Applications of CFD Simulations on Studying the Multiphase Flow in Microfluidic Devices

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APPLICATIONS OF CFD SIMULATIONS ON STUDYING THE MULTIPHASE FLOW IN MICROFLUIDIC DEVICES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in

Cain Department of Chemical Engineering

by

Yuehao Li
B.S., East China University of Science and Technology, 2009
M.S., Louisiana State University, 2013
December 2014
To my Parents

Mr. Xiaobai Li & Ms. Xiaolian Chen

my wife

Ms. Xiaoxia He

and our baby boy

Ethane Li
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Abstract

Microfluidics has been extensively investigated as a unique platform to synthesize nanoparticles with desired properties, e.g., size and morphology. Compared to the conventional batch reactors, wet-chemical synthesis using continuous flow microfluidics provides better control over addition of reagents, heat and mass transfer, and reproducibility. Recently, millifluidics has emerged as an alternative since it offers similar control as microfluidics. With its dimensions scaled up to millimeter size, millifluidics saves fabrication efforts and potentially paves the way for industrial applications.

Good designs and manipulations of microfluidic and millifluidic devices rely on solid understanding of fluid dynamics. Fluid flow plays an important role in heat and mass transfer; thereby, it determines the quality of the synthesized nanoparticles. Computational fluid dynamics (CFD) simulations provide an effective approach to understand various effects on fluid flows without carrying out complicated experiments.

The goal of this dissertation is to utilize CFD simulations to study flow behaviors inside microfluidic and millifluidic systems. Residence time distribution (RTD) analysis coupled with TEM characterization was applied to understand the effect of reagent flow rates on particle sizes distribution. Droplet-based microfluidics, as a solution to the intrinsic drawbacks associated with single-phase microfluidics, depends on proper manipulation of the flow to generate steady droplet flow with desired droplet / slug sizes. The droplet/slug formation process inside a millifluidic reactor was investigated by both experiments and numerical simulations to understand the hydrodynamics of slug breaking. Geometric optimization was carried out to analyze the dependency of slug sizes on geometric dimensions. Numerical simulations were also performed to quantify the mixing efficiency inside slugs with the aid of mixing efficiency index. In some circumstances, the droplet sizes are difficult to control via manipulating the flow rates. By applying external electric field to the conventional droplet-based microfluidic systems, the electric force induced on the fluid interface can reduce the droplet sizes effectively.

This work provides insight to understand fluid flow inside microfluidic and millifluidic systems. It may benefit the design and operations of novel microfluidic and millifluidic systems.
Chapter 1 Introduction

1.1 Microfluidics and millifluidics

What is microfluidics? Prof. George Whiteside defines microfluidics as the science and technology of systems that process or manipulate small \((10^{-9} \text{ to } 10^{-8} \text{ liters})\) amount of fluids, using channels with dimensions of tens to hundreds of micrometers\(^{[1]}\). After the first conceptual introduction by Manz et al. at the 5\(^{th}\) International Conference on Solid-State Sensors and Actuators\(^{[2]}\), microfluidics has been developed into a multidisciplinary field, attracting numerous interests from both scientific and commercial communities.

The realization of microfluidics depends on miniaturization that develops small-scale products, devices or components with similar performance or better functionality as their macroscopic components. The most successful example is the miniaturization of micro-electronics. Every year electronic industries bring in more efficient, reduced weight and cost-effective portable devices using sophisticated micro-fabrication techniques. Since two decades ago, the concept of miniaturization has been extended to chemical, biological and bio-medical applications. The micro-scale devices are integrated onto one chip, and the chip may perform same functions as what are originally conducted inside laboratories. These devices are termed as Lab-on-a-Chip (LOC).

LOC devices, also named as micro-total analysis systems (\(\mu\)-TAS) because of their first applications on chemical analysis, are demonstrated to be capable of carrying out conventional analysis laboratory tests within a single chip\(^{[3, 4]}\). As depicted in Figure 1.1, a typical LOC system usually contains various sub-components such as pumps, reactors, separation devices and waste treatment devices on micron size scale. Besides providing similar functions as their
macroscopic counterparts, the small scale of the sub-components offers remarkable benefits in terms of reduced size, enhanced mobility, less sample / reagent consumption and shortened analysis time.

