below a value of zero. As pointed out by Jones [45], the reduction of the contact angle is merely a characteristic of the response of conductive liquids to electromechanical forces. Furthermore, the maximum force acting on a droplet is not necessarily limited by contact angle saturation based on the above discussion.

The third advantage is that the electromechanical model does not pinpoint the location of the force. Using contact angle models, it is tempting to attribute the electric force to the contact line. In the derivation of the electromechanical force, the force is sensitive only to changes of the system capacitance, so it is not necessary to localize the electrical body force.

Lastly, the electromechanical model regards all interfacial tensions as constants, while some other models suggest a voltage dependent solid-liquid interfacial tension. This controversy finds expression in the existence of a ‘local’ contact angle that is not affected by the electric-field. As the ‘local’ contact angle has been distinguished from an ‘apparent’ contact angle which follows the EW equation [68,69], the electromechanical approach proves to be a more generally applicable model in predicting the translational mechanics of liquid moves.

Chapter 4 Experimental study for on-chip droplet dispensing

This chapter provides a description of EWOD and/or DEP-based liquid actuation and droplet dispensing experiments. Droplet dispensing refers to the process of extracting a droplet from a large volume of liquid in a reservoir. Droplet generation is a critical first operation in many lab-on-a-chip devices. In the application of foam target fabrication, droplet dispensing is of paramount importance because the accuracy of all subsequent liquid handling operations is largely determined by the initial liquid volume control.

In droplet-based microfluidics, two schemes of on-chip liquid dispensing are reported: 1) direct droplet dispensing from on-chip reservoirs [12,31,32,36] and 2) droplet dispensing with capacitance feedback [33,70]. The feedback control brings about an improved uniformity of the dispensed droplet volume, and is useful for applications requiring precise liquid handling, such as drug discovery or quantitative analysis. According to our previous discussion based on Figure 2.2, target fabrication requires droplet volume variations no greater than 5%. Such a droplet volume precision can be achieved by simple control over electrical signal switching [70,71], so we focus on direct dispensing in this work.

4.1 Introduction

Aqueous droplet dispensing has been demonstrated in parallel-plate structures

filled with oil [31] or in air [32]. In typical EWOD droplet dispensing, a liquid column is drawn from a large reservoir droplet. Liquid pinch-off occurs by activating the electrode at the front end of the liquid finger and the reservoir electrode, while deactivating the “cutting” electrodes in between until the liquid front is separated from the liquid bulk. This sequence of droplet dispensing is shown in Figure 4.1.

Fig. 4.1 Top view of an on-chip dispenser showing the sequence of droplet dispensing. (a) The reservoir and an already-formed droplet; (b), (c) and (d) the liquid finger is formed, and meanwhile the first droplet is delivered away; (e) the pinch-off occurs; (f) a new droplet is formed.

With this approach, the dispensed droplet volume reproducibility is usually no better than 5% because the droplet volume is affected not only by operating parameters but also factors such as surface roughness, hydrophobic coating uniformity, dielectric layer aging, and environmental humidity. To improve reproducibility, Ren et al. [33] developed a system consisting of droplet dispensing from a syringe pump and capacitance based droplet volume metering. With this feedback control scheme, the

pumped liquid volume is monitored by on-chip capacitance measurement. Recently, Gong [70] has developed an all-electric feedback control system for droplet generation on multilayer printed circuit board (PCB) EWOD device. Also using capacitance feedback control, this scheme achieved a reproducibility better than $\pm 1\%$. However, there are many fabrication complexities for these systems.

Although EWOD-based water droplet dispensing has been widely studied, dielectric droplet (oil) dispensing has not received much attention. In this Chapter we repeat EWOD-based dispensing of water droplets before demonstrating DEP-based dispensing of oil droplets, and we present results on the dispensing reproducibility as a function of certain operational parameters.

4.2 Chip fabrication and experimental setup

Refer to Figure 3.1 for the basic features of microfluidic droplet manipulation systems. The lower actuation electrode structures are fabricated on 3-inch square glass substrates. The substrate is evaporatively coated with 100 nm aluminum. Next, the aluminum layer is photolithographically patterned into a two dimensional electrode array, and then spin-coated with (i) 0.5 μm of polysiloxane-based spin-on-glass (SOG) (Futurrex IC1-200) as the dielectric layer and (ii) 1 μm of amorphous fluoropolymer (DuPont Teflon-AF) as a hydrophobic coating. The spin coating process and subsequent baking treatment parameters are detailed in Table 4.1. The top substrate is an ITO coated glass plate purchased from SPI Supplies and Structure Probe, Inc. The ITO layer is 15-30 nm thick and the entire plate is used as a ground electrode. A 1 μm

Teflon-AF layer is applied on top of the ITO layer to provide hydrophobic coating.

In operation, the bottom substrate is placed on a horizontal fixture and Pogo pins are used for voltage connection to the pads patterned on the substrate. The top substrate is positioned above the bottom substrate by appropriate spacers. A block diagram of the experimental setup is shown in Figure 4.2. Experiments are performed using AC voltages supplied by a power amplifier (Krohn-Hite 7602 or Fluke 5205A) driven by a function generator (Leader LG1301). By adjusting the output of the function generator, the Krohn-Hite amplifier can provide 0 to 180 Vrms AC voltages over a range of frequencies from 10 Hz to 100 kHz, while the Fluke amplifier is used for voltages from 100 to 500 Vrms at DEP frequencies in the range of 80 ~ 100 kHz. Activation of electrodes is controlled by a LabVIEW-based control system. The relay control circuit is diagrammed in Figure 4.2(b). Because the LabVIEW signal generator (NI USB 6009) cannot provide enough current to actuate the relays (IMO 4021), an external 5V DC voltage source (B&K 1651) is used to input more current to drive the relays.

Table 4.1 Spin coating and baking parameters for SOG and Teflon-AF.

Material	Spin rate (rpm)	Spin time (sec)	Bake temperature (°C)	Bake time (min)
SOG	2500	40	200	3
Teflon-AF	3000	30	80	5

A custom-made observation system equipped with imaging lenses (Edmund

EVA8X) and a CCD camera (JAI CV-S3200) is used to record droplet actuation and dispensing experiments at 30 fps. Selected video frames are processed with a Matlab routine to determine droplet volumes.

(a)

(b)

Fig. 4.2 (a) Block diagram of the experimental setup for droplet actuation and dispensing. AC voltage is applied to electrodes through relays controlled by a LabVIEW program. The video is captured by a CCD camera and processed by PC for quantitative analysis. (b) The control circuit for driving voltage actuation relays.

4.3 Results and discussion

Before starting an experiment, the liquids are introduced and voltages are applied to the reservoir electrode to hold the oil and DI water in their own reservoir areas. Next, by sequentially applying sufficient voltage on the reservoir electrode and the driving electrodes, liquid is drawn from its reservoir, and a droplet is generated on the receiving electrode next to the cutting electrode. Refer to the Figure 4.3 for the typical electrode structure for droplet dispensing.

Fig. 4.3 Typical dispensing electrode structure. L : length of the cutting electrode; a : length of a standard electrode.

Because of the differences in the actuation mechanism, oil droplet manipulation by DEP requires much higher voltages than EWOD dispensing of water droplets. For EWOD-based water actuation, low-frequency AC voltage, typically <100 V, is employed. For oil DEP actuation, AC voltage between 50 Hz and 100 000 Hz is used, but usually >250 V.

4.3.1 Water droplet dispensability

One way to understand the physics of the EWOD based droplet dispensing process is in terms of liquid pressure differences. Ren [71] proposed that the condition for successful dispensing involves achieving the required internal pressure difference between the liquid in the reservoir and the necking point of the liquid finger. As shown in Figure 4.4, the pressure in the liquid is related to the principal radii of curvature of drop by the Laplace equation:

$$\begin{aligned} P_1 - P_a &= \gamma \left(\frac{1}{r_1} + \frac{1}{R_1} \right) \\ P_2 - P_a &= \gamma \left(\frac{1}{r_2} + \frac{1}{R_2} \right) \end{aligned} \quad (4-1)$$

where $r_1 = \frac{-D}{\cos \theta_0 + \cos \theta_v}$, and $r_2 = \frac{-D}{\cos \theta_0 + \cos \theta_0}$. The pinch-off condition $P_2 > P_1$

can be rewritten as: $\frac{\cos \theta_v - \cos \theta_0}{D} \geq \frac{1}{R_1} - \frac{1}{R_2}$ (4-2)

Fig. 4.4 Breaking the liquid neck to form a droplet in a parallel plate structure.

where $1/R_2$ is negative at the boundary of pinch-off. By substituting the Lippmann-Young equation into (4-2), the condition for droplet formation becomes:

$$\frac{\frac{\epsilon_0 \epsilon_r}{2t\gamma_{LG}} V^2}{D} \geq \frac{1}{R_1} - \frac{1}{R_2} \quad (4-3)$$

From equation (4-3), it is clear that there exists a maximum gap height D above which dispensing is not possible [32,34,42]. Furthermore, if D is too large, then the voltage requirement is unrealizable and EWOD actuation is impossible [34]. Equation (4-3) also reveals a minimum voltage threshold for dispensing, which is determined by liquid properties and device geometry. The most important requirement for liquid property is to have large contact angle change due to EWOD. Note that liquid surface tension does not control the dispense capability [42].

In general, equation (4-3) shows that smaller gap height, a larger electrode size, and a longer cutting electrode all favor dispensing. In geometrically-similar devices, electrode size (a) determines the dispensed droplet size, and is proportional to the reservoir size, and thus approximately proportional to R_1 . Ren showed that larger pitch size required smaller actuation voltage to induce liquid protrusion, and then concluded that a large aspect ratio (a/D) is favorable for pinch-off [71].

Previous studies by Ren [12,71] and Berthier [42] were concerned with small droplets ($a < 1\text{mm}$). This size is too small for IFE laser target, so here we have studied the minimum pinch-off voltage for large electrodes, ranging from 1 mm to 6 mm. Figure 4.5 shows the experimental results. For 1 mm electrode, when the gap varies from 85 μm to 155 μm , the minimum actuation voltage varies from 58 V to 97 V, consistent with equation (4-3). For electrodes ranging from 2 mm to 6 mm, the actuation voltage does not change much with varying the gap. This result indicates

that there exists a maximum aspect ratio beyond which actuation voltage could not be lowered. See Figure 4.5.

Fig. 4.5 Minimum required pinch-off voltage for different electrode sizes. All tests were done with DI water, and each test structure was maintained equimultiple with $L=2a$, and reservoir width= $4a$. The voltage applied was 100Hz AC voltage.

Generally, a longer cutting electrode improves the dispensing function because the length L is related to R_2 . Ren [71] has proposed $|R_2| = ((L/a)^2 + 1) * a/4$, but this relation may be invalid for large L . It has been found experimentally that $|R_2|$ may be smaller than L when $L/a \geq 3$ as shown in Figure 4.6, which indicates the existence of a maximum $|R_2|$ for certain liquid and electrode structure, irrespective of the cutting electrode as long as it is sufficiently long.

Fig. 4.6 The moment of pinch-off of DI water dispensing on 2mm electrode. Length of cutting electrode is $L=3a$. The gap between top and bottom substrates was $85\mu\text{m}$, and the voltage applied was 100Hz 90Vrms AC voltage.

4.3.2 Oil droplet dispensability

Unlike EWOD based aqueous droplet dispensing, dielectric droplet (oil) dispensing has not been widely studied or reported. Here we demonstrate repeatable dielectric droplet dispensing on the same microfluidic chip as EWOD.

The condition for EWOD dispensing was described previously in equation (4-2). By substituting the electrowetting force (per unit length) $F_E = \gamma_{LG}(\cos \theta_v - \cos \theta_0)$ into this equation, the dispensing condition is described:

$$\frac{F_E}{\gamma_{LG}D} \geq \frac{1}{R_1} - \frac{1}{R_2} \quad (4-4)$$

Thus for a given device geometry, the competition between the electric actuation force (per unit length) and liquid surface tension determines the dispensing condition. In the case of DEP dispensing, one might make the hypothesis that the competition between dielectrophoretic force (per unit length) and oil surface tension guarantees good dispensing for oil droplets. Whether this condition is true or not is still under

investigation. The dielectrophoretic force (per unit length) can be calculated from the previously derived equation (3-13):

$$F_{DEP} = \frac{\epsilon_0 k_{eff} w}{2} V^2 \left(\frac{k_L}{k_L (2d' + d) + k_{eff} D} - \frac{k_{air}}{k_{air} (2d' + d) + k_{eff} D} \right) \quad (3-13)$$

We have performed dispensing experiments with different oils, the minimum voltage for oil dispensing is listed in Table 4.2.

Table 4.2 Properties, threshold driving voltages and minimum dispensing voltages of oil droplets actuated by DEP in a 85 μm high gap between parallel plates.

