A Novel Monolithic 3D Printed Axisymmetric Co-flow Single and Double/Compound Emulsion Generator

By

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THESIS
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<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DIW</td>
<td>Direct Ink Writing</td>
</tr>
<tr>
<td>DLP</td>
<td>Digital Light Processing</td>
</tr>
<tr>
<td>FDM</td>
<td>Fused Deposition Modeling</td>
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<tr>
<td>IDT</td>
<td>Interdigitated Transducer</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl Alcohol</td>
</tr>
<tr>
<td>MEMS</td>
<td>Microelectronics and Microelectromechanical Systems</td>
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<tr>
<td>MJF</td>
<td>MultiJet Fusion</td>
</tr>
<tr>
<td>PDMS</td>
<td>Poly Dimethyl Siloxane</td>
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<tr>
<td>PR</td>
<td>Photoresist</td>
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<tr>
<td>SAW</td>
<td>Surface Acoustic Wave</td>
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<tr>
<td>SLA</td>
<td>Stereolithography</td>
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<tr>
<td>SLS</td>
<td>Selective Laser Sintering</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>WGM</td>
<td>Whispering Gallery Modes</td>
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Abstract

Droplet microfluidics has been attracting interests of users in diverse fields of study such as cosmetics, pharmaceutical, and food industries due to its versatility in applications. This vast interest in droplet-based microfluidics is rooted in its specific capabilities to encapsulate biological and chemical reagents inside tiny amount of fluids, offering precise control over specific processes by considering efficiency of mass and heat transfer. In addition, droplets can play a significant role in an emerging field of opto-microfluidics. The softness of the droplet surfaces offers a unique structure for trapping light into a so-called Whispering Gallery Mode (WGM). In such a mode, the droplets serve as soft resonators, exhibiting unique optomechanical properties. Over the years, producing a device which is easy-to-use, cost-effective, and with sub-millimeter-droplet generation ability has always been a challenge among innovators in microfluidics. In our study, we have designed and fabricated a novel droplet generator device which can produce single droplets, and single/multiple droplets in a droplet by implementing monolithic 3D axisymmetric co-flow structure. We used a recent fabrication approach in microfluidics field, additive manufacturing, to fabricate the droplet generator. A commercial, low-cost Stereolithography 3D printer, which is able to offer acceptable transparency, small channel size, and high resolution of printing, produced this device. The device is user-friendly, and any inexpert person can conveniently utilize it. The design of the device is in a “Plug-and-Play” manner, which facilitates the connecting process of tubes to the device, overcoming a traditional issue of microfluidic devices which is fluid leakage. We took deionized water and mineral oil as popular immiscible fluids and tried different combination of generating emulsions, Water in Oil (W/O), Oil in Water (O/W), and Water in Oil in Water (W/O/W). We also investigated the impacts of change in flow rate of each immiscible fluid, which was used as inner, middle, or outer fluid, in the droplet (emulsion) generation. Also, we evaluated the size of emulsions which was influenced by flow rates and we extended our research to study possibility of generating complex droplet structures involving multiple droplets encapsulated in one outer droplet. Lastly, computational modeling of emulsification using phase field method has been performed to understand the fluid dynamics of the emulsion generation process. Overall, by using our novel 3D printed monolithic co-flow droplet generator device, generating single emulsion, monodispersed double emulsion, and multiple complex emulsions is now easier than traditional approaches and the device can be readily applicable in industry for many applications.
Chapter 1 Introduction to Microfluidics and Emulsion Generation in Microfluidic Systems

1.1 Introduction to Microfluidics

1.1.1 What is Microfluidics?

The science and technology of integrated channels on the microscale systems, in which small quantities of fluids can flow in a controlled manner through the designed configurations, is called microfluidics. It is originated from the requirement of planarization and miniaturization in bio(chemical) analysis (Whitesides). Since the fluid dimensions reduce to the microscale from those of macroscopic, diverse behaviors are introduced, which can be categorized by significance of surface tension due to the increase of surface area, efficient mass-heat transfer, and relative dominance of viscous over inertial forces. These features have introduced a systematic way to control and manipulate fluids and their interfaces interactions (Squires and Quake; Atencia and Beebe; Darhuber and Troian).

1.1.2 Droplet Microfluidics

The area of microfluidics has attracted attentions in recent years due to its multidisciplinary research in chemical, biological, medical, physical, and engineering fields of study. Droplet microfluidics is one of the significant subcategories of microfluidics, which generates and manipulates discrete droplets through immiscible multiphase flows inside microchannels (Teh et al.). Its rapid development, both theoretically and technically, in recent 20 years is due to contributing to huge scope of applications. In addition, fabrication and droplet dynamics have been studied in depth since they play a significant role in the process of droplet generation.
1.1.3 Application of Droplets

The interest of using droplet-based microfluidics is based on the droplet’s unique and versatile capabilities. Encapsulating biological processes and chemical reactions and offering such great control through heat and mass transfer over the processes, and isolating compartments of biological and chemical samples are the significant capabilities of the droplet-based microfluidics (Y. H. Hwang et al.).

1.2 Droplet (Emulsion) Generation

1.2.1 Single and Compound Emulsions

Emulsions, fine dispersions of droplets of one liquid in another immiscible liquid, have been utilized in a wide range of industries, including cosmetics, pharmaceuticals and foods. Various colloidal and granular materials have been produced by using emulsions as prepared without further solidification or subjected to further processing (Lee et al.). The emulsion drops can contain smaller drops inside them to form drops-in-drops dispersed in a third continuous phase, which are called double-emulsion drops. We refer to drops which are composed of single compartment as the single emulsion drops or double emulsion drops. It is possible to have additional levels of hierarchy as multiple/compound emulsion drops. The double emulsion has a drop-in-drop configuration, where the inner and outer drops are immiscible; the inner drops and the continuous phase are not necessarily immiscible because the inner drops are completely isolated from the continuous phase by the outer drop. The inner drops can contain additional immiscible drops to give a three-level hierarchy of drops-in-drops-in-drops, which are called triple-emulsion drop. In the current work, we will refer to emulsion drops with a level of hierarchy of two or above as compound emulsions.
1.2.2 Process of Droplet Generation

The process of generating single/compound droplets can be described in general as design and fabrication of a device which is able to generate droplets by following rules of droplet generation, implementing immiscible fluids through the channels of the designed and fabricated device, and observing/collectiong the emulsions generated. Each step of the process can also have sub-steps, for instance, choosing the fabrication method to produce the device is one of the steps which should be taken in the fabrication process, also the wettability features of the device can be changed in this process.

1.2.2.1 Passive and Active Methods

Emulsion generation process can be categorized into passive and active method. The interface of emulsion is deformed under certain flow fields in the passive method and the pinch-off process of the emulsion is naturally achieved as a result of interfacial instabilities, therefore, there would be no energy supply in the process of emulsion generation (Zhu and Wang). On the other hand, local actuations can be exerted during the breakup process of emulsion. Thus, external energy is provided for the excess interfacial energy. The actuation methods can be categorized to thermal, electrical, magnetic, acoustic, and mechanical forces, which can provide more delicate control such as on-demand droplet generation (Shang et al.).

1.2.2.1.1 Passive Generation methods

In the passive method, the immiscible dispersed and continuous fluids meet at a junction and droplet breakup and formation happens due to the geometrical design of the microchannel junction, where local fluid fields and interface deformations are determined at. Droplet formation can be classified into co-flow, crossflow, and flow focusing categories (Christopher and Anna). The fluid
behaviors can be characterized through some dimensionless numbers, which are corresponding to fluid properties, condition, and geometric feature of the device and fluids. One of the dimensionless numbers is the Reynolds number, Re, which measures the ratio of inertial to viscous forces. In general, droplet formation can be described as two competing effects: the deformation and extension of the interface which is caused by local shear stress and the resistance of deformation achieved through capillary pressure. Thus, the crucial forces in droplet microfluidics are viscous forces and interfacial tension. The dimensionless number which can be introduced to address the forces in droplet formation is the capillary number, Ca, which is the relation between strength of viscous to interfacial forces. Another helpful number is the Weber number which is relates inertial force to interfacial tension. The dimensionless numbers and forces mentioned above are the most important ones in droplet formation. However, there are several other forces which become significant under circumstances, such as gravity, buoyancy, and elastic effects, which can be defined as dimensionless numbers (Shang et al.).