Figure 1.1 Schematic of a typical Lab-on-a-Chip (LOC) device with various sub-components

Microfluidics promises numerous opportunities for commercial successes. With the advantage of small scale, they can enable novel applications that conventional devices cannot achieve. Nowadays one typical commercial interest is the plastic fabrication for single-use disposable microfluidic devices. For example, the diabetes test strip, also called glucose test strip, is one kind of widely used plastic microfluidic chip. The fantastic attributes, such as fast and precise analysis, cost-effectiveness and etc., have ensured a huge market for glucose meter manufactures. In a similar way, microfluidics might also change the way instrument companies conduct business, which may initiate a revolution on chemical analysis. Instead of selling a few expensive analysis systems, companies may sell cheap, disposable microfluidic devices. Making analysis instruments, tailored drugs, and disposable drug dispensers available for everyone will secure a huge market similar to that of computers today[5].
As a response to the commercial potential, microfluidics has attracted research interests from academic communities. A variety of disciplines, such as chemistry, biology, medicine, material science and engineering (chemical, mechanical, electrical etc.), are applying microfluidic to their research; their contributions have developed microfluidics into a truly multidisciplinary field. One application in chemical engineering is the development of micro-devices for traditional chemical synthesis. Taking advantage of their intrinsic property of small length scale, microfluidic devices offer favorable heat and mass transfer\cite{6,7}. Hassel et al. have utilized a micro-mixer within a microfluidic reactor for Phenyl Boronic Acid process and found 25\% higher yield, higher selectivity and less energy consumption compared to stirred tank process\cite{8}. Although various researches have shown promising results, it is still impossible to scale up micro-reactors to a mass chemical production facility. Massive parallelization of miniaturized systems (numbering up) is suggested as a possibility but integration and assembly of such a system remains a challenge. If massive parallelization is achieved, it could possibly be the next milestone of chemical engineering for massive manufacturing of chemicals utilizing microfluidic devices.

Several disadvantages have been encountered when apply microfluidic technology to industry. One is the high cost for fabricating complicated microfluidic devices. They are usually fabricated by lithography or etching inside a clean room. Recently, researchers have turned to millifluidics which has presented considerable advantages. Millifluidics is referred to those microfluidic devices that are scaled up to millimeter size. Millifluidic fabrication usually proceeds following steps in normal conditions: using precise micromachining to fabricate metal mold inserts, injection molding for cost-effective chip replication, and lamination for adequate sealing of the devices/chips. Recently, Panizza and his co-workers have demonstrated their work
to produce hierarchically organized larger emulsions by using combinations of modular millifluidic devices[9]. Their setup included an assembly of capillaries or flexible tubes connected together with elementary home-made modules. The tubes and modules could be assembled and disassembled easily; therefore, modular set-ups could be designed on demand in a short time[10, 11]. This method promises a great versatility to set up new millifluidic systems for various applications. Tachibana et al. have adopted a millifluidic system to produce microporous silica ceramic particles[12]. They claimed that utilization of multiple millifluidic reactors in parallel could pave the way to an industrial integrative formulation of dispersed materials with very large characteristic sizes ranging from typically 100 µm to several mm and new complex architectures. Since millifluidics is scaled up from microfluidics and the major difference between them is the dimensional scale only, microfluidics is used in general for the following sections that illustrate their applications in material synthesis.