Oil	Dielectric constant, ϵ	Viscosity, ν (cP)	Surface tension, γ (mN/m)	Measured threshold voltage to initiate motion, (V)	Measured minimum voltage for pinch off, (V)
Decane	2	0.92	23.6	265	410
Mineral oil	2.2	~35	28.1	340	670
Silicone oil 1.5 cSt	2.36	1.4	17.7	140	260
Silicone oil 10 cSt	2.64	9.34	20.1	170	320
Silicone oil 50 cSt	2.71	48	20.7	235	340
Sunflower oil	3.05	~37	31	225	360
Corn oil	3.12	35	34.6	250	440
Tetrachloroethylene (TECE)	2.5	0.89	31.7	275	370

To evaluate the transport of different dielectric droplets, we first measure the minimum driving voltage required to observe droplet motion. The droplet velocity at the threshold voltage can be as low as 5 $\mu\text{m/s}$, so it may take more than 3 minutes to drive a droplet from one electrode to another. From equation (3-13), the DEP force for a given w (1 mm) and D (85 μm) is only dependant on the dielectric constant ϵ of the oil droplet. It might seem that a dielectric droplet with higher dielectric constant would require a lower threshold voltage and vice versa; however, the measured

threshold voltages presented in Table 4.2 do not correlate with ϵ .

In droplet-base microfluidic schemes, researchers have correlated the threshold voltage to contact angle hysteresis (CAH) forces [72-74], which is related to surface tension, contact angle, and CAH. So these three factors all play a role in determining threshold voltages.

Table 4.2 also shows that an oil droplet requiring higher threshold voltage usually requires high voltage for dispensing, too. But it is not easy to find a quantitative expression between the minimum dispensing voltage and oil properties.

4.3.3 Droplet dispensing reproducibility

Laser target fabrication imposes strict requirements on droplet dispensing reproducibility because the uniformity of subsequently formed DE droplets is largely determined by controlling the initial water and oil droplet volume. This section reports droplet dispensing precision and reproducibility results. The reproducibility of on-chip dispensing depends on the following operational parameters: liquid surface tension, viscosity, dispensing frequency, length of the cutting electrode, applied voltage, mother droplet size, and the effect of having connecting lines beside the actuation electrode on single conductive layer device.

It has been observed that the final extracted drop volume is usually somewhat larger than the volume subtended by a square electrode ($a \times a \times D$) [34,71]. The reason is that a liquid tail formed after separation forces an extra amount of liquid into the already formed droplet. It is this effect that creates variability in the dispensed droplet

volume.

Ren [71] studied dispensing reproducibility as a function of the surface tension of the liquid in the reservoir, finding that lowering the interfacial tension between the liquid and medium fluid (oil) degrades reproducibility. This is because a more rapid pinch-off occurs for low surface tension solutions, thereby reducing the influence of electrode shape on the radius of curvature in the pinch-off region. Ren also found that volume control depends on the length of the cutting electrode. Berthier [42] further concluded that the reproducibility is satisfactory when the length of the cutting electrode is less than the size of the receiving electrode in the electrode array. Another factor is that the dispensed volume increases as the reservoir volume decreases [42,70,71] because the initial liquid shape influences the shape of the pinch-off. This result amplifies the importance of tail volume for droplet volume variations.

In this research we investigated the effects of applied voltage, and cutting electrode on droplet volume control for an on-chip dispensing system, because they both impact the tail volume directly. The effect of connecting traces is discussed under the condition of high applied voltage.

Effect of applied voltage on droplet volume variations.

We investigated the dependence of dispensed water drop volume upon the actuation voltage in a structure with 1 mm square electrodes. The droplet volume becomes sensitive when the applied voltage is close to the minimum required value for pinch-off. For example, when applied voltage decreased from 62.5 V to the minimum pinch-off voltage of 55.0 V, the droplet volume dropped by almost 30%, as

shown in Figure 4.7. The same result is observed with both square and circular dispensing electrodes. This voltage dependence traces back directly to the shape of the tail during pinch off. As shown in Figure 4.8, a smaller tail is observed at lower voltage, and the pinch-off position also moves closer towards the individual droplet. The shape of the tail changes because the necking of the liquid finger depends on the electrowetting force, which in turn is directly related to applied voltage. [12]

Fig. 4.7 The normalized (normalize to the droplet volume at 62.5 V) volume variation of a series of droplets generated by different applied voltages. All tests were done with DI water. The gap between top and bottom substrates was 85 μm , and the voltage applied was 100 Hz AC.

In general the liquid tail plays a more important role in determining droplet volume variation, but Figure 4.8 (c) and (g) shows that with square electrodes, a smaller area of the receiving electrode is filled by liquid during pinch-off at lower

Fig. 4.8 The effect of applied voltage on droplet volume variation. (a), (b) Square and circular dispensing electrodes used for the dispensing experiments. The square electrode is $1\text{mm} \times 1\text{mm}$ and the diameter of the circular electrode is 1mm. The length of the cutting electrode is 2mm. (c), (e) Pinch-off and the formed droplet on the square electrode by applying 62.5 V_{rms}, 100 Hz AC voltage. (g), (i) Pinch-off and the formed droplet on the square electrode by applying 55 V_{rms}, 100 Hz AC voltage. (d), (f) Pinch-off and the formed droplet on the circular electrode by applying 62.5 V_{rms}, 100 Hz AC voltage. (h), (j) Pinch-off and the formed droplet on the circular electrode by applying 52.5 V_{rms}, 100 Hz AC voltage. In all cases, the gap between top and bottom substrates is 85 μm.

voltage than at higher voltage. This smaller portion of droplet on receiving electrode may also contribute to reduced dispensed droplet volume. No obvious change in the portion of droplet on receiving electrode is observed for circular electrode structures, as shown in Figure 4.8 (d) and (h), but the droplet volume remains very sensitive to voltage change.

Effect of cutting electrode on droplet volume and reproducibility.

We tested electrode structures using cutting electrodes of varied length (L) to investigate the effect of this parameter on droplet volume and reproducibility. As shown in Figure 4.9, the dispensed droplet volume increases directly with L . Droplets with average volume of 103 nL and 183 nL were dispensed on a 1mm×1mm square electrode using cutting electrodes of lengths $L = 2\text{mm}$ and 3mm , respectively. These droplet volumes are greater than the volume subtended by one electrode- (85 nL). The increase in droplet volume is due to the larger tail formed upon longer cutting electrodes during pinch-off. Similar behavior is also observed on 2mm×2mm square electrodes.

Fig. 4.9 Average droplet volume versus cutting electrode length. All tests were performed with DI water. The gap between top and bottom substrates was 85 μm , and the voltage applied was 90 Vrms 100 Hz AC voltage.

Droplet volume reproducibility suffers as L is increased. As indicated in Figure 4.9 and Table 4.3, the coefficient of variation ($\text{CV} = \text{standard deviation} / \text{mean} * 100\%$) increases significantly when the ratio of the cutting electrode length to standard electrode length (L/a) approaches $L/a = 3$. This behavior is due to the reduced influence of the cutting electrode on the radius of curvature in the pinch-off region. In fact, the pinch-off position becomes indeterminate for sufficiently large L/a . Large droplet volume variation ($\text{CV} = 40\%$) is observed when $L/a=3$ on 2 mm $\times$ 2 mm electrode due to the indeterminacy of the pinch-off position. See Figure 4.10.

Table 4.3 Effect of cutting electrode length on volume reproducibility for droplets dispensed on 1mm and 2mm dispensing electrodes and a 85 μm channel gap. In all cases, the voltage applied was 90 Vrms 100 Hz AC.

Electrode size	$L/a=1$	$L/a=2$	$L/a=3$
1mm $\times$ 1mm		4.7%	12.7%
2mm $\times$ 2mm	3.0%	5.3%	40%

Fig. 4.10 Instability of the pinch-off position for droplet dispensing on 2 mm standard electrode and a 6mm cutting electrode. The gap between the top and bottom substrates was 85 μm , and the voltage applied was 90 Vrms 100 Hz AC.

The best reproducibility (CV = 3.0%) is achieved for a cutting electrode of the same length as that of the standard electrodes. According to our previous sensitivity analysis based on Figure 2.2, this reproducibility is adequate for laser target fabrication.

Effect of connecting traces on droplet volume variations.

Dispensing structures fabricated photolithographically with single conductive layer on the substrate require connecting traces between the actuation electrodes and the contact pads. Even narrow traces can affect the droplet volume at higher actuation voltages. During the dispensing operation, a portion of the liquid may move onto connecting traces, and this liquid influences reproducibility by merging the dispensed drop volume. Figure 4.11 shows very large droplet volume variation that can result

from this effect. Fan [76] has found that there exists a minimum voltage for liquid to pass a narrow region such as a connecting trace. This voltage is linearly proportional to the square root of device aspect ratio: $V_{\min} \propto (D/w)^{1/2}$. Thus a narrower connecting trace, and a larger gap height help to reduce the connecting trace effect.

Fig. 4.11 Effect of connecting traces on dispensing reproducibility. The dispensed silicone oil droplets were obtained at actuation voltages of 400 V, 350 V, and 330 V. All tests were performed on 1mm×1mm dispensing electrode and a 85 μm channel, and the voltage applied was 100 Hz AC.

A better solution would be patterning the connecting traces in a different dimension. Gong and Kim [77] has reported the building of such a scheme based on a printed circuit board (PCB). As shown in Figure 4.12, the connecting traces are fabricated underneath the electrodes in multiple layers so that they do not interfere with dispensing. A drawback with their scheme is that the PCB-based device requires high voltages to overcome the high movement resistance due to surface topography and roughness. For our coplanar electrode design, one must be very careful in selecting actuation voltage to avoid large volume variation due to connecting trace effect.

Fig. 4.12 EWOD device fabricated on four-layer PCB. (a) Optical top view of the PCB substrate. (b) Optical cross-sectional view of the PCB substrate. (c) Cross-sectional schematic of the PCB-EWOD plate with top cover plate on and a droplet in position. (d) Part of the 8×8 array PCB-EWOD device, showing big electrodes as liquid reservoirs and 5×4 driving electrodes. [77]

4.4 Conclusion

In this chapter, we have demonstrated dispensing experiments of both aqueous and non-aqueous liquid droplets from reservoirs on a microfluidic chip. The droplet formation process is analyzed to establish the static conditions under which droplets can be successfully pinched-off. In the dispensing process, droplet volume reproducibility has been tested over a range of operational parameters, including applied voltage, the length of the cutting electrode and the effect of connecting traces. We find that drop volume variability is mainly caused by variability in the tail volume during pinch-off. When the length of the cutting electrode is increased, volume reproducibility is degraded, because longer cutting electrodes reduce the influence of the electrode shape on the radius of curvature in the pinch-off region. These results provide important guidance for optimizing device design and selecting operation parameters.

Chapter 5 Manipulation of oil droplets through negative DEP

This chapter introduces a new method for low-voltage manipulation of dielectric (oil) droplets using “negative” DEP actuation. The electromechanical model predicts that the oil droplet actuation force using negative DEP can be compatible with EWOD-based water droplet manipulation, thus opening the way to fully automated formation of single-emulsion droplets on a parallel-plate microfluidic platform. The following sections describe the microfluidic operations of transporting, splitting, merging, and dispensing of oil droplets at voltages less than ~ 100 V.

5.1 Introduction

By integrating droplet based EWOD and DEP microfluidics, it becomes possible to manipulate both conductive and dielectric droplets on the same chip.[44,78] However, DEP actuation of dielectric droplets usually requires voltage much higher than EWOD. DC or low-frequency AC voltage in the range of 11-100 V [78-82] is usually adequate for EWOD actuation, but the voltage required for DEP actuation is higher than 200 ACV [53] or 260 DCV [44] in the same parallel-plate devices. This high voltage requirement for liquid DEP severely restricts its broader applications. Many people have made efforts to reduce the actuation voltage. Wu [73] employed an electret in a parallel-plate device as the virtual voltage source to transport dielectric droplets, thus reducing the control voltage to as low as 5 DCV. However, electret

surface charge decays with time and the electret charge stability need to be improved.

For application in target fabrication, the high voltage requirement for liquid DEP makes it very difficult to integrate DEP with EWOD because different voltage sources are needed to achieve concurrent actuation of water and oil droplets. In this chapter, we present a scheme that exploits “negative” DEP actuation for dielectric droplets. Using this new scheme, we reduce the DEP driving voltage for oil droplets to the EWOD level.

5.2 Principle and modeling

As shown in section 3.2.1, the parallel-plate microfluidic configuration can be modeled as an equivalent RC circuit and the electromechanical force then evaluated using the coenergy function: $f^e = \left. \frac{\partial W_e'}{\partial x} \right|_V = \frac{1}{2} V^2 \frac{\partial C(x)}{\partial x}$. Previously, it has been assumed that the ambient is an insulator, usually air or oil. But it is possible to change the medium to a conductive liquid. There are in fact four distinguishable configurations for a droplet-in-medium system: water droplet in air medium, water droplet in oil medium, oil droplet in air medium, and oil droplet in water medium. For the first three the medium is purely insulating, but for the last one, the external medium is a conductive liquid. To evaluate the electromechanical force for all geometries, we need the more general model shown in Figure 5.1, where the medium is represented as a resistor and capacitor in parallel.

Several studies have reported that for a droplet-in-medium configuration, a thin film of the medium liquid is usually trapped between the droplet and substrates.

[68,83-87] Because this layer is much thinner than the spacing between two substrates [68], it is neglected in the circuit model.

Fig. 5.1 Equivalent circuit model for the parallel-plate microfluidic device. The medium is represented as a resistor and capacitor in parallel.

Using the same method discussed in Section 3.2, we evaluate the electromechanical forces acting on all the four geometries as shown in Figure 5.2. For ease for comparison, the applied voltage is set to be 100 V_{rms}, and the spacing between two substrates is 170 μm . Force is plotted versus voltage for frequencies ranging from 10 Hz to 1 MHz.