1.2.2.1.1 Passive Method Structures

When the dispersed fluid phase is introduced into an inner channel and the continuous phase flows into an outer concentric channel, in the same direction, the co-flow droplet formation set up is made. In the crossflow category, the continuous and dispersed fluids are meeting at an angle. The most common case in which dispersed and continuous phases flow through orthogonal channels and meet at a cross junction is called the T-junction. In this approach of droplet generation, the dispersed phase partially blocks the continuous phase, a shear gradient is established, and the dispersed phase elongates and eventually breaks into droplets. It is important to note that the size of droplet is highly dependent on the shear stress. Another passive approach that is depending on the geometry and structure of channel inside the microfluidic device is the flow focusing in which
continuous and dispersed phases flow coaxially through a contraction region and generate an elongation filament that eventually breaks into droplets. The narrow region is having the function of shear-focusing and contributes to uniform droplet generation.

**Figure 0.1** Three passive structures for droplet generation

a) Co-Flow b) Crossflow c) Flow Focusing

### 1.2.2.1.2 Active Generation Methods

Active methods for generation of droplets can be categorized to thermal, electrical, magnetic, acoustic, and mechanical forces (Chong et al.). Electrical control methods in the process of droplet formation can be classified to two different types of current, direct current (DC) and alternating current (AC) (Tan, Semin, et al.; Link et al.). The electrodes used in this process are directly contacting with the liquids or through a metal wire (Link et al.; H. Kim et al.). In most of the experiments reported, the electric field was located in parallel to the flow direction, however, one perpendicular electrical field was studied numerically (Y. Li et al.). The electric field adds stress
on the interface of the two immiscible fluids which promotes the dispersed phase to pinch off. It is also possible to implement electrodes in a way that they do not need to contact the liquid, by aligning them at both upstream and downstream positions (Tan, Semin, et al.).

Magnetic control of droplet generation is another active method in which a ferrofluid which contains nanomagnetic particles is used and it can be magnetized by external magnetic field, such as magnet, electromagnet, and demagnetized when magnetic field is off (Kahkeshani and Di Carlo; Liu et al.). The location of magnetic field can be either at upstream, downstream, parallel, or perpendicular to the flow direction (Tan, Nguyen, et al.; Y. Wu et al.; Liu et al.).

Another method, which is non-contact method in droplet formation is acoustic control method. In this method, an interdigitated transducer (IDT), which generates surface acoustic wave (SAW), is impacting the liquid-liquid interface and liquid pressure, therefore, the pinch-off process of the droplet is affected (Schmid and Franke; Franke et al.).

The properties of most of the fluids, such as viscosities and interfacial tension, decrease by increasing the temperature. Hence, it is possible to control the droplet generation by changing temperature (N. T. Nguyen et al.). There are multiple approaches to implement increase of temperature in this process, for instance, implementing a focused laser beam to heat the fluids interface, or using a resistive heater which can be located at the junction where droplets are produced to vary the fluid properties (Baroud et al.).

The physical deformation of the channel resulting from piezoelectric or pneumatic actuation is classified as mechanical control method of droplet formation (Xu and Attinger). The channel, which is usually made of elastic materials such as PDMS, can be easily deformed. A pneumatic controller can be placed at upstream or at the junction to help droplet formation (Abate et al.;
Willaime et al.). Also, a fast vibration from a piezoelectric disc can vibrate the fluid inside the device to actuate pinching off process (Zhu, Tang, and Wang; Zhu, Tang, Tian, et al.).

1.3 Motivation

1.3.1 Optical Whispering Gallery Mode (WGM)

Optical Whispering-Gallery Modes (WGM) are a special type of electromagnetic excitations existing in dielectric objects with an axial symmetry (Vahala; Oraevsky; Ward and Benson). Qualitatively, they can be described as electromagnetic waves propagating along the internal surface of a resonator under the condition of total internal reflection (Chylek; Huber and Frost). WGMs are usually excited by use of special optical elements, such as prisms or tapered fibers (Little et al.; Cai and Vahala; Spillane et al.), which provide evanescent coupling between the incident wave and the WGMs of the resonator (Gorodetsky and Ilchenko). They can also be excited using fluorescent molecules as, for instance, in the case of WGMs observed in liquid droplets (Campillo et al.). WGM resonators have enjoyed intense attention during the last decade due to their importance for a variety of applications such as nonlinear optics (generation of optical combs for ultraprecise metrology (Chembo et al.; Chembo and Yu), ultra-low-threshold lasing (Min, Kippenberg, et al.; Min, Kim, et al.), etc.), single particle/single molecule optical sensing (W. Kim et al.; L. He et al.), near-field optical displacement sensors and related devices (force, temperature, etc. sensors), optical antennas (Kraemer and Jones), optomechanics (Kippenberg and Vahala; Anetsberger, Weig, et al.), quantum metrology (Arcizet et al.; Anetsberger, Gavartin, et al.), etc.

All these applications exploit high resonance’s $Q$-factors of the resonances and a high concentration of the highly confined field within a small volume encompassing the surface of the resonator (Povinelli et al.). WGM resonators come in various forms and shapes, such as disk resonators fabricated of silicon or semiconductor materials (Borselli et al.; Soltani et al.), toroid
resonators made of silica (Ilchenko et al.; Armani et al.) or crystalline nonlinear materials (Ilchenko et al.), and spherical resonators made of silica (Vollmer and Arnold; Martín et al.; Hanumegowda et al.) or crystalline dielectrics such as lithium niobite (Savchenkov et al.). Despite the fact that high resonance’s -Q WGMs were initially observed in liquid spherical droplets (Campillo et al.), the majority of recent studies have focused on solid-state resonators due to difficulties in controlling the position of the droplets and exciting their WGMs. However, liquid resonators may have significant advantages over their solid counterparts by offering reduced surface scattering and certain novel capabilities unavailable with solid resonators. To benefit from these advantages, however, one has to solve the problem of stabilizing the spatial position of a droplet and exciting WGMs by a tapered fiber or a prism. This problem can be solved by utilizing recent advances in optofluidics – an emerging technology seeking to integrate photonic and fluidic devices (Wolfe et al.; Valentino et al.).

1.3.2 WGM and Droplet Microfluidics

Droplets have unique structures and they have attracted attentions in this field of study due to their mechanical modes which are characterized by softness parameters for WGM resonators, which are a million times softer compared to what current solid-based technology allows. Liquid structures, therefore, are characterized by record values of optomechanical coolability, and will allow extending optomechanical phenomena to a unique regime, which cannot be achieved with any other optomechanical system. Additionally, droplets can be combined in droplet-inside droplets structures yielding new types of optical and mechanical resonators, which are specific to liquid droplets and droplet structures.

Modern microfluidic techniques have allowed fabricating complex structures, in which one or more small droplets of one material are enclosed in a large droplet of a different material. Sizes
and refractive indexes of the droplets can be selected to allow for excitation of WGM in all droplets. Smaller droplets in these structures can also be replaced by air bubbles, which will then serve as internal scatters for WGMs excited in an encompassing droplet. All these structures possess rich collections of optical and mechanical modes with new and unusual properties. For instance, in optical domain, one can design structures with optical spectra possessing exceptional points, where both real and imaginary parts of two different WGM modes coincide. In the mechanical domain, in addition to acoustic and capillary waves in individual internal droplets, such structures will possess mechanical modes associated with relative motion of the droplets as well as with collective surface capillary waves. Since all these types of mechanical modes lie in different frequency regions, they can be excited and studied separately resulting in distinct mechanical and optomechanical phenomena. The richness of mechanical and optical properties of these structures will translate in novel optomechanical phenomena.