1.2 Microfluidic reactors for controlled synthesis of nanomaterial

Nanoparticles exhibit a variety of size-, shape-, and crystal-structure-dependent physical and chemical properties; therefore, synthesis of nanoparticles requires superior controls over reactions, both kinetically and thermodynamically, so as to produce materials of required features and properties[13-16]. Wet-chemical synthesis, involving liquid phase reactions in simple equipment, is a traditional but an effective approach to produce a large amount of nanoparticles coated with organic stabilizers to protect them from aggregation or oxidation[17]. With proper controls over the process, wet-chemical synthesis can address several particular challenges in nanoparticle synthesis, for example, the uniformity in particle size distribution. In this study, metal salt reductions are adopted to synthesize metal nanoparticles.
Conventional wet-chemical syntheses are carried out in batch reactors such as stirred flasks. The turbulence created from the mechanical or magnetic agitators usually results in poor control over reaction conditions, producing nanoparticles with broad size distribution. In the past decade, there has been a strong shift towards the utilization of microfluidic devices to synthesize nanomaterial under continuous flows. Microfluidic reactors have several unique features for controlled synthesis of nanoparticles.

One is the thermal and chemical homogeneity pertained through the entire reaction volume inside microfluidic reactors. Microfluidic reactors are manipulated in laminar regime: the absence of turbulence enables a homogeneous environment for particle synthesis. Micromixers are usually integrated into the system to enhance mixing and thereby improve the yield. Edel et al. demonstrated the synthesis of CdS nanoparticles in a continuous-flow microfluidic reactor with a micromixer based on distributive mixing[18]. In contrast to the nanoparticles synthesized in traditional flask reactors, nanoparticles synthesized in their microfluidic reactors showed a sharp decline in poly-dispersity tending toward mono-dispersity by manipulating the flow rates of the reagents. Song et al. also reported that Pd nanoparticles obtained from a polymer-based microfluidic reactor with mixing components had smaller particle diameters and narrower size distribution than those obtained from batch process[19]. Over all, downsizing the reactor from bulk to microfluidic reactor is sufficient to improve the mono-dispersity of the nanoparticles.

In addition to the homogeneous environment, microfluidic systems may also provide unique platforms for studying the fundamental reaction process through spatially resolved analysis of nanoparticle formation process within the micro-channels. Since the reaction time of chemical reactions inside batch reactor is fundamentally same as the residence time inside microfluidic reactor, implementing insitu analysis to microfluidic reactors may provide kinetic
information of the reaction[20]. Zinoveva et al. probed the cobalt nanoparticle formation utilizing synchrotron-radiation-based X-ray absorption spectroscopy at three different locations of a PMMA microfluidic reactor[21]. The particle formation was depicted by the spectra recorded at these locations together with the reference spectra of the precursor and the final product collected at the outlet of the micro-reactor.

Another advantage of using microfluidic reactor is the ability of adding additional reagents downstream as required; therefore, pre and post treatment and multistep synthesis in a single microfluidic chip are achieved by such a unique feature. Shestopalov et al. carried out a multistep synthesis of Q dots at room temperature using the microfluidic droplet reactor shown in Figure 1.2[22]. Two aqueous reagents R\textsubscript{1}, R\textsubscript{2} and a separation stream S were injected upstream to initiate reactor 1. Taking advantage of rapid mixing using wind channels, a homogeneous environment was attained inside droplets. The reaction time, same as the residence time, was controlled by manipulating the flow rate of oil. The second reaction was initiated when the third reagent R\textsubscript{3} was injected from another side channel and added to the aqueous droplets. Multiple purposes can be realized, such as quenching the reaction or withdrawing part of the product, through proper operations on the side channel. The core/shell nanoparticle synthesis using such microfluidic devices have been demonstrated to have the ability to control overcoat thickness, avoid secondary nucleation and aggregation, and maintain a narrow size distribution[22, 23].