For water the electric field distribution across the liquid layer depends on the frequency of applied voltage. This is because of the conductive nature of water. A transition into dielectric behavior is clearly revealed in Figure 5.2 for the water-in-air, water-in-oil, and oil-in-water geometries. On the other hand, because oil and air are highly insulating, the force acting on oil droplet in an air medium is independent of frequency.

Fig. 5.2 Frequency dependency of the electromechanical force for four liquid combinations in the parallel-plate geometry. f_{W-in-A}^e : water droplet in air, f_{W-in-O}^e : water droplet in oil medium, $|f_{O-in-W}^e|$: oil droplet in water medium (absolute value), and f_{O-in-A}^e : oil droplet in air. The oil liquid used in the calculation is mineral oil. The device parameters and liquid properties are provided in Table 3.1.

In the air medium, the force acting on an oil droplet is much smaller than that on a water droplet under the same applied voltage. This result shows why actuation of oil droplets usually requires higher voltages. The difference in the voltage requirement is plotted in Figure 5.3, where the square law relationship between actuation force and applied voltage is shown for both water and oil droplet in air medium. According to our experiments, the minimum voltage required to initiate water droplet actuation is 35 Vrms, corresponding to an actuation force of 1.6 μ N. To achieve a similar force for mineral oil actuation requires hundreds of volts. The minimum driving voltage for mineral oil-in-air obtained from experiments is as high as 340 Vrms.

Fig. 5.3 The electromechanical force acting on a water droplet and an oil droplet in the parallel-plate device when the medium is just air. The oil liquid used in the calculation is mineral oil. The applied voltage frequency is set to be 100 kHz.

While the actuation force for an oil droplet in air is not strong, an oil droplet in water experiences a large electric force, the same in fact as a water droplet in oil. Note, however, that this force acts to the opposite direction: from high field to low field. The absolute values of the actuation forces for oil-in-water and water-in-oil geometries overlap each other. For the oil-in-water geometry, the electromechanical force is an example of “negative” DEP. The liquid droplet has a dielectric constant smaller than that of the surrounding medium and is repelled from stronger field regions to weaker fields. We can thus exploit low voltage oil actuation by ‘pushing’ the droplet away from the activated electrodes, so that continuous movement can be achieved by sequential activation of the addressable electrodes.

5.3 Results and discussion

To manipulate an oil droplet in a water medium, aqueous solution is introduced into the gap between the top and bottom substrates of the parallel-plate device. The surfactant Silwet L-77 (0.0625 wt%) is used in the water phase to lower its surface tension and thus stabilize the mineral oil droplet in the water. In the electrode design shown in Figure 5.4, side electrodes are used to contain the dielectric droplets on the track.

Fig. 5.4 Layout of the transport electrodes for moving oil droplets in water medium. When energized, the electrodes on the sides keep the dielectric droplet centered on the track.

5.3.1 Oil droplet transport

Figure 5.5 shows a sequence of video frames demonstrating operation of the oil droplet transport scheme in water. The oil droplet initially sits on electrode 1 as shown in Fig. 5.5 (a). All the electrodes are initially turned off. When electrode 1 and the side electrodes are activated, the oil drop is pushed to the left. See Figure 5.5 (b). After the droplet reaches electrode 2, this electrode is now activated forcing the oil

droplet to continue moving left to the next electrode. In this way, continuous movement is easily achieved.

Fig. 5.5 Sequence of video images of mineral oil droplet transport viewed from above through the top plate. Transport electrodes are 1 mm square, the spacing between the top and bottom plates is 170 μm , and the applied voltage is 50 Vrms at 100k Hz AC.

5.3.2 Oil droplet splitting and merging

Droplet splitting is achieved by activating the electrode on which the droplet resides while deactivating its two neighbors. In Figure 5.6 (a), a large oil droplet is initially situated on electrode 2 as shown. By activating electrode 2, the oil drop starts to split, moving towards electrode 1 and 3. See Figure 5.6 (b). Eventually the oil drop splits in two. Merging is achieved simply by reversing the splitting operation. When electrodes 1 and 3 are activated, the two small oil drops are pushed back together onto

electrode 2. When the two drops come into contact, they spontaneously merge into a single drop.

Fig. 5.6 Sequence of video images of splitting and merging a mineral oil droplet. Addressable electrodes are 1 mm square, the spacing between the top and bottom plates is 170 μm and the applied voltage is 70 Vrms at 100k Hz AC.

5.3.3 Oil droplet dispensing

Figure 5.7 provides a demonstration of oil droplet dispensing from a large reservoir. To contain the oil, both the reservoir electrode and transport electrode array are surrounded by side electrodes. The oil initially covers the large reservoir electrode. When this electrode is activated, with the side electrodes also turned on, oil is drawn outward onto the transport array to form a liquid column. See Figure 5.7 (b). Liquid pinch-off is achieved in Figure 5.7 (c) by activating the electrode next to the reservoir and deactivating the reservoir electrode. The portion of the liquid to the left forms a droplet which can then be transported away. The process may be repeated to dispense

a stream of droplets.

Fig. 5.7 Sequence of video images showing the dispensing of an oil droplet of ~ 230 nanoliter. The spacing between the top and bottom plates is $170\ \mu\text{m}$, and the applied voltage is $70\ \text{V}_{\text{rms}}$ $100\ \text{kHz}$ AC. Note the thin film of oil in (c) that for a short time connects the dispensed droplet to the much larger reservoir volume.

5.3.4 Discussion

In the experiments described, we successfully manipulated oil droplets in immiscible fluid media by applying voltages at DEP frequencies, demonstrating the principle of using negative DEP as an effective driving force for oil droplet actuation. As predicted in the electromechanical model, a “negative” EWOD force should be able to drive oil droplets, too. However, our experiments to manipulate dielectric droplets under low frequency voltages are not very repeatable. A full understanding of the reason for the failure is still lacking. We tested chips with atomic-layer-deposited

alumina instead of SOG as dielectrics, but obtained the same results. The alumina layer is a pinhole free material, so there must be some other explanations for failure instead of pinholes. Another possible explanation would be some interactions between the Teflon layer and the surfactant solution at low frequency. Further investigation into this issue is needed for clarification.

In the dispensing process, a very thin “tether” of oil connecting the dispensed droplet to the reservoir persists for a time. See Figure 5.7 (c). Eventually this tether ruptures. No such tether forms in the dispensing of mineral oil in air. Though the mechanism for tether formation remains unclear, it is apparent that aqueous Silwet solution enhances its stability. Similar tether structures are found when aqueous Silwet solutions are dispensed in air, and so does some dielectric liquid. More discussion of this phenomenon is provided in Chapter 6.

5.4 Conclusion

In this chapter, we use the electromechanical model to calculate the electric actuation forces on droplets surrounded by different mediums in parallel-plate devices. The model explains why oil droplet actuation usually requires high voltages, and also predicts possible low voltage oil actuation in water medium using ‘negative’ actuation scheme. Various oil manipulations in this scheme are demonstrated experimentally, including oil droplet transporting, splitting, merging, and dispensing.

Although all the operations have been demonstrated separately, they can be monolithically integrated on a single chip to provide a versatile platform to

manipulate many different types of oils, thus enabling a low-voltage oil droplet microfluidic actuation.

Chapter 6 On-chip double emulsion droplet formation

This chapter presents a Gibbs free energy model to study the conditions for spontaneous emulsification to form DEs and then experimental results demonstrating both water-in-oil-in-air (W/O/A) and oil-in-water-in-air (O/W/A) DE droplet formation. For O/W/A DE formation, surfactants must be added to lower the surface tension of the water phase. We find that a tether is formed during the dispensing of surfactant added water, preventing the formation of individual droplets through direct dispensing. We first solve the tether problem by mechanical disruption method using a second liquid finger, however, the tether severely degrades dispensing reproducibility. We further develop alternative dispensing methods to avoid tether formation.

6.1 Gibbs free energy model

In a double emulsion (DE), the inner dispersed droplet is separated from the continuous phase by another phase (usually liquid). In this work, we form “droplet within a droplet” systems in air. While these are not real DEs, they later can be dispersed in an immiscible continuous phase to form DEs as required for target fabrication operations.

When two immiscible droplets are brought together, a DE droplet forms spontaneously if the Gibbs free energy of the surface is reduced by the emulsification process. The Gibbs energy change (ΔG) is a convenient criterion for testing the

likelihood of DE formation. A negative ΔG means DE formation is favored. In the following, we develop a simple model to calculate the Gibbs surface energy changes associated with DE formation.

In this work, the combination of two immiscible droplets takes place either in a parallel-plate (closed) structure or in a single-plate (open) structure. Due to the difficulty in evaluating the surface profile of DE droplets in open structures, we calculate the DE total surface energies in air and in parallel-plate structures.

6.1.1 Stable surface energy of DE droplets in air

The naturally stable state of a droplet in a continuous medium is a sphere. This shape minimizes the surface area and thus the Gibbs energy. In the DE formation process shown in Figure 6.1, the Gibbs interfacial energy change between initial and final states is

$$\Delta G = G_{DE} - (G_A + G_B) \quad (4-1)$$

where G_{DE} = total Gibbs interfacial energy of a DE droplet

G_A, G_B = Gibbs surface energies of the individual A and B droplets before emulsification.

The Gibbs surface energy is a sum of the products of interfacial tensions and corresponding surface areas. Assume liquid A is to be ingested into B,

$$\Delta G = (\gamma_{AB}S_A + \gamma_B S_B') - (\gamma_A S_A + \gamma_B S_B) \quad (4-2)$$

where γ_{AB} , γ_A , and γ_B are interfacial tensions for the A-B, A-air, and B-air interfaces, respectively. S_A is the surface area of droplet A, S_B and S_B' are liquid B-air surface

areas before and after DE formation. Note that after DE formation, the interface between liquid A and air is supplemented by the interface between two liquids, and the outer area of liquid B increases.

Fig. 6.1 Formation of double emulsion droplet in air.

Table 6.1 Interfacial tension data at room temperature. (mN/m)

Interface	Interfacial tension
Water / air	74
Silicone oil (20 cst) / air	20.6 ^a
Mineral oil / air	28.1
Silicone oil (20 cst) / water	35 ^b
Mineral oil / water	49 ^c
Water / Teflon	49 ^d
Silicone oil (20 cst) / Teflon	5.6 ^d
Mineral oil / Teflon	10.25 ^d
Teflon / air	18
W _{S-t} / air	24.7 ^e
Mineral oil / W _{S-t}	4.5 ^b
W _{S-t} / Teflon	2.46 ^d

W_{S-t}: Silwet-treated water (0.0625 wt%)

a. Dow Corning 200 [®] Fluid data sheet..

b. Interfacial tension was determined using an Easy Dyne Tensiometer.

c. Reference 91.

d. Interfacial tension was calculated from Young's equation.

e. Reference 90.

Using the interfacial tension data from Table 6.1, we can calculate ΔG for water-in-silicone oil (20 cst) and water-in-mineral oil DEs. Refer to Figure 6.2 where ΔG is expressed per unit total liquid volume versus the ratio of the water phase volume to the total volume of the DE. ΔG is negative for water-in-Silicone oil (20cst) DE formation for values of the water phase volume ratio ranging from 1% to 99%. This result means the DE formation is always favored and the two liquids always form DE droplet spontaneously. On the other hand, the water and mineral oil droplet system exhibits negative ΔG for the water phase volume ratio between 1% and 94%, but goes positive ΔG above 94%. Thus there is a limit for water-in-mineral oil DE formation: very large water droplet cannot form a stable DE droplet with mineral oil.

Fig. 6.2 Surface Gibbs energy change for water-in-silicone oil (20 cst) and water-in-mineral oil DE formation in air.

Because silicone oil has an interfacial tension lower than mineral oil, a greater Gibbs surface energy change is observed for water-silicone oil system than for the water-mineral oil system, indicating an even more favorable condition for the formation of water-in-silicone oil DEs. We also find that maximum ΔG change occurs at different volume ratios for different water-oil systems: maximum ΔG occurred at 87% water phase volume for water-silicone oil system, but at 41% for water-mineral oil system.

As noted above, a water droplet and an oil droplet usually form a water-in-oil DE, but we can alter this tendency by adding surfactant into the water. The surfactant reduces the effective surface tension of water so that it becomes possible to form oil-in-water DEs. We use a nonionic surfactant Silwet L-77 in our study. As listed in Table 6.1, the interfacial tensions for Silwet-treated water at the surfactant concentration of 0.0625 wt% is still greater than silicone oil, but lower than mineral oil. Therefore, instead of silicone oil, we chose mineral oil for the oil-in-water scheme. The calculated result shown in Figure 6.3 confirms the possibility of forming oil-in-water DE droplet when proper surfactant is introduced into the water-oil system. ΔG is negative for mineral oil volume ratio varying from 1% to 98%, and the maximum $|\Delta G|$ is at 47% mineral oil volume ratio.

Fig. 6.3 Surface Gibbs energy change for mineral oil-in-Silwet-treated water DE formation in air.