1.4 Scope of Research

Droplet microfluidics has been attracting the interest of researchers in diverse fields of study such as cosmetics, pharmaceutical, and food industries due to its versatility in applications. This vast interest in droplet-based microfluidics is rooted in its specific capabilities to encapsulate biological and chemical reagents inside tiny amounts of fluids, offering precise control over specific processes by considering efficiency of mass and heat transfer. In addition, droplets can play a significant role in an emerging field of opto-microfluidics. The softness of the droplet surfaces offers a unique structure for trapping light into a so-called Whispering Gallery Mode (WGM). In such a mode, the droplets serve as soft resonators, exhibiting unique optomechanical properties. Over the years, producing a device which is easy-to-use, cost-effective, and with sub-millimeter-droplet generation ability has always been a challenge among innovators in microfluidics. In our
study, we have designed and fabricated a novel droplet generator device which can produce single droplets, and single/multiple droplets in a droplet by implementing monolithic 3D axisymmetric co-flow structure. We have focused on the ability of this device on the production size of droplets and its behavior during the process. Overall, by using our novel 3D printed monolithic co-flow droplet generator device, generating single emulsion, monodispersed double emulsion, and multiple complex emulsions is now easier than traditional approaches and the device can be readily applicable in industry for many applications.
Chapter 2 Experimental and Fabrication Methods and Technology

2.1 Introduction to Fabrication

In the past 20 years, the microfluidic chip fabrication has benefited from the introduction of new materials and fabrication techniques. In addition, droplet microfluidic chips have experienced a transition from simple two-dimensional microchannels to multifunctional three-dimensional microchannels. Thus, one of the most important steps in the process of droplet (emulsion) generation is fabricating a device which is following the design criterions of droplet generation. This process is requiring demand-driven selection of materials in coordination with appropriate fabrication methods. Currently, there are many techniques for fabrication of microfluidic chips such as polymer-based replica molding, glass/silicon-based micromachining, commercial modular assembly and newly developed 3D printing. These fabrication techniques will be discussed in detail in the following sections.

2.1.1 Micromachining

The silicon-based industry of microelectronics and microelectromechanical systems (MEMS) has progressed during past decades and met with bio(chemical) requirements for μTAS applications (Whitesides; Nge et al.; Stone et al.; Mark et al.). This progress resulted in shaping the microfluidics and first-generation of chips which were fabricated on silicon/glass substrates through standard micromachining (Abgrall and Gué). Micromachining process normally has 3 steps. First, lithography, in which a substrate is cleaned and spin-coated with a photoresist (PR) layer and then the PR layer is covered by mask with patterns, which are designed in favor of the application, of transparent and opaque areas. The PR is selectively eliminated after the exposure and development, and the micropattern on the mask is transferred onto the substrate. Etching is
the second step which is taken under certain etchant. Microchannels with the desired geometry are generated by selective elimination of substrate in this process and finally the PR is removed. In the last and third step, two micromachined substrates are aligned and made to cling to each other. This step is necessary to create closed channels rather than open ones. For bonding the two substrates, adhesive bonding or thermal fusion can be used to assemble the device and seal it properly. This type of fabrication is offering thermal stability under high temperature for some droplet-based chemical syntheses. Also, it is solvent resistant for an organic environment for many droplet-based reactions. In addition, the specific properties of this fabrication method offer high thermal conductivity, and electroosmotic flow stability. On the other hand, the large-scale production of microfluidic chips using this fabrication technique is hindered by high cost, demand for clean-room equipment, and time-consuming process (Shang et al.).

2.1.2 Molding Replication

The polymer replica molding technique has been introduced in droplet microfluidics to satisfy the demand for rapid prototyping and mass fabrication of the chip. In addition, this technique helps both laboratories and industries who need low-cost and disposable chips in the fields of biomedical and clinical droplet microfluidic application (Kuo and Chiu). Among the all techniques in replica molding, soft lithography is the most representative one, which refers to a set of techniques using a soft elastomeric material replica, typically poly (dimethyl siloxane) (PDMS), to transfer structures or patterns from a master. The procedure includes preparing a transparent mask with a generated pattern, transferring pattern through photolithography to a photoresist layer, and finally casting the PDMS prepolymer on the mold and thermally curing to obtain the micropatterned channel (McDonald et al.). PDMS is also offering intrinsic advantages such as making the sealing process of the chip simpler, using air or oxygen-plasma oxidation without implementing high
temperature or pressure. However, PDMS has its limitations in some aspects. The small molecular adsorption, high-pressure intolerance, and organic incompatibility hinders the usage of this material in certain situations (Shang et al.).

2.1.3 Modular Assembly

The interest of using modular assemblies for droplet microfluidics originated from the problems with conventional polymer chips based on quasi-2D planar microchannels, in which droplets are susceptible to contact the channel walls and the generation of the droplets becomes unstable. To overcome this issue, the selection of surfactants which can modify the wettability of the channels is required, however, this process is laborious and complicated. Therefore, constructing 3D droplet microfluidic channel, using a geometrical approach, was introduced by researchers. A typical device which is using a modular assembly technique in fabrication of droplet microfluidic chips could be cylindrical glass capillaries that are inserted into PDMS channel molds (Takeuchi et al.). These capillaries, either cylindrical or square shape, can be assembled in different alignments such as axisymmetric flow-focusing or in a sequential co-flow manner. The chemical resistance of the glass capillaries would allow the droplet generating in either hydrophobic or hydrophilic systems (Shah et al.). In addition, capillary channels can be assembled into multichannel junction or sequential insertion regimes for parallel and hierarchical processing. In addition to capillary assembly, there are other types of modules for constructing droplet microfluidic chips, such as using Teflon tubes and micro ferrules which were assembled into a hydrodynamic focusing nozzle, a micropipette tip and self-setting rubber, or needles and tubes for a faster and cheaper fabrication (Terray and Hart; P. Wu et al.; Lapierre et al.).
Figure 2.1 Different techniques of fabrication used for producing droplet microfluidic chips. a) Four SU-8 molds fabricated by the UV lithography process and using PDMS sheets in the module molding process. The PDMS modules were aligned and bonded manually after oxygen plasma treatment to produce the droplet microfluidic device. b) Microfluidic chip prepared by using a seven-bored capillary array as the injection tube (Bartolo et al.). c) the microfluidic chip fabrication through fiber embedment in PDMS and capillary insertion (Takeuchi et al.). d) Microfluidic channels were assembled by commercially available components (Teo et al.). e) Aligned glass capillaries for generation of different types of emulsions (Herranz-Blanco et al.).
2.1.4 3D Printing

3D printing is a flourishing field in droplet microfluidics which involves techniques for generating 3D structures, such as valves and pumps, in a single step procedure to promote industrialization processes that require high-throughput performances, and multiple functions of droplet microfluidic chips (Au et al.; Ho et al.; Yazdi et al.; Blow). In addition, this brand-new technology can play an alternative role for soft lithography fabrication technique since it is offering low cost and time efficient procedure. Various techniques in microfluidic 3D printing for delivering a successful chip have been introduced based on the manner of the raw material deposition. The extrusion-based method, vat polymerization, photocurable polymer printing, and powder bed fusion based printing are the techniques which have been used in microfluidics field of study (Shang et al.).

2.1.5 Other Methods for Chip Fabrication

Implementing new technologies and materials in droplet microfluidic chips can promote new techniques for the chip fabrication. Paper-based microfluidic chips are one of the approaches that enabled pump free operation, facile preparation, and surface-related reactions (Martinez et al.; Thuo et al.). In addition, by using “Origami” technique, paper folding, microfluidics chips can be made (Liu and Crooks). Paper materials have an intrinsic merit in fabrication of chips such as biocompatibility, abundant resources and porous structure. On the other hand, combining different fabrication techniques would result in a hybrid fabrication method which can enable improvement of the chip functionality, such as combining elements (optical components or microheaters) in the chip (Bertassoni et al.; Blazej et al.).
2.2 3D Droplet Microfluidics

Recent development of additive manufacturing, that is, 3D printing, opened a new door for fabrication of microfluidic devices. This technique has attracted the attention of researchers due to its freedom of designing novel structures, capability of building truly 3D structures, easy to learn and implement the fabrication learnings, and digital design and fast prototyping. As a result, a tremendous growth in implementing 3D printing in microfluidics has occurred in recent years. Here, we introduce the classification of this technique based on the raw material deposition and recent 3D printing development in passive droplet microfluidics.