Microfluidic reactors have another potential advantage to control the properties of nanoparticles by controlling their formation. One possible way is to separate the nucleation and growth stage to obtain nanoparticles of desired size and size distribution. The generally accepted mechanism of particle formation in a wet-chemical synthesis process, as proposed by Lamer and
Dinegar[24], consists of four distinct stages: supersaturated solute formation, nucleation, growth and aggregation. As the solute concentration formed by chemical reactions exceeds the super saturation limit and eventually reaches a critical concentration, numerous nuclei are generated in a short burst by nucleation. At growth stage, the solute deposits on particle, thus its concentration decreases to a value below critical concentration; therefore, the number of nuclei is halted during growth stage. Particles continue to grow until all the solutes have been consumed so as to lower the overall free energy of the system (particles and solutes). During this stage, aggregation

Figure 1.2 A micrograph of microfluidic device for performing droplet-based two-step synthesis with millisecond control. Reproduced from Reference 16 with permission from *Royal Society of Chemistry*. 

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might also occur since aggregation of individual particles also lowers the free energy of the system. The particles tend to coagulate and precipitate out of the solution[24, 25]. Nanoparticles of desired size and size distribution can be produced only if the amount of reagent is controlled so that the growth stage stops at the proper time, and suitable stabilizer is utilized to avoid aggregation. Investigations by Sounart et al. suggested the possibility to separate the nucleation and growth stage: the homogeneous reaction, solute formation and nucleation are diffusion limited and occur instantaneously; in contrast, the growth stage occurs on a longer time scale (seconds)[26]. Similar observations were also demonstrated by Wager et al. in the case of gold nanoparticle synthesis[27-29] and also by Khan et al. in the case of silica nanoparticle synthesis[30, 31].

1.3 Droplet-based microfluidics

Conventional microfluidic devices are operated with continuous flow in laminar regime. They are associated with several inherent problems. One is the large residence time distribution (RTD) due to the velocity variance in cross section. In laminar regime, a parabolic profile is established along the cross section of the channel with high velocity in the center and no-slip assumption at wall. Since the fluid elements in the center region have large velocity, the residence time is small; in contrast, those fluid elements near wall have smaller velocity thus in turn longer residence time. The distribution in residence time leads to distribution in particle growth time and concomitantly poly-dispersity in particle size. Another disadvantage is the low yield resulted from poor mixing of the reagent: mixing in laminar regime without any mixer is based on molecular diffusion, which is much slower compared to convection. Additional external micromixer must be integrated into the system, but it in turn arguments the complexity for fabrication. Traditional single-phase microfluidic reactor suffers from fouling, i.e., the deposition
of solid material on channel surface, eventually leading to the blockage of the channel[32]. Surface treatment on channel walls is an effective approach to eliminate fouling. Wagner reported[29] that fouling was successfully prevented by carrying out reactions at elevated pH values and by making the internal channel surface hydrophobic through silanization. However, this method may not be applicable for other material synthesis, and suitable treatment must be adopted based on particles being synthesized as well as channel material.

“Droplet-based microfluidics” has been firstly introduced in 2003 as an alternative method to address these problems simultaneously[33]. The typical setups of the droplet-based microfluidic reactor are illustrated in figures as seen in Figure 1.2 and Figure 1.3. The aqueous reagents are encapsulated inside nanoliter–scale droplets and segmented by oil plugs. Two immiscible phases are involved: aqueous phase and oil phase (or carrier fluid). Since the aqueous droplets are segmented by oil plugs, the two phases are also termed as dispersed phase and continuous phase respectively. The setups illustrated in Figures 1.2 and 1.3 are typical microfluidic T-junction devices: aqueous reagents are injected from the side channel while oil is injected from another channel; discrete droplets are sequentially pinched off from the aqueous solution at the junction region. As depicted in Figure 1.3, droplet-based microfluidics has several advantages over single-phase microfluidic reactors: rapid mixing, no dispersion and minimized surface deposition. The strong convection enables rapid mixing inside droplets without presence of eternal micro-mixers. Vortices are generated inside droplets due to velocity distribution and immiscible condition: fluid elements in the center are moving faster than those near channel walls; circulating occurs since the fluid elements in the center are forced to move backward because they cannot penetrate the fluid interface. If a homogeneous environment is required
within a short time, wind channels are integrated into the microfluidic system to further enhance mixing by taking advantage of chaotic advection\cite{34}.