6.1.2 Stable surface energy of DE droplets in parallel-plate structure

When a droplet is sandwiched between parallel plates, its surface shape is strongly affected by the contact angle against the substrate and the spacing between top and bottom substrates. For the ideal geometric model shown in Figure 6.4, the droplet volume is

$$V = 2 \int_0^h \pi x^2 dz = 2\pi[(x_0^2 + R^2)h - \frac{1}{3}h^3 + 2x_0R^2(\frac{1}{2}\theta_0 + \frac{1}{4}\sin 2\theta_0)] \quad (4-3)$$

where $\theta_0 = (\theta - \pi/2)$,

θ = contact angle on a hydrophobic surface ($\theta > 90^\circ$),

$R = (-h/\cos\theta)$,

and the spacing between substrates is $2h$.

Fig. 6.4 Side view of the droplet geometry when sandwiched between parallel plates. The flattened droplet has a circular profile with a radius of (X_0+R) from above.

The lateral surface area and base areas are then

$$S_L = 2 \int_0^{\theta_0} 2\pi(x_0 + R \cos \theta') R d\theta' = 4\pi R(x_0 \theta_0 + R \sin \theta_0) \quad (4-4)$$

$$S_B = 2\pi(x_0 + R \cos \theta_0)^2 \quad (4-5)$$

When $\theta < 90^\circ$, the droplet volume and droplet surfaces are

$$V = 2\pi[(x_0^2 + R^2)h - \frac{1}{3}h^3 - 2x_0R^2(\frac{1}{2}\theta_0 + \frac{1}{4}\sin 2\theta_0)] \quad (4-6)$$

$$S_L = 2 \int_0^{\theta_0} 2\pi(x_0 - R \cos \theta') R d\theta' = 4\pi R(x_0 \theta_0 - R \sin \theta_0) \quad (4-7)$$

$$S_B = 2\pi(x_0 - R \cos \theta_0)^2 \quad (4-8)$$

where $\theta_0 = (\pi/2 - \theta)$, and $R = (h/\cos \theta)$.

Several studies [83-87] have reported that, for a water-in-oil DE droplet in the parallel-plate structure, oil forms a thin film underneath the inner water droplet as illustrated in Figure 6.5(b). We analyzed the Gibbs surface energy change for the cases of the water droplet directly in contact with the Teflon surface and also contained by a thin layer of oil. Figure 6.5 (c) shows ΔG calculations using equations (4-3) to (4-8) and the interfacial tension data from Table 6.1 for water-in-silicone oil (20 cst) DE. ΔG per unit total liquid volume is plotted as a function of the ratio of the

volume of water to the total volume of water and oil in the DE. For both configurations $\Delta G < 0$, but the case of the oil entrapped underneath the water is energetically favored.

Fig. 6.5 Water-in- silicone oil (20cst) DE droplet in the parallel-plate structure: (a) The inner water droplet rests on the Teflon surface; (b) The inner water droplet rests on a thin layer of oil; (c) ΔG of DE formation for both the cases of (a) and (b).

Mineral oil is used as the inner oil droplet for oil-in-water DE formation in the parallel-plate structure. Figure 6.6 plots ΔG for mineral oil-in-Silwet-treated water as

a function of the volume ratio of mineral oil. Again, the requirement for DE formation, $\Delta G < 0$, is met. There are also two possible configurations for the oil-in-water DE droplet as shown in Figure 6.6 (a) and (b). We calculated ΔG for both cases. Figure 6.6 (c) shows that the energy is lower when the inner oil droplet is separated from

Fig. 6.6 Mineral oil-in-Silwet treated water DE formation in parallel plates. (a) The inner oil droplet rests on the Teflon surface; (b) The inner oil droplet rests on a thin layer of water; (c) ΔG of DE formation for both the cases of (a) and (b).

Teflon surface by a layer of water. Experimentally we have observed some evidence for the existence of the water film as shown in the mineral oil-in-water DE formation process in Figure 6.7. When the water droplet was first in contact with the Silwet-added oil droplet ($t = 0$ s), there was no water film underneath the oil drop. After 11 seconds, the oil drop was surrounded by water droplet to form oil-in-water DE and some water started to go between the oil drop and the substrate. See Figure 6.7 (d). The water film became larger and larger with time as shown in Figure 6.7 (e) and (f). Unlike the oil film in water-in-oil scheme, the formation of this surfactant-treated water film is a very slow process.

Fig. 6.7 Water film observed during an oil-in-water DE droplet formation process. (a) Right: a pure water droplet; left: a 0.5% (v/v) Silwet-added mineral oil. (b) The water droplet is delivered to the oil droplet. (c) The water droplet is in contact with the oil droplet, this moment is set to be $t = 0$ s. (d) 11 seconds later, the oil-in-water DE is formed and the water film start to appear under the oil drop. (e),(f) The water film becomes larger and larger with time.

6.2 Experiments for water-in-oil DE formation

We tested the electric-field actuated formation of water-in-silicone oil DE as

shown in Figure 6.8. Two silicone oil droplets were first dispensed from the left reservoir using DEP by applying 330 Vrms 100 Hz AC voltage to the lower array of electrodes. Then, two DI water droplets were dispensed from the right reservoir via EWOD actuation using 85 Vrms 100 Hz AC voltage on the upper array of electrodes. The water droplets were then transported towards the oil droplets as shown in Figure 6.8 (c) and (d). When the water droplets touched the oil droplets, they were immediately engulfed by the oil droplets to form DE droplets. After formation, it was possible to transport these DE droplets using low-voltage EWOD. The transport mechanism is the same reported by R. Garrell [92]. The EWOD force on the water droplet drags the surrounding oil with it.

Fig. 6.8 The formation of water-in-silicone oil double emulsion droplets. (a) Two silicone oil droplets are dispensed through DEP actuation by applying 330 Vrms 100 Hz AC voltage; (b) two DI water droplets are dispensed by EWOD actuation by applying 85 Vrms 100 Hz AC voltage; (c), (d) and (e) the water droplets are delivered and combined with oil droplets to form DE droplets; (f) the water droplets pull the whole merged water-in-oil DE droplets by EWOD actuation.

6.3 Experiments for oil-in-water DE formation

Experimental demonstration of oil-in-water DE droplet formation is more challenging. We use a commercially available trisiloxane surfactant, Silwet L-77, in this research to help form oil-in-water DEs. Silwet surfactant has effective wetting capabilities when used in aqueous solutions. Surface tensions as low as 20~21 mN/m can be attained using Silwet [88,89]. Also, as a nonionic surfactant, Silwet is not likely to interfere with electric actuation.

6.3.1 Dispensing low surface tension water

We first investigated the wetting property of water-based Silwet solutions on Teflon surfaces. Five solutions of varying Silwet concentration were prepared ranging from 0.00625 wt% to 0.125 wt%. Figure 6.9 shows the measured equilibrium contact angle values. It is clear that the addition of Silwet to water greatly reduces the contact angle values. It is clear that the addition of Silwet to water greatly reduces the contact angle of pure DI water on Teflon. The equilibrium contact angle of a pure DI water drop on Teflon is 115°, while the lowest contact angle achievable with Silwet is 51°. Although the critical micelle concentration (CMC) is unknown for Silwet as it is a commercial mixture of trisiloxane molecules with additives, the data in Figure 6.9 indicate that CMC is between 0.0125 and 0.025 wt%.

Fig. 6.9 Equilibrium contact angles of water-based Silwet solutions on Teflon surface.

Of the five different Silwet solutions, only 0.00625 wt% Silwet solution could be dispensed smoothly. All the others formed a remarkably persistent “tether” during the pinch off process. As shown in Figure 6.10 (a), the thin liquid tether formed between the reservoir and the droplet prevents separation. A full understanding of the tether formation is still lacking, but low contact angle ($< 90^\circ$) is one necessary condition. When surfactant-treated water is placed in the oil medium where a high contact angle could be maintained, similar experiments show that surfactant-treated water can be successfully dispensed without tether formation. [42,71]

Fig. 6.10 Breaking the tether with a second water liquid finger. (a) The second liquid (DI water) in a reservoir. (b) The second liquid finger approaches the tether. (c) The tether breaks inside the second liquid finger. (d) The entire tether disintegrates into many satellite droplets.

One way to break the tether is to use a second liquid finger to disturb it, as shown in Figure 6.10. The secondary liquid used was pure DI water. When the pure water finger touches the tether, apparently the Silwet solution in the contact area is locally diluted and the tether breaks because of the increased surface tension as revealed in Figure 6.10 (d). The entire tether disintegrates into many satellite droplets due to hydrodynamic instability.

This method does not work when the Silwet concentration exceeds 0.125 wt%, in which case the second water finger joins with the tether instead of breaking it up. Figure 6.11 shows this phenomenon. Apparently the local dilution is not sufficient to

increase the surface tension when the Silwet concentration is far above CMC. Another problem with the tether formed during dispensing is that the electrode shape loses some of its influence in defining the pinch-off curvature, resulting in poor volume reproducibility.

Fig. 6.11 Tether breaking experiments with 0.15 wt% Silwet solution. (a) The second liquid finger (DI water) approaches the tether. (b) The second liquid finger touches the tether. (c) The second liquid finger joins with the tether after contact.

6.3.2 Other possible solutions to the tether problem

A second method to avoid tether formation is by taking advantage of the pH effect on spreading of Silwet solutions. Radulovic [90] found that the wetting ability of Silwet solutions is drastically reduced with the addition of acetic acid, possibly due to the polarization of the trisiloxane head. Based on this property, we have demonstrated that the addition of acid to Silwet-treated water can avoid the tether formation. Then, the dispensed droplet is neutralized by mixing with another base droplet. In this way, the required low surface tension is recovered. The droplet, now containing some salts, can be used for oil-in-water DEs. The problem with this method is that the reverse process using a base solution takes a long time, typically

more than an hour. This waiting time would be a major disadvantage for mass production of DE droplets. Also, evaporation of water during such a long period would have to be prevented.

A third approach would be to add the surfactant to the oil to avoid tether formation. We have found that Silwet has little influence on the wetting property of oils, and Silwet-doped oil can be dispensed smoothly. As shown in Figure 6.12, when a pure water droplet and a Silwet-doped oil droplet are placed together, an oil-in-water DE droplet can be formed, apparently because the Silwet tends to diffuse into the water phase. Unfortunately, DE droplet formation is slow because the Silwet diffuses gradually across the interface from the oil phase into the water phase. Using 0.125% (v/v) Silwet-added mineral oil and DI water droplets, the process takes several minutes. When a 0.5% (v/v) Silwet-modified mineral oil drop is used, the diffusion time is reduced to about 10 seconds.

Fig. 6.12 Formation of an oil-in-water DE droplet. (a) Left: a pure water droplet; right: a 0.125% (v/v) Silwet-added mineral oil. (b) The water droplet is delivered to the oil droplet. (c) 5 minutes later, the oil-in-water DE is formed.

6.3.3 More about the tether issue.

Shown in Figures 5.7 and 6.10, a thin liquid tether is formed during the dispensing process of Silwet-treated water in air medium and of mineral oil in water medium. We performed additional dispensing experiments with other oils and their mixtures and found that for several oils the tether exists. The test results are listed in Table 6.2. The common property of the liquids with which a tether forms is not apparent. Mineral oil and sunflower oil have similar surface tensions and contact

Table 6.2 Tether formation for oil mixtures when dispensed in air.

Oil type	Tether existence
Mineral oil	No
TECE	Yes
Mineral oil + TECE ^a	Yes
Mineral oil + TECE + Silwet ^b	Yes
Mineral oil + Silwet ^c	No
Silicone oil	No
Silicone oil + TECE ^a	No
Sunflower oil	Yes
Sunflower oil + TECE ^a	No
Corn oil	Yes

TECE = carbon tetrachloride

a: the mixture is prepared at 1:1 v/v.

b: Mineral oil and TECE is first mixed at 1:1 v/v, then 0.0625 wt% Silwet is added.

c: 0.0625 wt% Silwet is added in mineral oil.

angles on Teflon surface, but only sunflower oil forms a tether during dispensing. TECE added to mineral oil forms a tether, but eliminates it when added to sunflower oil. The surfactant Silwet produces a persistent tether when added in water, but has no such effect in mineral oil.

We compare the dispensing processes with and without tether in Figure 6.13. As can be seen, there is always a thin film of liquid formed at the moment of pinch-off. Also see Figure 4.8 and 4.11. Usually this thin film breaks quickly because it is not a hydrodynamically stable structure. But in some cases this thin film persists and becomes a long stable tether. To form a tether structure, the liquid surface tension must be relatively low so it becomes a less dominant force and there might be some interactions between liquid molecules and the solid surface to help maintain the tether structure. To better understand the mechanism, further research is needed to demonstrate the underlying interactions.

Fig. 6.13 A thin liquid film forms at the pinch-off step of dispensing. (a) Mineral oil. The liquid film is short and breaks quickly. (b) Mixture of mineral oil and TECE. The liquid film is persistent and forms the tether structure.

6.4 Conclusion

In this chapter, we presented theoretical predictions and experimental results for on-chip DE formation in parallel-plate structure. We use the Gibbs free energy change to test the ability to form stable DE droplets. The calculations show that water-in-oil DE droplets formed through spontaneous emulsification, and oil-in-water DE droplets also can be formed by the addition of surfactant and the proper selection of oil. Experimental results reveal the formation of water-in-oil DE droplets. Using simultaneous DEP and EWOD actuation on a microfluidic chip, oil and water droplets are dispensed, and merged, and the transport of the merged water-in-oil DE droplet is also demonstrated.