2.2.1 Extrusion Based Method

The widely used technique of 3D printing is extrusion-based method which includes Fused deposition modeling (FDM) and Direct Ink Writing (DIW). For FDM process, a material, which is thermoplastic, is heated in the printing nozzle and then extruded and cooled down immediately. This process forms layers of the thermoplastic material. In DIW method, pressure is driving the material, usually liquid, and photocuring or chemical crosslinking it leading to solidification (Pranzo et al.). In general, extrusion-based technique in 3D printing is offering low cost production, simple process, and wide range of materials for using in microfluidic applications. However, the transparency and resolution of the printed devices are low which limits its application (Yazdi et al.).

2.2.2 Vat Photopolymerization

Stereolithography (SLA) and Digital Light Processing (DLP) used in conjunction are forming the Vat Photopolymerization method in 3D printing (Kuo et al.). Resin, which is a photosensitive liquid, is used as the material that can be cured by ultraviolet (UV) light. SLA technique is using
a laser beam to scan the liquid resin and its tracks are determining the layer structure which is cured on the lift. In the next step, the lift elevates for laser to scan another liquid layer which is cured on the previous layer. This process is repeated until the whole object is built on the platform. For DLP, the light, from laser or a UV lamp, is exposed to the liquid resin through a mask which determines the layer structure. The whole object is built by multiple exposures instead of layer by layer scanning in SLA method. The mask is not necessarily physical, and it can be digital. In general, the Vat Photopolymerization is widely used in droplet microfluidics since it is offering better resolution and transparency (H. H. Hwang et al.).

2.2.3 Photocurable polymer printing

Another technique for printing objects is by using a photo resistive liquid resin and using a printer like the commercial inkjet printer (F. Li et al.). The droplet of liquid resin is extruded through the inkjet nozzle and then cured by UV light to form a layer. This procedure is repeated until the whole object is successfully printed. This technique is known as photocurable polymer printing, or inkjet 3DP or photopolymer inkjet printing (PolyJet), and its advantage is its capability to use wide variety of materials, such as soft or hard plastics, with high resolution of printing, which in nature is favorable for integrated microfluidic devices (Y. He et al.).

2.2.4 Powder bed fusion based method

This process of 3D printing includes Selective Laser Sintering (SLS) and MultiJet Fusion (MJF). Since this type of 3D printing is offering rough and non-transparent surface, they are rarely used in droplet microfluidic devices (Amin et al.).
Figure 2.2 3DP techniques used in droplet microfluidics (Zhang, Ji, et al.). a) Fused deposition modeling (FDM). b) Direct ink writing (DIW). c) Stereolithography (SLA). d) Digital light processing (DLP). e) Photopolymer inkjet printing (Polyjet).
2.3 Passive Droplet Generation Using 3D Printing in Droplet Microfluidic Systems

2.3.1 Passive Droplet Generation in 3D Printing: Single Monolithic Devices

The idea of generating droplets in a microfluidic device using a simple and straightforward approach is to print the device via a 3D printer rather than fabricating it with conventional methods, such as soft lithography (SLA) etc. Various structures were designed, such as coflow, flow focusing, etc, using different materials as highlighted in the following lines. A SLA 3D printer was used to print T-junction and flow-focusing structures (Figure 2.3 a) (Bhargava et al.). A Polyjet 3D printer was used to print a T-junction producing droplets (Figure 2.3 b) (Donvito et al.). FDM printer was used also to fabricate flow-focusing structures (Figure 2.3 c) (Morgan et al.). These three experiments were the pioneers in 3D printing for droplet microfluidics. However, the structures of the aforementioned devices still formed 2D flow fields for droplet generation. A 3D printed structure which could introduce 3D flow fields was introduced designed as an improvement over the previous three designs (Figure 2.3 e, f) and it could generate different types of single emulsions, Oil-in-Water and Water-in-Oil emulsions, and even double emulsions by implementing the additive manufacturing fabrication technique (Zhang, Li, et al.). Overall, single chips for generating droplets using different passive method structures either in 2D or 3D flow fields have been reported in many studies.
Figure 2.3 Current 3D printing technologies applied in droplet microfluidics. a) A flow focusing structure printed by SLA 3D printer. b) A T-Junction structure printed by using Polyjet technology. c) A flow-focusing structure built by using FDM printing technology. d) a non-planar structure built by SLA 3D printing technology e) Different types of emulsions were produced by a non-planar structure.

2.3.2 Passive Droplet Generation in 3D Printing: Hybrid and Modular Devices

Hybrid devices can be defined as using 3D printing to form a configuration in which needles, glass capillaries, and tubing are in such an arrangement that at least two immiscible phases can form droplets (Qiu et al.). 3D printing can help the assembly of conventional glass capillaries to form a suitable flow configuration for droplet generation. Normally, assembling glass capillaries for the purpose of droplet generation requires a delicate manual process, which cannot be reproducible. Therefore, 3D printing can help in assembling complex glass capillaries. In addition, achieving comparable channel dimensions by current 3D printer’s resolutions is difficult, so manipulating both glass capillaries and 3D printing can be taken into consideration to achieve droplet size of conventional methods and overcome the manual assembling difficulties of glass capillaries. A set of grooves and connection fasteners were designed, and 3D printed in order to enable a precise and controlled assembly of flow-control modules (Figure 2.4 a ) (Meng et al.).
In another investigation, a screw-nut structure to align the capillaries (Figure 2.4 b) (Martino et al.). Low-cost commercial needles and tubes were connected and configured by printing manifolds to produce single and double emulsions (Figure 2.4 c) (Vijayan and Hashimoto). A SLA printer was used to produce a chamber in which tubing was inserted to form a gap (channel) that can generate droplets (Figure 2.4 d) (Zhang, Aguirre-Pablo, et al.). A modular device was designed and fabricated to have the flexibility of using different size of capillaries which can offer wide range of droplet size (Zhou et al.). In this process, different modules were introduced for generation of single, double, Janus emulsions by replacing each module for introducing different liquid inputs. A flexible T-junction was introduced by using a screw and nut system, which was 3D printed, and the droplets were generated at the gap which was formed by screw and the channel wall (H. Van Nguyen et al.). In this device, production of different size of droplets is dependent on the gap size which can be tuned (Figure 2.4 e). Furthermore, modular 3D printed devices have been introduced in the droplet microfluidics. For instance, A SLA 3D printer was used to build blocks, including single and double inlet modules, which can be integrated through detachable notch structure (Figure 2.4 f) (Ji et al.). In another study, A set of modular printed parts were used to produce single and double emulsions by connecting the modules through screw threads and form a droplet generator (Figure 2.4 g) (Morimoto et al.). In summary, the hybrid and modular droplet generator devices have been demonstrated to have advantages, such as overcoming conventional difficulties in fabrication and offering multi functionality by using 3D printing.
Figure 2.4 Hybrid and Modular Devices for Passive Droplet Generation using 3D Printing. a) A 3D-printed groove and connection fastener for assembly of flow modules to produce multiple emulsions. b) A 3D-printed holder mold for flexible alignment of the glass capillary for generating double emulsions. c) A 3D-printed chamber combined with commercial tubing to create smaller droplets. d) 3D-printed chamber combined with a nut and a commercial screw. e) A T-junction structure built by a 3D-printed chamber with a nut and a commercial screw. f) A notch structure with an O-ring connected each 3D printed module printed by a SLA 3D printer. g) Assembled 3D-printed modules to produce multiple emulsions with screw-thread as connection.
2.4 Design and Fabrication of Single and Double/Compound Emulsions Generator

3D printing has the unique capability of fabricating arbitrary complex 3D geometries for microfluidics applications. As we discussed in previous sections, this fabrication technique can overcome conventional fabrication difficulties of droplet microfluidic chips, such as the demand for delicate manual fabrication of glass capillaries and its reproducibility, high-pressure intolerance of replica molding, and the demand for clean-room equipment of micromachining. In addition, Computer-aid as an important role in integrating digital design, automated fabrication and fast prototyping are the advantages of the 3D printing method which allow researchers and designers to integrate different channel types and even introduce new designs and novel devices in droplet microfluidic field of study.