![Figure 1.3 Advantages of using droplet-based microfluidic reactor. Reproduced from Reference 24 with copyright from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.](image)

Dispersion is eliminated as reagents are isolated within droplets. With the aid of rapid mixing, homogeneity in heat and mass is attained, thus each isolated droplet is served as an individual batch reactor. Since they travel with same speed, all droplets have same residence time; therefore, the reaction / growth time inside each “batch” reactor is same. Consequently, uniform residence time distribution leads to narrow size distribution of the synthesized nanoparticles\cite{20}.

Another advantage offered by microfluidics is the ability to prevent surface deposition because of a thin lubricate layer. If the reagents are in aqueous phase, the channel walls are accordingly fabricated by hydrophobic material, thus a thin layer of the continuous phase is developed between the translating droplets and the channel walls. This thin layer prevents
deposition of nanoparticles on channel walls[35, 36]. The existence of the thin layer has been indicated through experiments, but a definitive optical evidence for the film thickness and its consequential effect on nanoparticle synthesis has not been reported yet[37, 38].

Droplet-based microfluidics has gained much research interests from multi-disciplines due to its advantages and superior controls. Numerous publications demonstrating its applications on various research fields[20, 39-41] have been reported within these ten years. Particularly in nanoparticle synthesis, it has shown fantastic capability for synthesizing nanoparticles with mono-dispersity and controlled morphology. Duraiswamy and Khan[42] have applied droplet-based microfluidics to synthesize anisotropic metal nano-rods with controlled aspect ratios as shown in Figure 1.4. Xu et al.[43] has also reported their syntheses of polymer nanoparticles with controlled shapes and sizes as shown in Figure 1.5.

![Figure 1.4 TEM images of rod-shaped nanoparticles with varying aspect ratios. The corresponding aspect ratios are: (a) 2.3±0.5 (b) 3.2±0.5 (c) 4±0.5 and (d) 2.7±0.3. Reprinted from reference 29 with copyright 2009 from Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.](image-url)
Figure 1.5 Monodispersed particles with controlled shape and sizes generated in droplets. (a) polymer microsphere (b) a crystal of polymer microspheres (c) polymer rods (d) polymer disks (e) polymer ellipsoids (f) agarose disks (g) bismuth alloy ellipsoids. Reprinted from reference 30 with copyright 2005 from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Droplet-based microfluidics has encountered several disadvantages that limit its applications. One arises from the requirement to find a suitable choice of reaction fluid and carrier fluid, since they should be immiscible over all the range of experimental conditions (pressure, temperature, pH value, etc.)[40]. Another disadvantage is the further separation downstream to separate the product from oil, which has been conditionally addressed by adding an in-line phase separator[44, 45]. It is worthy to point out that liquid-liquid flows in microfluidic channels may exhibits other flow patterns rather than droplet flow; therefore, suitable operating conditions, i.e., flow rate, viscosity ratio, interfacial tension, must be selected to operate droplet-based microfluidic in droplet flow regime.

1.4 Apply numerical simulations to microfluidics

With the development of computational power and simulation techniques, numerical simulations have opened a new approach to investigate microfluidics. Since the flow characteristics inside microfluidic devices are important, computational fluid dynamics (CFD)
simulations provides an easy way to study those flow behaviors that are difficult to observe through experiments.

Fluid flows are described by Navier–Stokes (N-S) equation, which is a set of partial differential equations with time and space dimensions. The idea of CFD simulations is to obtain the flow field inside those microfluidic devices by solving N-S equation through numerical methods. Typical numerical methods include finite difference method (FDM), finite volume method (FVM) and finite element method (FEM). Many commercial CFD software or packages are available now, i.e., ANSYS Fluent, ANSYS CFX and Comsol Multiphysics. There are also open source numerical solvers such as OpenFoam, Fluent and OpenFoam are based on FVM while Comsol and CFX adopt FEM methods.