The formation of mineral oil-in-Silwet treated water DE droplets is demonstrated. We find that a tether is formed during the dispensing of Silwet-treated water. Although the tether can be broken by the disturbance of a second liquid finger, it interferes with the dispensing operation and degrades dispensing reproducibility. Other methods to avoid the tether include taking advantage of the pH effect on Silwet solutions, and adding the surfactant to the oil phase. Using the pH effect, the recovery of wetting ability (the contact angle reversal) is very slow. Alternatively, adding the surfactant to the oil phase is a much faster method to form oil-in-water DE droplets.

Chapter 7 Water droplet movement between closed and open systems

To form DE droplets water and oil droplets dispensed in closed sections of the microfluidic system are delivered to an open section of the device before they are combined. Though many studies have demonstrated droplet manipulation on a single-plate (open) structure [37-41], detailed study of droplet movement between closed and open sections is lacking. This chapter presents theoretical models and experimental results for transferring a water droplet from a closed into an open section. We use a force analysis method to determine the condition required for a droplet to cross the open/closed edge and we successfully demonstrate droplet movement using EWOD actuation. A bevelled edge on the upper substrate makes it possible to minimize the contact area between water drop and the upper ITO plate, thus easily detaching the droplet.

7.1 Introduction

In contrast with the more conventional parallel-plate (closed) microfluidic devices in which ground potential is supplied via a top electrode, single-plate (open) devices actuate droplets on a substrate that contains both the actuation and ground electrodes. While the open scheme lacks the capacity of splitting or dispensing droplets [42], it has the advantages of faster mixing [38], the ability to move larger droplets on a given electrode, and easier access to droplets for further handling or

optical detection [41].

Many different designs of ground wires/ electrodes of open scheme devices have been investigated [37-41,93]. The configuration of the ground wires influences the electric field distribution upon the droplet and in turn the actuation forces. Abdelgawad et. al. [94] compared the actuation forces for six different open structure designs and found significant force variations among them. In our work, we use structures with a line of ground electrodes parallel to the actuation electrodes. See Figure 3.2. This structure is easy to fabricate and then integrate with parallel-plate (closed) structures and it provides relatively large actuation forces.

Because a water droplet has a large contact angle (115°) on Teflon, there occurs a large change in shape as a droplet moves from the closed to the open structure, that is, from a flattened to a sessile form. A large change in Gibbs surface energies can be expected. A calculation of the Gibbs energies of a water droplet in closed and open sections is shown in Figure 7.2. The calculation for closed section is the same as the previous model described in section 6.1. When it is in the open section, the droplet is approximated as a spherical cap as shown in Figure 7.1. The height of the droplet is related to the sphere radius R and the contact radius a by

$$h = R(1 - \cos \theta) = a \tan\left(\frac{\theta}{2}\right) \quad (7-1)$$

The volume and surface area of the spherical cap are respectively

$$V = \frac{\pi}{6} h(3a^2 + h^2) \quad (7-2)$$

$$S = \pi(a^2 + h^2) \quad (7-3)$$

Note all these equations can be used for the case of both hydrophobic and hydrophilic droplets, that is $0^\circ < \theta < 180^\circ$.

Fig. 7.1 Cross section of a micro-drop on open section. The droplet must be sufficiently small to be a spherical cap.

Fig. 7.2 Gibbs surface energy of a 100 nL water droplet in parallel-plate structure (the line) and single-plate structure (the red dot). When the gap height is large, our model is less accurate due to droplet distortion. The Gibbs surface energy for this portion is plotted as dashed line.

Figure 7.2 plots the Gibbs surface energy for a 100 nL water droplet as a function of the spacing between parallel plates. For simplification, this calculation assumes that no energy barrier exists at the closed/open boundary. It is clear that the surface energy falls rapidly with the increase of gap height. The Gibbs surface energy in the open section is plotted for comparison. It is much lower than that for a closed section when the gap height is $\sim 100 \mu\text{m}$. This result indicates that it should be easy to move a water droplet from closed to open sections. On the other hand, a large energy input will be required to move a droplet from an open substrate to the closed structure.

7.2 Force analysis of water droplet at the closed/ open interface

To evaluate the prospect of droplet movement between closed and open systems by electrical actuation, we conduct force analyses to compare the driving forces with resisting forces. These results provide an estimate for the required voltage for a droplet to move back and forth.

7.2.1 Moving a water drop from closed to open section

The forces exerted on the droplet at the closed/open interface are illustrated in Figure 7.3. We can distinguish two distinct contributions in the plane of the structure: the capillary force and the EWOD force. The capillary force is

$$F_c = F_1 |\cos \theta| + F_2 |\cos \theta| \quad (7-4)$$

and the EWOD force is

$$F_{EWOD} = F_3 |\cos \theta_v| + (F_1 - F_5) |\cos \theta| \quad (7-5)$$

where $F_1 = F_2 = \gamma w$, $F_3 = \gamma a$, $F_5 = \gamma(w-a)$. w and a are contact lengths of the droplet in closed and open sections respectively. θ_v and θ are the droplet contact angle with and without applied voltage. We can avoid use of contact angles by employing the previously derived electromechanical model to calculate F_{EWOD} . Refer to equation (3-9).

Fig. 7.3 Force analysis of a water droplet at the closed/open boundary when it is being moved toward the open section.

In Figure 7.3, where the water droplet is being moved from the closed section to the substrate, because there is no motion for the upper portion of droplet that contacts the edge of the ITO plate, the influence of F_4 is neglected. Thus, the total force acting on the drop is:

$$F_{total} = F_3 |\cos \theta_v| + (F_1 - F_5) |\cos \theta| + F_2 |\cos \theta| \quad (7-6)$$

Here, the three force components help move the droplet toward the open section, so it is understandable that the droplet gets out the closed section easily. In fact, the water droplet tends to move out even without external applied voltage, in which case the

total lateral force is $F_2 |\cos \theta|$. Still, one might anticipate a metastable state at the closed/open boundary if $F_2 |\cos \theta|$ is not large enough to overcome contact angle hysteresis. In any case, the electric force can easily overcome any metastable state that might exist.

7.2.2 Moving a water drop from open to closed section

Figure 7.4 depicts the force components when a water droplet is being moved back into the closed structure. Now, the total force becomes:

$$F_{total} = F_1 |\cos \theta_v| + (F_3 + F_5) |\cos \theta| - F_2 |\cos \theta| - F_6 |\cos \beta| \quad (7-7)$$

F_4 is not included because the effect of F_4 is just to pull the droplet up and down, its horizontal component is compensated by the ITO plate. F_6 is the resisting force from the top ITO plate due to droplet deformation. We estimate that the lateral portion of F_6 is equal to $F_5 |\cos \theta|$. Then

$$F_{total} = F_1 |\cos \theta_v| + F_3 |\cos \theta| - F_2 |\cos \theta| = \gamma w |\cos \theta_v| + \gamma a |\cos \theta| - \gamma w |\cos \theta| \quad (7-8)$$

A numerical example is useful here. For a 100 nL water drop, the contact diameters in the closed (with 100 μm gap height) and open sections are, respectively, 1.1 mm and 0.56 mm. Using $w \approx 1.1$ mm, $a \approx 0.56$ mm, and $\theta = 115^\circ$, $F_{total} > 0$ gives $\theta_v < 78^\circ$. This contact angle is achievable by EWOD actuation, but it is close to the saturation limit. Equation (7-8) shows that a large gap between parallel plates, corresponding to a small w , is favored to move the droplet back into the closed region.

Fig. 7.4 Force analysis of a water droplet at the closed/open boundary when it is being moved toward the closed section.

7.2.3 Detaching a water drop from the ITO plate

When the droplet emerges from the closed section, it still tends to stick to the Teflon-coated ITO glass due to the low interfacial tension between water and Teflon. See Figure 7.5 (a). To detach the drop successfully, the electrical actuation force is needed to overcome F_4 :

$$\begin{aligned}
 F_{total} &= F_E - F_4 \sin \theta = (F_1 |\cos \theta| + F_3 |\cos \theta_v|) - F_4 \sin \theta \\
 &= \gamma a (|\cos \theta| + |\cos \theta_v|) - \gamma (2a + 2t) \sin \theta
 \end{aligned} \tag{7-9}$$

where t is the thickness of ITO plate.

Using $t = 1.12 \text{ mm}$, $a = 0.56 \text{ mm}$, $F_{total} > 0$ gives $\cos \theta_v > 5.02$, which is physically impossible. This calculation demonstrates the limit of the contact angle model in EW theory that the contact angle cannot be reduced below zero. As discussed in section 3.3, using the electromechanical model avoids this apparent paradox. By substituting the droplet and device parameters into equation (3-9) where the electric force F_E is

expressed by applied voltage, we obtain the condition $V > 244V$. This voltage value is consistent with our experiment which will be described in next section. Based on equation (7-9), we can reduce the voltage by using a larger droplet (increasing a) or a thinner upper plate (reducing t). While the droplet volume is usually fixed, we bevel the edge of ITO glass to reduce water/Teflon contact area ($t = 0$) as shown in Figure 7.5 (b). With this method, F_4 is reduced to γa and the required voltage is only 105 V.

(a)

(b)

Fig. 7.5 Force analysis of a water droplet at open section but stuck to the upper ITO plate. (a) A normal ITO plate; (b) ITO plate with sharp edge.

7.3 Experimental results

Roux [36] has demonstrated that water droplets in an oil medium can be moved back and forth readily between closed and open systems. Here we test such manipulations in air. Figure 7.6 shows video frames demonstrating water droplet movement from the closed to the open section. A droplet is first injected into the

Fig. 7.6 Moving a water drop from closed to open section. (a) The water droplet is initially placed in closed section. (b) The droplet is moved towards closed/ open boundary by EWOD actuation using 100 V_{rms} 100 Hz AC. (c) The droplet enters open section as soon as it arrives at the boundary. (d) The droplet completely acrosses the boundary. (e)-(h) Different voltages are applied to remove the droplet from ITO plate: (e) 100 V_{rms} (f) 120 V_{rms} (g) 180 V_{rms} (h) 300 V_{rms}. (i) The droplet is successfully removed after applying 300 V_{rms} voltage. The spacing between two plates for the closed section is 90 μ m. All the voltages applied are 100 Hz AC.

closed section, and then moved toward the closed/open boundary by EWOD actuation. When the droplet reaches the boundary, it is ejected rapidly but still clings to the upper plate. See Figure 7.6 (d). The droplet's movement across boundary (between Figure 7.6 (b) and (d)) only takes 0.24 second. We then apply voltages ranging from 100 to 300 V_{rms} to detach the droplet from the upper ITO plate. Detachment is successful at 300 V_{rms} , in reasonable agreement with the predictions in section 7.2.3 that voltage must be > 244 V.

Fig. 7.7 Removing a water drop from ITO plate with sharp edges. The voltage applied is 90 V_{rms} 100 Hz AC.

To reduce the voltage needed for detachment, we use an ITO plate with a beveled edge. As shown in Figure 7.7, the droplet is easily removed at 90 V_{rms} , which is somewhat lower than the predicted value of 105 V, probably because the direction of the resisting force F_4 in Figure 7.5 (b) is not exactly horizontal.

As presently envisioned, the target fabrication process will not require moving a droplet from an open surface back into a closed section. Nevertheless, this scheme might prove useful for other microfluidic applications involving droplets in

parallel-plate structure. Figure 7.8 shows water droplet movement from open to closed section. A metal wire is used to provide ground potential in the open section. The water droplet is successfully driven into closed section by an actuation voltage of $100\text{ V}_{\text{rms}}$. Using the Lippmann-Young equation we find this actuation voltage corresponds to a contact angle of 61° without considering the saturation effect. This value is at least consistent with the previous force analysis result in section 7.2.2 that θ_V must be $< 78^\circ$.

Fig. 7.8 Moving a water drop from open to closed section.. The voltage applied is $100\text{ V}_{\text{rms}}$ 100 Hz AC.

7.4 Conclusion

In this chapter, we compared the Gibbs surface energy of a water droplet in closed and open structures. The droplet movement from closed to open section is shown to be an energy minimizing process. Using force analysis method, we predict the possibility and required condition to achieve water droplet movement between closed and open sections. These analysis lead to two major results. First, it is easy to move water droplet from closed to open section, and the reversing movement is also

achievable by EWOD actuation. Second, a high voltage is required to remove the water droplet from the edge of upper ITO plate, but this voltage can be greatly reduced by using a sharp edged ITO plate.

Experiments to test the model have been done to demonstrate water droplet movement between closed and open sections. The applied voltages to achieve each scheme agree rather well with the predictions.

Chapter 8 Manipulation of oil droplets on oleophobic surfaces

Oil droplets have low surface tension and usually form a small contact angle on solid surfaces. As a consequence, it is likely that an oil droplet will find its way into cracks or small channels due to the capillary effect. We must overcome this behavior in order to move oil droplets from a closed channel to an open section. In this chapter, we first analyze the requirements to achieve such movement for oil droplets and determine the need for oleophobicity of the structure surface. We then discuss how to realize and fabricate oleophobic surfaces, and present some experimental results.