Over the years, producing a device which is easy-to-use, cost-effective, and with sub-millimeter-droplet generation ability has always been a challenge among innovators in microfluidics. In our study, we have designed and fabricated a novel droplet generator device which can produce single droplets, and single/multiple droplets in a droplet by implementing monolithic 3D axisymmetric co-flow structure. We used a recent fabrication approach in microfluidics field, additive manufacturing, to fabricate the droplet generator. A commercial, low-cost Stereolithography 3D printer, which can offer acceptable transparency, small channel size, and high resolution of printing, produced this device. The device is user-friendly, and any inexperienced person can conveniently utilize it. The design of the device is in a “Plug-and-Play” manner, which facilitates the connecting process of tubes to the device, overcoming a traditional shortcoming of microfluidic devices which is fluid leakage.
2.4.1 Design of the Device

Different approaches in the design of channels for passive droplet generation in microfluidic chips have been shown in section 2.3. Introducing new designs and devices have been challenging the researchers in the past few years since the droplet generation approaches have been settled for almost 20 years. However, the technology of materials and machinery is advancing and attracting scientists to implement these new technologies in different fields of study. We have designed and fabricated a novel droplet generator device which can produce single droplets, and single/multiple droplets in a droplet by implementing monolithic 3D axisymmetric co-flow structure.

The design of channels has been illustrated in Figure 2.5. For generating single emulsions, two units (B,C) of this device can be used in which unit B is responsible for directing the dispersed phase to the orifice, whose diameter is 750 micrometer, and unit C is directing the continuous phase to the outlet. When two phases are meeting at the orifice, the droplet formation is happening. For generating double/compound emulsions, unit A should be used, simultaneously with units B and C, for inserting the most inner fluid. It should be taken into consideration that all the units, A, B, and C, have been printed in a single process which defines this device as a monolithic 3D printed one.

Figure 2.5 The designed emulsion generator with three units (A, B, and C). a) The three-dimensional view of the designed device. b) Units A, B, and C are shown. Section D is the outlet and inlets are shown as arrows.
We used Solidworks from Dassault Systèmes company to 3D design the device and make STL files, which are the files readable into a 3D printing software. Finally, we transferred the STL files to PreForm software, a software which is an interface between the printer and computer.

2.4.2 Fabrication

3D printers have made the process of fabricating microfluidic chips easier since they are offering single step procedure of production, meaning the designed device or channels could be fabricated automatically by the 3D printer and it is ready to use immediately after printing process is done, however, for achieving a satisfactory result for the favorable application, post processing is needed in some cases.

The designed device is printed with an inexpensive commercial 3D printer, Form3 (Formlabs, Inc) which only costs $3000, and it is based on the stereolithography technique to print structures. The great advantage of using this printer is its clear resin which provides excellent transparency and thus allows researchers to observe internal fluids and develop various applications of microfluidics, such as emulsion generation, which requires optical access. In addition, the Young’s modulus of post cured clear resin is 2.8 GPa which is greater than PDMS, $0.75 \times 10^{-3}$ GPa. Therefore, the device is capable of withstanding higher liquid flow rates and input pressure.

To achieve the best resolution and transparency of the printed device, we chose the highest possible resolution of the 3D printer which is 25 microns. This resolution is defining each layer’s thickness in the process of printing and it would result in a smooth surface finish of device that would provide a transparent clear droplet generator. Therefore, during the process of inserting the fluids inside the device, we can control the sequence of inserting and prevent wetting of unfavorable surfaces, since wetting is impacting the droplet size.
Another important factor in STL 3D printing is the clogging issue of channels. Since the resin is liquid and it is curing during 3D printing process by a UV light, the design of channels should be in a way that it can let the resin flow out of it otherwise the resin would be clogged in the channel which is not desirable. To prevent the clogging of the channels, we designed the smallest channel of the device, the Unit A’s orifice with 600 microns diameter, as small as possible the printer can print without clogging. In addition, washing the final product with Isopropyl Alcohol (IPA) can help the uncured resin to dissolve and help us to make sure there is no blockage of channel in the device.

2.4.3 Materials and Apparatus

In our study, we could generate single, double, and compound emulsions of water and oil. We used three different liquids, namely, deionized water, mineral oil, and ethanol, for generating different combinations of emulsions including single oil-in-water (O/W) emulsions, double and compound water-in-oil-in-water (W/O/W) emulsions. In this process, we added surfactants to the continuous phases for stabilizing the emulsions and prevent the coalescence and rupture of emulsions. To investigate and measure the emulsion’s size, we collected them in a transparent borosilicate glass beaker (Kimax) which was filled with the continuous phase fluid.

In the production of single and double emulsions, using appropriate surfactants plays important role in the stability of the emulsions. We could stabilize the O/W emulsions by using Polyglycerol Polyrincinoleate 90 (PGPR 90) 1% (DanisCo) in mineral oil and using a solution of ethanol-water with 0.1% of sodium dodecyl sulfate (SDS) (Fisher BioReagents). In addition, for producing double/compound emulsions, we used deionized water as the most inner phase to generate W/O/W emulsions.
The liquids were infused to the device by using three syringe pumps, Chemyx 3000 Nexus, and commercial syringes, Becton, and clear Tygon tubes, Saint-Gobain, for directing the liquids to the device. Collected emulsions were observed via Nikon Eclipse Ti -S microscope and pictures were taken by Phantom Miro M310 camera which was mantled on the microscope. The evaluation of emulsions’ size was performed by using ImageJ software.
Chapter 3 Single Emulsion Generation Using 3D Printed Device

3.1 Mechanism of Emulsion Generation

Single and double emulsions generation process is significantly dependent on the fluid’s properties, such as viscosity, density, etc., and hydrodynamic forces applied through the interaction of fluids. Numerous studies have been developed on the mechanism of droplet generation in microfluidic devices. Some authors classified the formation mechanism into the confined, unconfined, and partly confined breakup mechanism, which are called squeezing, dripping, and transition regime respectively (Bashir et al.; Seemann et al.; Korczyk et al.).

The factors influencing the dynamic behaviors of the emulsion generation are essentially affecting the process of single and double emulsion generation (Wang et al.). Therefore, we have shown the forces exerting on a growing head-on droplet in Figure 3.1. Primarily, a brief discussion on the forces acting on a head-on spherical droplet (O/W and W/O/W) was made to understand the behavior of the emulsion generation. As it is shown in the Figure 3.1, for the generation of single emulsions, the interfacial tension force, \( F_\gamma \), acting around co-flow interface where the droplet is expanding and getting detached, is described as a holding force. This force can be added to another similar force when we try to produce double emulsions, as it is shown in Figure 3.2 with \( F_\gamma \) and \( f_\gamma \), one for the inner interface and another one for the outer interface.

The effects of the detaching forces are more complicated in both single and double emulsion generation process, such as hydrostatic thrust of the outer fluids, gravity force, inertia forces (\( F_{\text{Inertia}} \)), Laplace pressure force (\( F_{\text{Laplace}} \)) of the inner and middle fluids in double emulsion generation and dispersed phase in single emulsion generation, and viscous shear force (\( F_{\text{Drag}} \)), driving the droplet breakup and detachment. The drag force of this process is depending on the
viscosity of the dispersed phase, its velocity and the continuous phase velocity, and droplet and orifice diameters. For the inertia force, the force is produced by the momentum transfer from the droplet phase when it is exited from tip of the orifice and entered the drop phase and this force is dependent on the properties of droplet, such as density, droplet phase flow rate, and the orifice size. Lastly, viscous resistance force is also indicated in Figure 3.1 due to the viscosity of the inner fluid.

![Figure 3.1 Mechanism of single emulsion generation in the 3D printed device.](image-url)
Among all the forces applied in the process of droplet generation, interfacial tension force and viscous resistance force are acting upward, while both drag force and inertia force are defined as the streamwise forces. In general, a typical dripping regime can have a force balance which is the basic mechanism of the drop formation.

\[ F_\gamma + F_{\text{viscous}} \approx F_{\text{drag}} + F_{\text{inertia}} \]

Two forces, gravity and hydrostatic thrust, have not been considered in this relationship since their impact on this process is insignificant. Single emulsion drops are forming at the tip of the orifice and then detach when they reach a size where the detaching force due to the continuous phase exceeds the holding force. After the droplets detach, the viscous shearing force due to the continuous phase carries the droplets downstream. For double emulsion droplets, the procedure is
like what we mentioned above but with few differences. Double emulsion drops would detach from the inner orifice when the detaching forces of the middle phase exceed the holding force and inner droplets would accumulate at the middle phase drop until the drop reaches a size where detaching force of outer phase overcomes the holding force.