CFD simulations have been adopted by researchers in microfluidic field in many respects. One is in the characterization of mixing performance in microfluidic devices. The experimental characterizations of mixing are often carried out by diluting dye or fluorescence with water [46]. In numerical simulations, the mixing performance can be investigated by N-S equation coupled with transport equations. As fluid flow inside microfluidic devices is laminar, the simplicity in flow patterns ensures a good agreement of the simulation results with the experimental observations. Many researchers have adopted numerical simulations to design novel microfluidic devices and test their mixing performances in order to save time and labor effort [47].

Another application of CFD simulation is to study the droplet formation process inside microfluidic devices which is critical for droplet-based microfluidics. Droplets in microfluidics are micrometer scale, and their formation process usually occurs within milli-seconds. Experimental investigations require sophisticated equipment such as microscope and high-speed cameras. Various factors affect the droplet formation process, increasing the complexity of
investigation. Recently, CFD simulations are attracting many attentions as an alternative. Researchers have adopted various numerical methods, i.e., volume of fluid method (VOF), level-set method (LSM), lattice-Boltzmann method to study the multiphase problem[48]. Numerical studies can help to understand the role of various effects and also save the efforts of fabricating chips and carrying out experiments.

1.5 Scope of this dissertation

This dissertation seeks to apply CFD simulations to understand the flow behavior inside microfluidic reactors so as to find suitable operating conditions and optimal designs for nanoparticle synthesis. The organization of this thesis is as follows: the second chapter discusses the spatial evolution of Au nanoparticle at various locations inside a millifluidic reactor. In the third chapter, numerical simulations were carried out to investigate the slug formation process inside a millifluidic flow-focusing reactor and analyze the effect of geometric dimensions on slug lengths. In the fourth chapter, mixing performances inside slugs were investigated under various operating conditions. In the fifth chapter, external electric field was utilized to control the droplet breakup process in a microfluidic flow-focusing device. The last chapter is the references been cited in this dissertation.
Chapter 2 Size Evolution of Gold Nanoparticles in a Millifluidic Reactor*

2.1 Introduction

Microfluidic reactors have gained extensively research interests from multi-disciplines, especially for synthesis of novel nanomaterial.[40, 49, 50] However, they usually rely on sophisticated fabrication techniques, for example, lithography or etching in a clean room, which increase their cost and hinder their applications. In addition, there remain a number of issues related to process scale-up in order to meet the requirements for industry-level applications. [13, 50]

Millifluidics, referred to those devices which have a length-scale larger than 500 µm, has emerged as a bridge between microfluidics and bulk systems.[11] In contrast to expensive microfluidic fabrications, the large scale of the channel size makes millifludic devices relatively easy to fabricate and consequently low cost. Another potential advantage of millifluidic reactors is that the fluid volume is many folds higher than that of microfluidic reactors while offering similar controls. The larger channel size also provides better opportunity than microfluidics for insitu characterization of nanocluster with various spectroscopies, especially when carrying out time-resolved insitu analysis using synchrotron radiation-based X-ray absorption spectroscopy where larger probe dimensions provide better signal to noise ratio[21]. Recently time resolution studies with microfluidic reactors have been carried out using a number of probes such as surface-enhanced resonance Raman spectroscopy (SERRS), Coherent Anti-Stokes Raman scattering microscopy, photoluminescence imaging and spectroscopy, and X-ray absorption spectroscopy probes.[21, 51] Applying these spectroscopic probes to millifluidics is believed to provide better performances.

* Reprint with permission from ChemPhysChem
These advantages have promised millifluidic reactors as an alternative to microfluidic reactors. Surprisingly, they have not been investigated thoroughly for their utility in general[52] and for nanomaterial synthesis in particular.[53]

In this work, a snake-shape millifluidic reactor is utilized as a platform to carry out spatial evolution analysis of Au nanoparticle formation inside millifluidic channel using Transmission Electron Microscopy (TEM) as a probe. Converting the spatial resolution information to time resolution, the size evolution of nanoparticle within the channel elucidates a general particle growth process. Numerical simulations are performed to compute corresponding residence time distribution (RTD) at different sampling locations under various flow rates. The correlation between RTD and particle size distribution (PSD) reveals the effect of flow rates on particle formation process.