8.1 Introduction

In Chapter 7 we demonstrated the movement of water droplets from closed to open sections of microfluidic devices. The same movement for oil droplets is, however, far more difficult to achieve. To appreciate this difficulty, we have done a calculation of Gibbs surface energies for two typical oils in both closed and open sections. The calculation method is identical to that described in section 7.1, and results for 100 nL silicone oil and mineral oil droplets are shown in Figure 8.1. In the closed section, the total surface energy of oil droplets decreases with the gap height as shown by the solid lines. This tendency is the same as for water droplet as shown in Figure 7.2. However, unlike water droplets, the Gibbs surface energy of sessile oil droplets in an open section is higher than that for a closed structure. In other words, an

oil droplet sandwiched between parallel plates is the more energetically favored state. Thus, it is easy to move an oil droplet from open section to closed section, but very difficult to achieve the reverse movement.

Fig. 8.1 Gibbs surface energy of a 100 nL oil droplet in closed structure (the line) and open structure (the dot). Red: mineral oil droplet; Black: Silicone oil (20 cst) droplet. When the gap height is large, our model is no longer valid due to droplet distortion so the Gibbs surface energy for this portion is plotted as dashed lines.

The tendency of a liquid to enter narrow channels is commonly recognized as the capillary effect. A classic textbook example is the liquid rising in a vertical glass tube. As shown in Figure 8.2 (a), the height of a liquid column, limited by gravitational forces, is given by:

$$h = \frac{2\gamma \cos \theta}{\rho g R} \quad (8-1)$$

where γ is the liquid-air surface tension, θ is the contact angle, ρ is the density of liquid, $g = 9.81 \text{ m/s}^2$ is gravitational field strength, and R is radius of the tube. For our apparatus, the liquid droplet moves horizontally and the goal is to use electrical actuation to overcome the capillary effect. To evaluate the requirements to accomplish this operation, we conduct a force analysis to compare the driving force and resisting forces as shown in Figure 8.2 (b). The total force acting on the oil drop is:

$$F_{total} = F_{DEP} - F_2 \cos \theta - F_4 \sin \theta + (F_3 \cos \theta + F_5 \cos \theta - F_1 \cos \theta)$$

$$\approx F_{DEP} - F_2 \cos \theta - F_4 \sin \theta \quad (8-2)$$

Fig. 8.2 (a) Force analysis for a capillary tube. (b) Force analysis of an oil droplet at the closed/open boundary.

The DEP force can be calculated using equation (3-9), with $F_2 = \gamma w$ and $F_4 = \gamma a$. w and a are contact lengths of the droplet in closed and open sections respectively. Using the parameters listed in Table 8.1, the minimum required voltage to achieve $F_{total} > 0$ is 1292 V and 1555 V for silicone oil and mineral oil, respectively. These

high voltages are much greater than the dielectric breakdown voltages of 750 V, so it is impossible to achieve the desired movement by direct actuation.

Table 8.1 Properties and profile parameters of oil droplets used for closed to open force analysis.

	Surface tension (mN/m)	Dielectric constant	Contact angle (°)	Drop volume (nL)	Gap height for closed section (um)	w (mm)	a (mm)
Silicone oil (20 cst)	20.6	2.68	53	100	100	1.1	0.98
Mineral oil	28.1	2.2	74	100	100	1.1	0.83

One proposed solution is to use non-parallel plates as shown in Figure 8.3 (a). Using a slightly tilted upper plate, it might be possible to drive the oil droplet from a narrow region to a wide region, and eventually to deliver the oil droplet to an open section. The total force acting on the oil droplet is:

$$\begin{aligned}
 F_{total} &= F_{DEP} - [F_1 \cos \theta + F_2 \cos(\theta - \theta_1) - F_3 \cos \theta - F_4 \cos(\theta + \theta_1)] \\
 &= F_{DEP} - 2\gamma w \sin \theta \sin \theta_1
 \end{aligned} \tag{8-3}$$

Because the upper plate is only slightly tilted, we still use the parallel-plate structure equation (3-13) to calculate the DEP force. From equation (8-3), it is clear that there is a maximum tilt angle θ_1 at given voltage above which $F_{total} > 0$ cannot be achieved.

For example, when a 100 nL mineral oil droplet is actuated by 400 V voltage, $F_{total} > 0$

gives $\sin \theta_1 < \frac{F_{DEP}}{2\gamma w \sin \theta} = 0.15$, so the maximum tilt angle θ_1 is just 8.6° .

Fig. 8.3 (a) Non-parallel two-plate structure to drive the oil droplet from narrow region to wide region by DEP. (b) Breaking up of the oil droplet in parallel-plate structure when the two plates are separated far enough from each other.

Although actuation of an oil droplet can be achieved in the non-parallel two-plate scheme when the tilt angle is small, there is still the problem of using this scheme for closed to open structure movement: the oil droplet tends to break up before reaching the open section. We can understand this issue by considering a quasi-static process where the two plates are slowly separated as shown in Figure 8.3 (b). The oil droplet sandwiched between parallel plates has a contact angle $\theta < 90^\circ$. The vertical component of the surface tension forces at the upper (or lower) edge and the middle of drop are respectively:

$$F_{edge} = \gamma 2\pi R \sin \theta \quad (8-4)$$

$$F_m = \gamma 2\pi r \quad (8-5)$$

As the plates separate, both R and r decrease. At some point F_{edge} will exceed F_m because r can approach 0. Then, the droplet breaks into two droplets, one each on the top and bottom substrates. In the non-parallel structure in Figure 8.3 (a), the oil droplet displays similar behavior and breaks into two after it arrives in the open section.

Fig. 8.4 Experimental demonstration of oil droplet separation when delivered from closed to open section. (a) Side-view of the experimental setup. (b)-(g) Selected video frames showing the oil droplet separation at the lower edge of plate A. The oil droplet used in this experiment is a 10 μL silicone oil (10 cst) drop.

This droplet break-up mechanism is demonstrated using the vertical two-plate structure shown in Figure 8.4 (a). Two overlapping glass slides are placed together and the oil droplet is drawn by gravity. A silicone oil droplet is pipetted on plate A and is pulled downward by gravity. The oil droplet enters the closed section very quickly as shown in Figure 8.4 (c), then travels down the channel between plates A and B. When the droplet arrives at the lower edge of plate A, most of the drop continues

down and enters the open section on plate B, but a small droplet is left on the edge of plate A, as shown in Figure 8.4 (f) and (g).

In contrast, we have shown successful closed-to-open movement for water droplets in Chapter 7. This is because, as shown in Figure 8.5, a water droplet has a contact angle $> 90^\circ$ on Teflon. Because $R < r$, the vertical component of the surface tension force at the upper (or lower) edge- ($\gamma 2R \sin \theta$) is always smaller than that at the middle of drop- ($\gamma 2\pi r$). In this case the droplet can detach from one surface without separation.

Fig. 8.5 The profile of a water droplet sandwiched between parallel plates.

In summary, contact angle plays an important role in keeping a droplet from separating during its closed-to-open movement. When the contact angle is $< 90^\circ$, the droplet has a “slim waist” profile in the parallel-plate structure and thus breaks up easily before entering the open section. A solution to this problem is to employ an “oleophobic” surface for one of the parallel-plate surfaces. In the next section, we

discuss how to design and fabricate oleophobic surfaces, and present oil droplet manipulations on oleophobic surfaces.

8.2 Designing oleophobic surfaces

The wetting behavior of solid surfaces by a liquid is governed by the free energy and the geometry of the surface. We here first consider the surface energy. For a flat surface, the surface tension required to achieve a contact angle greater than 90° for oils is determined by Young's equation:

$$\cos \theta = (\gamma_{SV} - \gamma_{SL}) / \gamma_{LV} \quad (8-6)$$

Thus for $\theta > 90^\circ$,

$$\gamma_{SV} \leq \gamma_{SL} \quad (8-7)$$

The interfacial tension γ_{SL} can be approximated by the empirical equation (8-8): [95]

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\sqrt{\gamma_{SV}\gamma_{LV}} \quad (8-8)$$

Combining equations (8-6), (8-7) and (8-8), we obtain $\gamma_{SV} \leq \gamma_{LV}/4$. Typical surface tensions for oils are 20~30 mN/m, thus the surface tension of the solid surface must be on the order of several mN/m. In nature solids rarely possess such a small surface tension. The trifluoromethyl group ($-\text{CF}_3$), with surface tension of 6 mN/m [96], is perhaps the only material to satisfy this requirement. By comparison Teflon, used in most of our experiments, has a surface tension of 18 mN/m.

One way to achieve high apparent contact angle is to use a micro- or nano-structured surface to change the wettability. [97-108] Two well-known models, developed independently by Wenzel [109] and Cassie and Baxter [110], are

commonly used to explain the effect of surface roughness on the apparent contact angle of liquid drops. Wenzel's model assumes that the liquid is in contact with the entire rough surface. The surface roughness increases the available contact area, thus amplifying the wetting property. The contact angle in the Wenzel model is

$$\cos \theta = R_f \cos \theta_0 \quad (8-9)$$

where θ is the apparent contact angle on a textured surface, R_f is the ratio of the roughened surface to the smooth surface, and θ_0 is the equilibrium contact angle on a smooth surface.

The Cassie-Baxter model corresponds to composite wetting, where the liquid, in contact with the solid surface, traps micro air pockets. If f_{SL} is the solid-liquid contact fraction, the apparent contact angle is given by

$$\cos \theta = f_{SL} \cos \theta_0 - 1 + f_{SL} \quad (8-10)$$

As applications for the Wenzel and Cassie-Baxter models, consider a microstructure with periodic arrays of cylindrical pillars of diameter D , height H and pitch P . Equations (8-9) and (8-10) now become

$$\text{Wenzel:} \quad \cos \theta = \left(1 + \frac{\pi DH}{P^2}\right) \cos \theta_0 \quad (8-11)$$

$$\text{Cassie-Baxter:} \quad \cos \theta = \frac{\pi D^2}{4P^2} \cos \theta_0 - 1 + \frac{\pi D^2}{4P^2} \quad (8-12)$$

According to equation (8-11), the Wenzel model predicts that a roughened surface makes a hydrophilic surface more hydrophilic, and a hydrophobic surface more hydrophobic. On the other hand, the Cassie-Baxter relation allows for the possibility of $\theta > 90^\circ$, even when $\theta_0 < 90^\circ$.

A general way to analyze the wetting properties of a textured surface is to plot a

wetting diagram. Such diagrams show the apparent contact angle of a liquid placed on the textured surface as a function of the equilibrium contact angle of a reference smooth surface. See Figure 8.6. The wetting states can be clearly identified from the diagram as different branches. The first branch (I) corresponds to the Cassie-Baxter state, where the liquid droplet is suspended on the top of textured surface. Branch II corresponds to the Wenzel state, where the liquid droplet wets the entire surface. Branch III corresponds to an inversion of the first branch. All the three branches show that texturing enhances natural wetting property of a surface.

Fig. 8.6 Wetting diagram for a crenelated surface. This diagram is adapted from [101].

The wetting diagram incorporates all the equilibrium states. As can be seen, a surface cannot exist in the Cassie-Baxter state for $\theta_0 < 90^\circ$. The creation of an oleophobic surface requires that $\theta_0 > 90^\circ$. These conclusions highlight the difficulty of developing oleophobic surfaces as there are no natural surfaces with a low enough

surface tension to enable $\theta_0 > 90^\circ$ for oils. However, various experiments with microstructured surfaces and corresponding free energy approaches [97-108] show the existence of “metastable” configurations that can be exploited. Further, Krupenkin et al. [111] have reported the possibility of reversible transitions between the Wenzel and Cassie-Baxter states. Studies of certain plant leaves [112,113] indicate the possibility of achieving highly nonwetting surfaces with texturing, even when $\theta_0 < 90^\circ$. Indeed, an oleophobic surface can be realized on metastable Cassie-Baxter states.

Strictly speaking, metastability only delays a transition, but if the metastable Cassie-Baxter state persists for long enough, it can be used to provide oleophobicity in many applications. “Re-entrant” geometries are usually used to exploit this metastability. A re-entrant structure is one where the surface has concave cross-sectional topography. Refer to Figure 8.7. Joly [101] calculated the wetting diagram for a re-entrant T-shaped structure and found that the first branch, the Cassie-Baxter state, reaches the lower right quadrant, indicating the possibility of $\theta > 90^\circ$ even though the intrinsic contact angle $\theta_0 < 90^\circ$. Because the intrinsic contact angle is $< 90^\circ$, the meniscus is pinned on the re-entrant surface and cannot penetrate all the way into the cavity.

Fig. 8.7 Basic principle of oleophobicity: the pinning of the meniscus at the re-entrant geometry ensures the metastability of the Cassie-Baxter state even for an intrinsically wetting surface.

Successful fabrication of oleophobic surfaces dates back to the 1990s. The earliest strategy for making oleophobic surfaces was to start with a sufficiently rough surface and then to immerse it into a chemical solution containing fluorinated compounds. Methods used to create rough aluminum surfaces include anodic oxidization [98,103], sand-blasting, and electrolytic etching [108]. Nowadays, microstructured surfaces are usually fabricated by microfabrication methods, for example, micro-hoodoo structures on silicon wafer [97], hierarchical silica sphere stacking layers [99], ion track etched silica film [100], and re-entrant structures on PDMS [102]. The bonding of the fluorinated chemical layer is done by either coating [98,102] or chemical vapor deposition (CVD). [97,100]

A different strategy for making oleophobic surfaces is to add fluorinated compounds to the structure materials before they form microstructured surfaces. Examples of these oleophobic surfaces can be found in electrospun fibers containing polyhedral oligomeric silsesquioxane (POSS) molecules [97], thin film obtained by electrochemical polymerization of highly fluorinated 3,4-ethylenedioxyppyrole

monomers [104], and spin coated film containing fluorinated silica nanoparticles [107].