3.2 Single Emulsion Generation in the 3D Printed Device

The generation of oil-in-water emulsions was performed in our study by varying flow rates of different liquid phases. In our study, different emulsion sizes were achieved by varying the dispersed and continuous liquid phases. Therefore, we need to first investigate the effects of changing flow rates, either dispersed or continuous, on the variation of emulsions size.

3.2.1 Experimental Setup and Its Performance

The experimental setup for generation of either single or double/compound emulsions is depicted in Figure 3.3. For the stable production of the emulsions, a vertical holder was used to grab the device and hold it during the entire experiment. Firstly, we placed the device in an orientation so that the air inside can exit the device. This would help us to reduce the air blockage in our system which can influence the process of emulsion generation. In addition, to prevent the detachment of tubes, which can result in air leakage in the device, we applied UV glue to the tubes connected to the outlet and inlets and cured it for few hours before using the device.

The continuous phase (water-ethanol solution) was first infused to wet the outer surface of the unit B. This would help us to prevent bigger size of emulsions. If the dispersed phase (oil) first wets the outer surface of the orifice, the droplets would expand on the surface and they would become larger in size. After the continuous phase wetted all the areas of unit B and exited from the outlet, we can start infusing the dispersed phase into the device and it reaches the orifice finally. Upon
generation of the first emulsion, we pause the experiment and change the orientation of the device in such a way that the outlet faces to the ground.

**Figure 3.3** The experimental setup and the generation of double emulsion.

The entire process which was explained in the previous paragraph would be repeated for double/compound emulsions generation with a difference before changing the orientation of the device. The sequence of liquid infusion would be first outer phase should wet the surface of unit C, then middle phase should wet the surface of the unit B, and finally inner phase can be infused to the device.
The generated emulsions were collected from the outlet into a transparent Borosilicate glass beaker and pictures of emulsions were taken immediately after the collection.

### 3.3 Evaluation of Emulsion Size

The first step to be taken in this part is to analyze the single emulsions’ behavior during the production process which is the requirement for achieving satisfied results in the next step, the double emulsions generation. Therefore, we will dig into the dripping regime behavior of the single emulsion production which we could observe in the experiments.

To investigate the effects of varying the dispersed and continuous phase flow rates on the droplet size, we considered three different flow rates for the dispersed phase and we kept increasing the continuous flow rate for each of these flow rates. After each set of flow rates, we collected three emulsions and took their pictures. After the collection of all varieties of emulsions, in various set of flow rates, we post-processed the data collected and measured the size of each emulsion with ImageJ software.
We started the oil emulsion generation process by infusing 40 $\mu L/min$ for the dispersed phase flow rate and 300 $\mu L/min$ for the continuous flow rate. After collection of the emulsion samples, the continuous flow rate was kept constant and the dispersed flow rate was increased to 70 $\mu L/min$. The increase in the dispersed flow rate was repeated once more by increasing the dispersed flow rate to 100 $\mu L/min$. The entire procedure of increasing the dispersed flow rate was repeated for various continuous flow rates, as illustrated in Figure 3.5.

Figure 3.5 shows the diameter of the collected emulsions corresponding to its dispersed and continuous flow rates. The dispersed flow rates are shown in diamond, square, and triangle that are corresponding to 40 $\mu L/min$, 70 $\mu L/min$, and 100 $\mu L/min$ flow rates respectively. The horizontal axis is indicating the continuous flow rate and the vertical axis is the measured droplet
size. We could achieve different range of emulsion size, from 1838 to 3090 micrometers, by varying the dispersed and continuous flow rates (continuous flow rate up to 4000 $\mu L/min$).

By analyzing the results of the Figure 3.5, we could understand the effect of the continuous flow rate on the droplet size: when the dispersed phase flow rate is constant, the droplet size would decrease when the continuous flow rate is increased. For better investigation of this fact, we kept the dispersed flow rate as 40 $\mu L/min$ and increased the continuous flow rate from 300 $\mu L/min$ to 11000 $\mu L/min$ to achieve the smallest emulsion possible from the orifice with diameter of 750 $\mu m$. We could achieve an emulsion as small as 1250 $\mu m$ in a continuous flow rate of 11000 $\mu L/min$. The range of emulsion diameter in Figure 3.5 is from 2680 $\mu m$ to 1250 $\mu m$. In addition, the trend line is having a decline trend in that indicates the droplet size decrease by increasing the continuous flow rate.

![Figure 3.5 Emulsion dimension ($\mu m$) and Continuous flow rate ($\mu m$) in 40 $\mu L/min$ dispersed flow rate.](image)

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The impact of changing the dispersed flow rate and keeping the continuous flow rate constant can be understood from Figure 3.6. For example, at the continuous flow rate of 300 $\mu L/min$, the 40 $\mu L/min$ dispersed flow rate has an average emulsion size of 2680 $\mu m$, the 70 $\mu L/min$ dispersed flow rate has an average emulsion size of 2790 $\mu m$, and the 100 $\mu L/min$ dispersed flow rate has an average emulsion size of 2994 $\mu m$. In another instance, at the continuous flow rate of 600 $\mu L/min$, the 40 $\mu L/min$ dispersed flow rate has an average emulsion size of 2537 $\mu m$, the 70 $\mu L/min$ dispersed flow rate has an average emulsion size of 2559 $\mu m$, and the 100 $\mu L/min$ dispersed flow rate has an average emulsion size of 2667 $\mu m$. Therefore, we can conclude that the higher dispersed flow rate at a constant continuous flow rate would result in bigger size of emulsions. This fact is due to the increase in amount of emulsion and as a result it requires more
viscous force to detach the emulsion. Since, the viscous force is constant, due to constant continuous flow rate, the emulsion is becoming bigger to finally pinch off and get into a stable form.

All three trendlines, which are corresponding to three different dispersed flow rates, are following declining trend. Therefore, we can conclude that in the dripping regime, by increasing the continuous flow rate, we can achieve smaller emulsion size. In addition, the emulsion size difference among three dispersed flow rates become smaller when the continuous flow rate value increases. For instance, at continuous flow rate of 3500 μL/min, the 40 μL/min dispersed flow rate has an average emulsion size of 1899 μm, the 70 μL/min dispersed flow rate has an average emulsion size of 1935 μm, and the 100 μL/min dispersed flow rate has an average emulsion size of 1970 μm. Therefore, in higher continuous flow rates, the emulsion size would be more uniform due to the significance of the drag force in the mechanism of emulsion generation.

3.4 Frequency of Emulsion Generation

During the experimentation, we could record the time of single emulsion generation and investigate its frequency. The time of generation was recorded by measuring the time from the beginning of pinching off an emulsion to the beginning of next emulsion pinch off. Figures 3.7 and 3.8 show the frequency of the single emulsion production on the vertical axis, versus the continuous flow rate on the horizontal axis. Similar to the Figure 3.6 in the previous section, three dispersed flow rates are shown in diamond, square, and triangle. From Figure 3.8, we can understand that the frequency of single emulsion generation is increasing either by increase of dispersed or continuous flow rate. The trendline for each of the dispersed flow rate is indicating the same fact because it is following an inclined trend with the increase of continuous flow rate.
Figure 3.7 Continuous Flow rate (μL/min) and Frequency (mHz) of single emulsion generation at rate 40 μL/min dispersed flow rate.

Figure 3.8 Continuous Flow rate (μL/min) and Frequency (mHz) of single emulsion generation at three different dispersed flow rates.

The increase in dispersed flow rate would result in a higher frequency production of single emulsion. For instance, at the continuous flow rate of 2000 μL/min, the 40 μL/min dispersed flow rate has an average frequency of 128.15 mHz, the 70 μL/min dispersed flow rate has an
average frequency of 206.79 millihertz, and the 100 $\mu L/min$ dispersed flow rate has an average frequency of 270.73 millihertz. To better understand the impact of continuous flow rate on a constant dispersed flow rate, we extended the increase in continuous flow rate while dispersed flow rate was 40 $\mu L/min$. Table () is showing that by increasing the continuous flow rate even to higher values, the frequency of the generation is increasing.

In general, understanding the frequency of the emulsion generation would help the researchers to achieve the appropriate number of droplets in a minute. For instance, if a person is looking for one emulsion generation in a minute, the frequency to look for is 16.67 millihertz. Therefore, the flow rates of continuous and dispersed phases can be estimated by checking the Figure 3.8 and tuning the infusion flow rates in syringe pumps.
Chapter 4 Double and Compound Emulsions Generation in the 3D Printed Device

4.1 Double and Compound Emulsions Generation Experiment

We extended our experiments to investigate the performance of our 3D printed device by infusing the inner phase, deionized water, to produce double and compound emulsions. The inner liquid was infused to the unit A with lower flow rate than the middle phase since the middle phase should play the continuous fluid role for the dispersed deionized water. Therefore, the infusion of three liquids, deionized water as the inner phase, mineral oil as the middle phase, and the water-ethanol solution as the outer phase, was taken place in our experiments by considering the lowest flow rate for the inner phase and higher flow rates for middle and outer phases.

The experiment was started with the middle phase flow rate of $10 \mu L/min$ and the outer flow rate of $30 \mu L/min$. To produce inner emulsions in a dripping regime, we chose $2 \mu L/min$ as the flow rate of the deionized water since it has lower value than the middle phase. In the process of double emulsion generation, the water-in-oil (W/O) emulsion was generated at the first orifice, unit A’s orifice, and then it moved to the second orifice, unit B’s orifice, where oil-in-water (O/W) emulsion has been generating. Since the orifice of the unit A is smaller than unit B, the emulsion size of W/O can be smaller, and it can be encapsulated by the O/W emulsion. In addition, by tuning the middle phase flow rate, the smaller and more W/O emulsion is possible to be encapsulated. This would be discussed in detail in the following sections of this chapter.

4.2 Evaluation of the Emulsions Size

Double and compound emulsions generation process is more complex than the single emulsion generation since one more phase is added to the process. The generated O/W emulsions can include single or multi water emulsions to provide water-in-oil-in-water (W/O/W) emulsion. As a result,
the number and size of the inner and outer emulsions are dependent on different factors. In this section, we try to investigate these factors in detail by showing the experimental results.

**Figure 4.1** Double/Compound emulsions generated in different sizes.

In the process of double/compound emulsion generation, the size of the inner and outer emulsions and number of the inner emulsions are highly dependent on the value of the flow rates, since the drag force of the continuous phase is dominating the interfacial force and causing the detachment of the emulsion from the orifice, the increase in flow rate of the continuous phase is playing a significant role in this process. In addition, as discussed in last chapter, the increase in the dispersed flow rate can also result in the change in size and number of droplets. Figures 4.2 and 4.3 are the experimental results for double and compound emulsions generation.
Figure 4.2 is showing the outer and inner size of emulsions in different middle and outer flow rates. The results are separately shown in this table by upper and lower data sets. The upper part is indicating the outer emulsion size and the lower part is showing the inner emulsion size. In this table, the inner flow rate was kept constant, 2 $\mu L/min$, to investigate the impact of increase in middle and outer flow rates on the emulsion size. The vertical axis is showing the emulsion size and the horizontal axis is showing the outer flow rate. In our experiment, we started with middle flow rate of 10 $\mu L/min$ and outer flow rate of 30 $\mu L/min$. Then, the middle and outer flow rates were increased from 10 $\mu L/min$ to 30 $\mu L/min$ and 30 $\mu L/min$ to 150 $\mu L/min$ correspondingly. Different middle flow rates are shown in different color dots.

The number of produced and collected inner emulsions are shown in Figure 4.3. Vertical axis is corresponding to the number of inner emulsions and the horizontal axis is showing the outer flow rate. The number of emulsions in some sets of middle and outer flow rates is varying because achieving a uniform production of specific number of emulsions needs tuning of the flow rates. Since we chose specific values, four values for the middle flow rate, we experienced this behavior in some sets of middle and outer flow rates.
Figure 4.2 Inner and outer emulsions size at 2 μL/min inner and different middle and outer flow rates.

Figure 4.3 Number of inner emulsions generated at constant inner flow rate of 2 μL/min and four different middle flow rates and different outer flow rates.
The outer emulsion size, O/W, can be impacted by different factors in the production process. The upper part of the Figure 4.2 is indicating the behavior of the outer emulsion in various middle and outer phases flow rates. We can understand from Figure 4.2 that by increasing the outer flow rate, outer emulsion size is becoming smaller. The trend lines are also indicating this fact. In addition, when we are comparing two emulsions in a same outer flow rate situation, the bigger emulsion size, O/W, could be resulting from three possible situations. These situations can happen at a same time or one of them can result in the bigger size of O/W emulsion. These situations can be classified as 1) the emulsion is including higher number of inner emulsions, or 2) the average inner emulsion size is larger, or 3) the flow rate of the middle phase is higher.

Here we discuss the results of experiments listed in Figures 4.2 and 4.3 and explain the reasons of the difference in outer emulsion size in 4 middle flow rates based on the reasons introduced in the last paragraph. At the outer flow rate of 15 $\mu L/min$, the increase in middle phase flow rate resulted in higher number of inner emulsions and bigger outer emulsion size. When we increased the outer flow rate to 30 $\mu L/min$, the 30 $\mu L/min$ middle phase flow rate still showed a bigger outer emulsion size. In addition, the outer flow rate of 25 $\mu L/min$ is having higher flow rate and number of emulsions, and bigger inner emulsions than the 20 $\mu L/min$ oil flow rate so it has bigger outer emulsion size. The 10 $\mu L/min$ is showing an average size close to 25 $\mu L/min$ and bigger than 20 $\mu L/min$ because of its significant bigger inner emulsion and slower flow rate which are resulting in the bulging of outer emulsion. In addition, the significant difference in both inner and outer emulsion size at 20 $\mu L/min$ is due to small inner emulsion which was resulted by the incomplete pinch off process. It means during this process the second inner emulsion was broken into two parts and one part encapsulated in the oil emulsion and the other part encapsulated in the next emulsion.
In three other outer flow rates, 60 $\mu L/min$, 75 $\mu L/min$, and 150 $\mu L/min$, the 10 $\mu L/min$ middle flow rate has shown smaller outer emulsion since it has bigger inner emulsion and the oil emulsion pinches off faster, as soon as the inner emulsion enters it. At the outer flow rate of 60 $\mu L/min$, the 30 $\mu L/min$ middle flow rate has shown smaller outer droplet size since it is including less and bigger number of droplets, same as the 10 $\mu L/min$ middle flow rate as described in this paragraph. For the 20 $\mu L/min$ and the 25 $\mu L/min$ middle flow rates, they showed a similar average size on the outer emulsion but with a difference in number of emulsions included and size. The 25 $\mu L/min$ middle flow rate has smaller and more inner emulsions. After increasing the outer flow rate to 75 $\mu L/min$, the 30 $\mu L/min$ and 25 $\mu L/min$ middle flow rates have shown similar behaviors in inner and outer average emulsion size and number of inner emulsions. This is due to the regime that inner phase enters which requires higher/lower drag force for making significant changes in the size and number of emulsions. The 20 $\mu L/min$ middle flow rate at this situation has less number of emulsions but bigger average size which result in faster pinch off since the oil drop reaches the point in which the drag and inertia forces are becoming significant to help the process. For the last scenario, the 150 $\mu L/min$ outer flow rate has shown similar behavior as the middle flow rates had at 15 $\mu L/min$.

The generation of inner emulsion is same as the generation of single emulsion, which we discussed in chapter 3, since it is considered as the dispersed phase for the continuous middle phase. Therefore, an increase in inner flow rate would result in an increase of inner emulsions size at a constant flow rate. In most of the experiments, we could observe the same thing, however, there are some exceptions due to other factors which impacted the process. For instance, at the outer flow rate of 30 $\mu L/min$, 30 $\mu L/min$ middle phase flow rate has shown bigger average droplet size. This is due to partial encapsulation of inner emulsions at 20 $\mu L/min$ middle phase flow rate.
and resulting in smaller average size of emulsions. Another example is the 30 $\mu L/min$ middle flow rate which could produce two bigger droplets than 20 $\mu L/min$ and 25 $\mu L/min$ middle flow rates. To address this situation, we are assuming that the flow rate combination of 2 $\mu L/min$ inner flow rate, 30 $\mu L/min$ of middle flow rate, and 60 $\mu L/min$ of the outer flow rate is resulting in uniform two inner emulsion generation.