8.3 Fabrication of oleophobic surfaces by electrospinning

Tuteja [97] has reported superoleophobicity on both the electrospun film with fluorodecyl POSS molecules and silicon surface with re-entrant microstructures. These processes seem well-suited to our purpose, so we have tried to duplicate them. The fabrication and experimental results are presented next.

Electrospinning is a simple but versatile method to produce continuous ultrathin fibers with micrometer and sub-micrometer diameters. The setup used for our electrospinning experiments is shown in Figure 8.8. A syringe containing a polymer solution is operated at a constant flow rate and a high DC voltage is applied between the syringe needle and polymer fiber collector. In operation, ultrathin fibers are formed by the stretching of the polymer jet associated with the onset of the whipping instability induced by the electric field.

To form uniform electrospun fibers, the polymeric solution must have appropriate viscoelasticity and electrical conductivity. Otherwise, the Rayleigh instability, which tends to break the polymer jet into droplets, leads to the formation of beaded fibers or individual microdroplets. In this study, we use poly(methyl methacrylate) (PMMA) (MW = 35k Da, Aldrich) as the polymer material and various fluorinated compounds as the low surface tension material. The material selection and operating parameters are listed in Table 8.2. For all the tests, ITO coated glass plates were used as the

receiver plate for the fiber mats. The distance between the syringe needle and the ITO glass collector was approximately 16 cm. Solution feeding rate was set at 0.25 mL/h and the temperature was around 25°C.

Fig. 8.8 The setup of electrospinning.

Table 8.2 Material selection and operation voltages of electrospinning experiments.

Sample index	Fluorinated compound	Solvent	PMMA concn (wt%)	Voltage (kV)
A1	1H,1H,2H,2H-Perfluorooctyl-trichlorosilane	Chloroform	5	7
A2	1H,1H,2H,2H-Perfluorodecyltriethoxysilane	Chloroform	5	8
B1	Fluorodecyl POSS	AK225	5	10
B2	Fluorodecyl POSS	AK225	7.5	10
B3	Fluorodecyl POSS	AK225	10	10

In tests A1 and A2, the resulting films exhibited no oleophobic behavior, even with increased concentration for the fluorinated compounds (from 5 wt% to 10 wt%). Both the fluorinated compounds in A1 and A2 have a chain structure and each molecule has one $-\text{CF}_3$ group at one end. Apparently these compounds do not have sufficiently low surface tension and the electrospinning process can not guarantee that

the $-\text{CF}_3$ group will face outwards from the surface. Next was tried Fluorodecyl POSS molecules (provided by ERC, Inc.), which has a cage-like structure surrounded by perfluoro-alkyl groups. See Figure 8.9. The high surface concentration of $-\text{CF}_2$ and $-\text{CF}_3$ groups combined with the symmetry of the structure results in a very low surface energy. Because the fluoroPOSS is not soluble in chloroform, both the polymer and fluoroPOSS are dissolved in a hydrochlorofluorocarbon solvent, Asahiklin AK-225 (Asahi glass co.) for electrospinning. The fluoroPOSS concentration is 5 wt%.

Fig. 8.9 Fluorodecyl POSS molecular structure. R_f group in the structure: 1H,1H,2H,2H- heptafluorodecyl.

Fiber mats with different morphologies are obtained by varying the concentration of PMMA during electrospinning. The morphologies are shown in the SEM (Zeiss-Leo DSM982) images provided in Figure 8.10. The contact angles of a mineral

oil droplet placed on these fiber mats are measured to be respectively 120° , 132° and 128° for samples B1, B2 and B3. All these electrospun surfaces are oleophobic and the best performance is achieved with 7.5 wt% PMMA concentration. At a concentration of 5 wt%, many microdroplets formed during electrospinning instead of

Fig. 8.10 The morphology of electrospun PMMA/ fluoroPOSS composite microfiber at different PMMA concentration. (a), (b) 5 wt%; (c), (d) 7.5wt% and (e), (f) 10 wt%.

polymer fibers, as shown in Figure 8.10 (a) and (b). This microdroplet formation is probably due to low solution viscoelasticity. At 7.5 and 10 wt% PMMA concentration, a “beads-on-string” morphology is formed. Ma [114] found this structure actually improves oleophobicity because the beads introduce a second level of roughness. Such roughness, spanning several dimensional scales, is favored for oleophobicity. When the polymer concentration is further increased, the average fiber diameter rises from 0.4 to 1.1 μm , which reduces the contact angle because the thicker fibers increase the solid-liquid contact fraction in the Cassie-Baxter model.

Although we have achieved reasonable oleophobicity on the electrospun PMMA/fluoroPOSS fiber mats, there are still two problems for their application to droplet manipulation. First, the uniformity of an electrospun surface is difficult to control. Our electrospinning method lacks control over mat thickness and also the density of fibers therein. As a result, adequate oleophobicity over the functional area of a microfluidic device cannot be guaranteed. This non-uniformity is evident from the fact that a droplet sliding down a tilted mat sometimes sticks due to pinning. Another problem encountered is that the oil droplets become contaminated by the fiber mat material, apparently because the fiber mat is not a compacted structure. Some of the fiber mat adheres to droplets as they roll over the surface. Because of these problems, we abandoned the electrospinning approach and tried to fabricate textured silicon surfaces with re-entrant microstructural profiles.

A very basic process for fabricating re-entrant microstructure on Si wafer is shown in Figure 8.11. A 300 nm thick silicon dioxide thin film is first deposited on a 4-inch Si wafer by PECVD (plasma enhanced chemical vapor deposition). Cap geometries are then defined via standard photolithography using Shipley S1805 as the photoresist. Using the photoresist as a mask, the silicon dioxide layer is etched with CF_4 plasma to expose Si. See Figure 8.11 (b). Etch depth is set to 350 nm to guarantee

Fig. 8.11 The fabrication of re-entrant structure on Si wafer. (a) A 300 nm silicon dioxide layer is deposited on the Si wafer. (b) The cap patterns is first formed on the photoresist layer via photolithography and then transferred onto the SiO₂ layer by CF₄ plasma etching. (c) SiO₂ caps are released by SF₆/O₂ plasma etching. (d) Severe re-entrance is achieved by XeF₂ isotropic etching.

exposure of bare silicon surface. Next, the silicon dioxide caps are formed using a SF_6/O_2 plasma reactive ion etching (RIE) process. See Figure 8.11 (c). Finally, vapor-phase XeF_2 isotropic etching is applied to the Si wafer to undercut the silicon dioxide caps and form the re-entrant profile.

Figure 8.12 shows SEM images of the re-entrant microstructure fabricated on a Si wafer. Figure 8.12 (a) and (b) are the structure just after the SF_6/O_2 etch. The feature depth is $7.8\ \mu\text{m}$ and the undercut for SiO_2 caps is only $600\ \text{nm}$ (inset, Fig. 8.12 (b)). After a second XeF_2 etching process, the undercut is enlarged to $\sim 2\ \mu\text{m}$. See Figure 8.12 (c) and (d).

Fig. 8.12 SEM images of the re-entrant microstructures on Si wafer. (a) Side-view of an array of T-shape pillars after the SF_6/O_2 etch. (b) Measurement of the feature depth and undercut for Fig. 8.12 (a). (c) Top-view of the cap patterns after XeF_2 etch. (d) Magnification view of Fig. 8.12 (c).

Three different SiO₂ cap patterns with lateral spacings (W) of 20, 40 and 60 μm were fabricated in order to vary the fractional surface coverage. The cap dimension is fixed at 10 by 20 μm and the spacing between them in y direction is 5 μm . The microstructure in Figure 8.12 (c) shows the cap pattern with 40 μm lateral spacing.

To achieve low surface energy, a fluorination treatment was carried out by chemical vapor deposition (CVD) of 1H,1H,2H,2H-Perfluorooctyl- trichlorosilane. Samples are placed in an oven with silane atmosphere and heated at 140°C for 50 minutes.

After silanization, we measured the Cassie-Baxter state apparent contact angle for the three cap patterns. As shown in Table 8.3, both water and mineral oil droplets have contact angles $> 140^\circ$. The contact angle for water is always greater than mineral oil due to its greater inherent hydrophobicity. According to the Cassie-Baxter equation (8-10), the apparent contact angle is determined by f_{SL} , the fraction of the solid surface wetted by the contacting liquid. Small f_{SL} results in large apparent contact

Table 8.3 Contact angle values for water and mineral oil droplets on re-entrant microstructures.

Lateral spacing between SiO ₂ caps, W (μm)	20	40	60
Solid-liquid contact fraction (f_{SL})	0.33	0.22	0.17
Equilibrium contact angle on smooth surface ($^\circ$)	¹ (92) and ² (78)		
Calculated contact angle from Cassie-Baxter model ($^\circ$)	¹ (133) and ² (127)	¹ (142) and ² (137)	¹ (147) and ² (143)
Apparent contact angle on textured surface ($^\circ$)	¹ (142) and ² (141)	¹ (145) and ² (143)	¹ (146) and ² (144)

¹For water.

²For mineral oil.

angles. This trend was verified from contact angle measurements. The largest contact angle is obtained at 60 μm lateral spacing. However, the large spacing also lead to more severe encroachment of liquid into the cavities, which allows for easier failure of the Cassie-Baxter state. In the next experimental section, we use the re-entrant microstructure with 40 μm lateral spacing for electric field assisted microfluidic manipulation of oil droplets.

8.5 Oil manipulation experiments

The analysis presented in section 8.1 predicts that it is easy to move an oil droplet from an open to a closed section. The experiment described here demonstrates this tendency for oil droplets moving into a capillary channel. Figure 8.13 (a) shows a water droplet initially placed in a closed section (right) and a large silicone oil droplet placed in the adjacent open section (left). When the water droplet is ejected from the closed channel into open section and makes contact with the oil droplet, the oil droplet tries to engulf the water drop and in so doing contacts the closed/open boundary. The oil droplet immediately moves into closed section with no external force applied. Contact with the water is retained but the entire oil drop stays in the closed section. In contrast to the oil droplet, the water droplet prefers the open section. A useful application can be deduced from this phenomenon: a Teflon coated closed/open interface is ideal for separating oil/water mixtures.

Fig. 8.13 Movement of oil droplet from open to closed section. (a) A water droplet placed in closed section (right) and a large silicone oil droplet placed in open section (left). (b) and (c) When the water droplet is delivered to open section, the oil droplet engulfs the water drop and moves into closed section. (d) Eventually, the oil droplet goes into closed section and the water drop stays in open section.

Since it is impossible to achieve closed-to-open movement simply with Teflon coated substrates, we use the textured Si wafer as the top substrate for this movement of oil droplets. Figure 8.14 shows a mineral oil droplet sandwiched between a Teflon coated glass substrate (bottom) and a textured Si substrate (top) actuated by DEP. When the oil droplet is delivered to the closed/open boundary, continuous actuation moves the oil droplet to the open section, see Figure 8.14 (c). Wu [73] reported a low resistance to motion when he manipulates a hexadecane droplet in a parallel-plate where textured Si wafer is used as the bottom substrate. For our device the textured

surface was on the top and we do not see a significant change in the resisting force since the actuation voltage is similar to the parallel glass plate device.

Fig. 8.14 Side view showing manipulation of a mineral oil droplet between Teflon coated glass substrate (bottom) and textured Si substrate (top). The spacing between two substrates is 200 μm . The applied voltage is 560 Vrms 100 Hz AC.

One important issue to be considered while using the textured oleophobic surface for oil droplet manipulation is the robustness of the Cassie-Baxter state. This state is metastable for oil droplets because the intrinsic contact angle is $< 90^\circ$. A transition from the Cassie-Baxter state to the Wenzel state occurs over time due to the sagging of liquid-air interface. To investigate this effect, we measured the persistence time of the Cassie-Baxter state apparent contact angles at for different oils. The results are listed in Table 8.4. This measurement is based on sessile droplets; the transition might occur more quickly for a droplet in motion. Figure 8.15 shows a different test: the behavior of a mineral oil droplet on textured oleophobic surface when it is moved back and forth. After 3 cycles, a tiny oil droplet comes off and adheres to the textured surface, indicating a local transition to the Wenzel state. See Figure 8.15 (b). By 7 cycles, more and more small droplets are adhering to the surface. After 10 cycles, the entire oil drop pins and becomes unmovable.

Table 8.4 The persistence time of Cassie-Baxter state apparent contact angles.

	Acetone	Corn oil	Sunflower oil	Castor oil	Mineral oil
Apparent contact angle (°)	132	130	124	146	143
Persistence time (min)	0.5	1	10	30	30

Fig. 8.15 Sliding of a mineral oil droplet on textured oleophobic surface. (a) The first cycle. (b) After 3 cycles. (c) After 7 cycles. (d) The 10th cycle.

Joly et. al. [101] used a finite element model to simulate the Cassie to Wenzel transition for a re-entrant structure. They found the liquid filling transition to originate in the spontaneous filling of the cavities with the liquid phase rather than due to a collapse of the meniscus. A local condensation of the liquid at the internal corners of the cavity is presumably the direct cause for the transition. This explanation is consistent with another test we performed using more volatile acetone, which stays in

the Cassie-Baxter state for the shortest time. According to this transition mechanism, an inverse-trapezoidal re-entrant microstructure without sharp internal corners could enhance the robustness of the Cassie-Baxter state. However, no easy process to fabricate such a structure on Si wafer was available to us. Further effort to perfect structured oleophobic surface is needed.