### 4.3 Evaluation of the Number of Emulsions Generated

Figure 4.3 is showing the number of inner emulsions in the double/compound emulsion generated via the 3D printed device. It should be taken into consideration that the numbers in the Figure 4.3 are based on few droplets collected. To understand the uniformity in number of droplets encapsulated during the process, further experimentation is needed in which more stable emulsions can be collected and measured. Here we try to investigate the effect of the flow rate on the number of emulsions encapsulated.

In general, the increase in continuous flow rate would result in higher frequency of emulsion generation, as we discussed in the previous chapter. Since the generated inner emulsions would be accumulated in the oil or outer emulsion, until it gets pinched from the orifice and produce double/compound emulsion, the increase in frequency of the inner emulsion production would result in more inner emulsion encapsulation in the outer emulsion. As we can see in Figure 4.3, the number of inner emulsions was increased by increasing the middle phase flow rates. For instance, the increase in middle phase flow rates, 25 $\mu L/min$ and 30 $\mu L/min$, at outer flow rate of 15 $\mu L/min$ resulted in generation of three inner emulsions. In some cases, we could observe various numbers of inner emulsions and it is because of the encapsulation process. This process
can behave different in some situations due to untuned flow rates and different inner emulsions size.

4.4 Frequency of the Emulsion Generation

The frequency of outer emulsion generation is shown in Figure 4.4. The vertical axis is showing the frequency of the generated double emulsion from the one emulsion pinch off to another one. The horizontal axis is indicating the outer flow rate and the data points which are shown in diamond, square, triangle, and cross are four different middle phase flow rates.

The trend of frequency of generation of double/compound emulsions is similar to single emulsion generation since the increase in either outer or middle flow rates resulted in higher frequency. The frequency in some combinations of middle and outer flow rates can have errors due to the process of encapsulation. For instance, at 75 μL/min outer flow rate and 25 μL/min middle flow rate, we can see higher fluctuation in the double emulsion generation. This is because of untuned set of flow rates which resulted in various number of encapsulated inner emulsions.

![Figure 4.4 Frequency (mHz) of double/compound emulsions generation in different middle and outer flow rates (μL/min).](image)

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Chapter 5 Conclusion and future work

5.1 Conclusion

In this thesis, we proposed a novel monolithic 3D printed axisymmetric co-flow single and double/compound emulsion generator. In chapter 1, we introduced the concept of droplet microfluidics and techniques for production of droplets. Later, we introduced the Whispering Gallery Modes and usage of droplet microfluidics in this application. In chapter 2, we explained the fabrication methods used in production of droplet microfluidic chips, and we introduced recent developments of 3D printed devices in this field of study. In addition, we described the design of our 3D printed device, its fabrication process, and materials and apparatus which were used for the experiments. In chapter 3, the mechanism of single and double emulsion generation in the device was explained and the process of generating emulsions in the device was introduced. Also, the experimental data of single emulsion production was shown in different figures and the size of emulsions and its frequency of generation were discussed. In chapter 4, we presented the results of experiments involving double/compound emulsion generation and discussed the factors impacting the change in size of inner and outer emulsions, number of emulsions encapsulated, and the frequency of double emulsion production.

In conclusion, we designed and produced a novel monolithic 3D printed axisymmetric co-flow device for generating single and double/compound emulsions. This device was successfully tested, and it could produce single emulsions with average diameter of 1250 to 3000 $\mu m$ in different dispersed and continuous flow rates. In addition, double/compound emulsions were produced with outer emulsion having an average diameter 2150 to 2930 $\mu m$ and inner emulsions having an average diameter of 488 to 1120 $\mu m$ by keeping the inner phase flow rate constant and varying middle and outer flow rates. We could also achieve compound emulsions and encapsulate more
than one, and up to six, inner emulsions inside the bigger emulsion by using this device. Overall, our emulsion generator would help any user to produce emulsions and achieve favorable emulsion size by varying the flow rates and the size of the orifice. Moreover, the device is designed in a “Plug-and-Play” manner and it is fabricated with a commercial and low-cost Stereolithography 3D printer. These design and fabrication features offer any user an accessible and easy-to-utilize device to produce single, double, and compound emulsions.

5.2 Future Work

Our device has shown a promising capability to produce different emulsions (single, double, and compound) and there are some improvements that can advance the capabilities of our novel monolithic 3D printed device to new areas of application. For instance, the stability of the double emulsions can be improved from about a minute (at present stage) to more than a few hours by investigating different surfactants and their ratios for generating stable double/compound emulsions. In addition, the mechanism of the emulsion generation can be studied in future to find out the relation between geometrical features of device and forces applied during the process of emulsion generation. Moreover, computational modeling of emulsification using phase field method has been performed using COMSOL Multiphysics software to understand the fluid dynamics of the emulsion generation process. In this computational study, we could achieve preliminary results and simulate different regimes of double emulsion generation (See Figure 5.1). The process of double emulsion generation can be studied and validated with the experimental results in future work.
Figure 5.1 Simulation results of double emulsion generation. Fluid A is demonstrated in red (Deionized Water), Fluid B is in green (Mineral Oil), and Fluid C is in blue (Deionized Water) 1.a) at t = 0 s, initial condition of 3 fluids in microfluidic device. 1.b,c) Double emulsion generated at two increments of time. 2.a) Squeezing regime and generation of double emulsion in an unstable situation. 2.b) Multiple double emulsions were generated; however, they are not stable by the time of detaching. 2.c) Jetting regime of fluid B and dripping regime of fluid A are demonstrated.
List of References


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Education
University of Illinois at Chicago (UIC) December 2020 Master of Science in Mechanical Engineering GPA: 4.0/4.0
Science and Research Branch of Islamic Azad University - Tehran, Iran. January 2018 Bachelor of Science in Mechanical Engineering GPA: 3.1/4.0

Certification
Engineer-in-Training [Fundamentals of Engineering Exam (FE)] December 2019

Course Work

Skills
Computer Skills: Solidworks, 3D design, Revit, AutoCAD, Comsol Multiphysics®, Abaqus, Ansys, MATLAB, Python, Simulink, HTRI Xchanger, Microsoft Office
Tools: Formlabs and FDM 3D printers, CNC Machine

Project Experience
Microfluidics Laboratory, Research Assistant, UIC August 2019 – Present
- Design and create a 3D printed device using micro glass capillary tubes to produce single and double water and oil emulsions.
- Investigate the effect of flow rate and surfactants ratio on size of single and double emulsion.
- Use Formlabs SLA 3D printer to produce microfluidic devices using resin.

Analysis of loads on mechanical structures Sep – Dec 2017
- Analyzed tension and stress of a beam, truss and frame with known characteristics under loads with Abaqus. (Computer aided design and manufacturing)
- Simulated forging and extrusion operations with Abaqus and demonstrated the appropriate load which should be implemented on the object. (Methods of manufacturing)

Simulation and programming using MATLAB Jan – May 2017
- Calculated energy distribution in a plate with interpolation method using forward polynomial method. (An introduction to computational fluids)
- Simulated a spool valve connected to hydraulic system with Simulink and derived the pressure of fluid in system by using given data like displacement of spool valve. (Automatic control)

Engineering Experience
Mechanical Engineer Intern, Kerman & Kavian Cable Industries – Tehran, Iran Sep. 2016 – Nov. 2016
- Investigated different kinds of cables and production process and machinery.
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Mechanical Engineer Intern, Kimiaqaran Company – Qazvin, Iran Mar 2016 – May 2016
- Provided appropriate solar water heater by considering the customer’s need like the water consumption.

Additional Experience
Mechanical Engineering Department, ABET Coordinator, UIC -Chicago, Illinois, United State June 2019 - Present
- Respond to Professors and Teaching Assistants inquiries and meeting with them.
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Memberships
• Mechanical and Industrial Engineering Graduate Association  
  2019 - Present
• Pi Tau Sigma, Mechanical Engineering Honors Society  
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• American Society of Mechanical Engineers  
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