8.6 Conclusion

In this chapter, we analyze the condition required to achieve closed to open movement for oil droplets. The force analysis result shows that it is impossible to drive oil droplets to open section by direct DEP actuation. Using the non-parallel two-plate scheme, we can move oil droplet from narrow to wide regions, but usually breaks the droplet before moving it to open section. Accordingly, an oleophobic surface is required to complete closed to open movement for oil droplets.

To design an oleophobic surface, two strategies are proposed: (i) to obtain a microstructured surface and then treat it with low surface tension material and (ii) to add low surface tension material to the structure materials before using them to form microstructured surfaces. Both methods combines the effects of surface free energy and surface geometrical structure on apparent contact angle to achieve optimized results.

Based on the designs, two types of oleophobic surfaces are fabricated: the electrospun fiber mats and the re-entrant structure on Si wafer. The electrospinning method intrinsically provides the required roughness for oleophobicity because of the

small fiber size. With the fluoroPOSS molecules, the electrospun fiber mats shows good oleophobicity but the uniformity and contamination issues limit their further application. The re-entrant structure on Si wafer also provides good oleophobicity for many types of oils. We present successful oil droplet manipulations using the textured surface. However, the robustness of the apparent contact angle needs to be improved.

Chapter 9 Conclusion and future work

The cryogenic laser targets used in inertial confinement fusion experiments are prepared from hollow, low-density polymer foam shells. By the very nature of the inertial confinement fusion reaction, stringent requirements are imposed on the sphericity and wall thickness uniformity of these shells. Currently, triple-nozzle droplet generators produce DE droplets for foam shell formation by controlling the liquid flow rate and matching liquid densities, but the method suffers from low yield. We have investigated the critical elements of a droplet-based microfluidic DE assembly-line for automated production of foam shells for laser target. This microfluidic assembly-line automates the production process to achieve droplet-by-droplet processing. Thus, in contrast to bulk processing methods now used, every DE droplet produced is expected to meet the specifications. Because it is electrically controlled, this scheme provides excellent flexibility and scalability, allowing for on-demand production of DE droplets from a selection of liquids.

9.1 Electrical actuation mechanisms

The electric field mechanisms used in the DE droplet assembly line are EWOD and DEP: the first actuates conductive liquids, while the second operates on insulating, polarizable media. We present a simple model to calculate these actuation forces using lumped parameter electromechanics. The electromechanical force is expressed as a function of controllable parameters: the thickness and dielectric constant of each layer

in the device, the gap height between parallel plates, the electrode size, the applied voltage and frequency, and the conductivity and dielectric constant of the liquid. Given its generality, this model can be used to predict the possibility to actuate particular liquids in devices of known geometry and to optimize device design and operating conditions to enable actuation of many liquids.

This model is more general than the contact angle model commonly used in EW theory. The electromechanical approach clearly reveals the frequency-dependent relationship between EWOD and DEP, that is, the electromechanical force exerted on a liquid droplet with finite conductivity transitions from EWOD regime to DEP regime as frequency is increased. Using the electromechanical model also avoids any need to evaluate contact angles and thus requires no attention to the electric field in the region of the contact line.

9.2 Droplet manipulation studies

Droplet manipulation of water and oil in parallel-plate structures is achieved by application of sufficient voltage. We first study the droplet dispensing process because dispensing is a fundamental enabling operation for the formation of DE droplets. The quasi-static condition to achieve successful dispensing is established. This condition, derived from hydrostatic analysis, shows that small gap height, large electrode size, and a long cutting electrode all favor successful dispensing. Droplet volume reproducibility is tested over a range of operational parameters, including applied voltage, cutting electrode length, and the effect of connecting traces. By optimizing

the operating conditions, we obtain a reproducibility of $\pm 3.0\%$, which is adequate for laser target fabrication according to our sensitivity analysis.

The force calculations predict and experimental results verify that oil manipulation require much higher voltages than water. We have demonstrated dispensing of many types of oils by DEP actuation, but have not succeeded to obtain a quantitative expression relating dispensing voltage and oil properties. We intended to establish a physical model relating the DEP force (applied voltage) to oil properties and device geometry to describe dispensing condition. The ratio of the DEP force to oil surface tension forces was first considered, but the analysis was not applicable to all oils. A more general model is needed to take into account other factors- contact angle hysteresis, viscosity, and absorption between oil and the Teflon surface.

To reduce voltage requirements to manipulate oil, we introduce a new method of actuating oil droplets in water medium that exploits negative DEP. The calculated actuation force on oil droplets using negative DEP is comparable to EWOD-based water droplet manipulation. These predictions have been borne out by the experiments reported. Microfluidic operations of transporting, splitting, merging, and dispensing of oil droplets are achieved at voltages less than ~ 100 V. By combining positive and negative DEP actuation, water and oil droplets can be manipulated concurrently with a single voltage level, thus opening the way to automated, on-chip formation of DE droplets.

9.3 DE droplet formation in parallel-plate structure

After dispensing water and oil droplets, these must be combined to form DE droplets. We present a Gibbs free energy model and experimental results for the on-chip DE formation process. The Gibbs energy change offers a convenient criterion for testing the likelihood of DE formation. The model shows that water-in-oil DE droplets form through spontaneous emulsification due to energy minimization and oil-in-water DE droplets form if the proper surfactants are added. Further, our energy model correctly predicts the configuration of liquid films for parallel-plate devices. The existence of this water-in-oil DE structure has been proved [84-87] and we have observed it in oil-in-water DE droplets. See section 6.1.2.

We present experimental results demonstrating both water-in-oil and oil-in-water DE droplet formation in parallel-plate devices. Water-in-oil DE droplets are formed by first dispensing individual droplets and then merging them. Oil-in-water DE droplets can be formed by merging surfactant-treated water and oil droplets. In the latter case, however, a tether usually prevents the successful dispensing of surfactant-treated water droplet. Although the tether can be cut using a second liquid finger, it interferes with the dispensing operation and degrades volume reproducibility. Other methods to avoid the tether include taking advantage of the pH effect on Silwet solutions and adding the surfactant to the oil phase. Using the pH effect, the recovery of wetting ability is very slow. Alternatively, adding the surfactant to the oil phase is a much faster method for oil-in-water DE formation. Further effort to explain and solve the problem of tethers is needed for future research.

9.4 Moving droplets from closed to open sections

Because droplet dispensing can only be done in closed parallel-plate structures, we deliver the droplets to an open section after formation. We use a force balance analysis to predict the condition required to eject a droplet from a closed section. This model shows that it is easy to move a water droplet from closed to open section, and that the reverse process is also achievable using EWOD actuation. On the other hand, oil droplets always tend to stay in a closed section. Driving an oil droplet from closed to open section by direct DEP actuation is impossible on Teflon coated surfaces. An oleophobic surface must be used to complete this movement for oil droplet.

Experimental testing of the various predictions is done to demonstrate droplet movements between closed and open sections. For water droplet, the applied voltages to achieve closed-to-open or open-to-closed movement agree rather well with predictions. To detach the water droplet from the upper plate, we use a bevelled edge to minimize water-Teflon contact area and thus reduce the applied voltage. For oil droplets, we investigated two types of oleophobic surfaces- electrospun fiber mats and re-entrant Si structures. Both have shown good oleophobicity. While the electrospun fiber mats are not very useful for droplet manipulations due to non-uniformity and possible particulate contamination, we successfully used the re-entrant Si structure to achieve closed to open movement.

9.5 DE droplet formation in open section

In addition to forming DE droplets in parallel-plate structure, we also investigated

water and oil droplet combination in open section. Figure 9.1 shows the water-in-oil DE droplet formation process. A water droplet is first dispensed from the left reservoir, and moved toward the closed/open boundary by EWOD actuation. When the droplet reaches the boundary, it is ejected very quickly. See Figure 9.1 (d) and (e). Next, after the ground ITO electrode on the upper substrate is disconnected, droplet detachment

Fig. 9.1 The formation of water-in-silicone oil DE droplet in open section. (a), (b) A water droplet is dispensed by EWOD actuation in closed section. (c) The water droplet is transported toward the closed/open boundary. (d), (e) The water droplet is ejected to the open section. (f), (g) The water droplet is detached from the upper ITO substrate. (h) The water droplet is delivered and combined with an silicone oil droplet to form DE droplet. (i) The water droplet pulls the whole merged water-in-oil DE droplet by EWOD actuation. The voltage applied through the entire process is 100 Vrms, 100 Hz AC.

is achieved by sequential voltage application to the coplanar electrodes. Refer to Figure 9.1 (f) and (g). Though not evident in the video frame the edge of the upper plate is beveled for easy detachment. The water droplet is then transported towards the previously placed oil droplet. When the water droplet touches the oil droplet, it is immediately engulfed by the oil droplet to form a DE droplet. After formation, the DE droplet is further transported by EWOD actuation as shown in Figure 9.1 (i).

Fig. 9.2 The formation of mineral oil-in-water DE droplet in open section. (a), (b) A water droplet is dispensed by EWOD actuation in closed section. (c), (d) The water droplet is ejected to the open section. (e) The water droplet is detached from the upper ITO substrate. (f) The water droplet is delivered and combined with a Silwet added mineral oil droplet (0.5% v/v). (g)-(i) The water droplet gradually engulfs the oil droplet and forms an oil-in-water DE in ~10 s. The voltage applied through the entire process is 100 Vrms, 100 Hz AC.

In the target fabrication process, mineral oil-in-water DE droplets are used. We demonstrate the formation of such a DE droplet in Figure 9.2. The dispensing and closed-to-open ejection process for a water droplet is the same as described above. Now, however, the oil droplet is a Silwet added mineral oil (0.5% v/v). When the water droplet contacts the oil droplet, its contact angle is quickly reduced due to surfactant diffusing into the water. See Figure 9.2 (f) and (g). The water droplet gradually engulfs the oil droplet and forms an oil-in-water DE in ~ 10 s. See Figure 9.2 (i). The delivery¹ of the formed DE droplet to an oil bath can be achieved by simply tilting the substrate and pouring the DE droplet. However, one must keep the DE droplet moving slowly to avoid rupture of the inner droplet. A more reliable way to achieve this transfer is needed.

9.6 Future work

A number of problems with different techniques have been encountered in this research. Solutions to them would greatly advance the effort to apply the microfluidic DE formation scheme in the target fabrication process.

More robust oleophobic surface treatments

The surface of the re-entrant Si structure is not robust enough for repeated use in oil manipulations. As discussed in section 8.2, the Wenzel state of an oil droplet on textured surface has a much lower free energy density compared to the Cassie-Baxter state, and is therefore the thermodynamically favored state. A transition from the metastable Cassie-Baxter state to the Wenzel state occurs over time and accordingly

¹ The next step would be to deliver the DE droplet to an oil bath for further centering process.

the oleophobicity is lost. According to Joly's [101] prediction, an inverse-trapezoidal re-entrant microstructure could enhance the robustness of the Cassie-Baxter state. Such a structure has been fabricated on PDMS [102], but we have not found a process to fabricate this structure on a Si wafer. Further effort to develop re-entrant structures without sharp internal corners is needed.

Integration of the chip with centering structures

We form DE droplets on a microfluidic chip in ambient air. The next step in the target fabrication process is electric centering and polymerization of the DE droplets to form usable foam shells. These processes are done with the DE droplet in a surrounding fluid with density closely matched with the DE droplet. A reliable way to deliver the DE droplet from air to liquid medium is needed. The DE structure must be maintained in the delivery without severe deformation and avoid popping of the inner droplet of the DE. G. Randall [115] has found that the stability of DE droplets depends on the selection of surfactant as well as the inner oil droplet. Further effort to optimize surfactant and oil selection is needed.

Other unsolved issues

In this study, we have encountered several issues that we do not fully understand. All of these seem to involve fundamental scientific problems that require further study. The principal of these are discussed below.

- (i) A tether is formed during certain dispensing operations, such as the dispensing of surfactant-treated water in air, mineral oil in surfactant-treated water, and certain oils in air. See table 6.2. The tether can be quite persistent and hard to

rupture. We have not found a common condition under which the tether is formed. As a theoretically unstable structure, the tether's formation mechanism might involve interaction between liquid and the solid surface. Further research is needed to demonstrate the underlying mechanism.

- (ii) We present a negative electric actuation scheme for oil droplets. As predicted by the electromechanical model, a negative EWOD force is greater than the negative DEP force under the same voltage, and should be able to drive oil droplets, too. However, our experiments to manipulate dielectric droplets under low frequency voltages are not repeatable. A full understanding of the reason for the failure is still lacking. We have excluded the possibility that pinholes are the reason for the failure. A possible explanation would be some interactions between the Teflon layer and the surfactant solution at low frequency. Further investigation into this issue is needed.
- (iii) Another unsolved frequency effect is found in liquid actuation on narrow electrodes. Fan [76] demonstrated this scheme of water actuation by applying voltage at DEP frequencies. We find that water actuated under EWOD frequencies does not follow the electrode-defined path at all. Thus a new advantage of DEP is found in configuring liquid profiles. Still, the reason for the entirely different behaviors between DEP and EWOD needs to be revealed.

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