2.2 Experimental method

The Au nanoparticles were synthesized in both batch and continuous processes by modifying a previously reported procedure.[54] The millifluidic reactor has a snake shape as shown in Figure 2.1 (purchased from Microplumbers) with channel dimensions of 2 millimeters width and 125 micrometers depth. Only the reaction channel on the right side of the chip was utilized in this work. The mixing length inside the channel is approximately 14 centimeters. The two reagents, DMSA (dimercaptosuccinic acid) and chloroauric acid (HAuCl₄) were injected into the millifluidic reactor with same flow rates from two inlets. The total injecting rate was set as 2mL/h, 6mL/h, 10 mL/h and 40 mL/h respectively through computer controlled syringe pumps (NE-500 OEM Syringe Pump from SyringePump.com; New Era Pump systems Inc.).
Figure 2.1 (a) Milli-fluidic chip (Left chip utilized for the synthesis) (b) schematic diagram of the milli-fluidic channel
The chloroauric acid was prepared by dissolving 1.7 mg of Au (III) gold salt dissolved in 5 mL deionized water. DMSA solution, serving as both reducing agent and stabilizer, was prepared by dissolving 1.8 mL of DMSA in 5mL deionized water. The final solution was collected from desired sampling locations inside small glass bottles and used for various characterization purposes.

Mixing between the two reagents was studied by a dilution process of the fluorescent dye with deionized water. Photographs of the millifluidic channel were taken with a Leica DM RXA2 fluorescence microscope equipped with a 5x N.A. 0.15 objective, a Cooke SensiCam QE digital camera as well as a Xenon lamp. Images were acquired and processed using Slidebook version 4.0 (Intelligent Imaging Innovations, Denver, CO). After post-processing the images in Adobe Photoshop CS5, the intensity of the fluorescence was measured across the channel by Image J. A typical acquired image is shown in Figure 2.2. Since the camera used to take the photos was not capable to measure the intensity in the depth, the measurements of Image J was taken to be the average value on the depth.

The millifluidic chip was dissects at two required locations, location 1 and 2 as shown in Figure 2.1 (b) to collect the nanoparticle product. The spatial particle size distribution (PSD) was investigated by collecting a drop of product solution from the dissected locations as well as from the outlet onto a TEM grid. After evaporating the solvent, TEM analysis of the samples was performed to provide information regarding on the size and size distribution evolution at these locations. This procedure was identical for all the samples collected at different locations and at different flow rates and therefore provided reliable information about relative growth of particles at different locations within the channels. It was also important to mention that the particle deposition on the channel wall was virtually eliminated as one chip was used only once to run the experiment at each flow
rate in order to avoid particle deposition, if any, on channel walls. This was one of the advantages of using “use and throw” and inexpensive polymeric millifluidic chips. In order to compare PSD between millifluidic and batch products, samples were taken from batch reactors at specified time same as the residence time of those samples taken from millifluidic reactors. TEM images were recorded at University of Texas in Arlington (UTA) using Hitachi H-9500 High-resolution TEM. Particle size and size distribution were obtained by analyzing TEM images using Image J.

Figure 2.2 A typical image of fluorescent mixing with water. The red line indicates where the intensity is measured by Image J after post processing the image with Photoshop.

2.3 Numerical methods

Numerical simulations were adopted to study the mixing inside the millifluidic reactor and analyze the residence time distribution (RTD) at various flow rates. The accuracy of the numerical model was estimated by comparing the prediction of mixing between two reagents to the observation in fluorescent dilution. The mixing process is governed by three equations:
continuity equation (2.1), incompressible Navier-Stokes equation at steady state (2.2) and steady-state species transport equation (2.3).

\[ \nabla \cdot \vec{v} = 0 \tag{2.1} \]

\[ \rho \vec{v} \cdot \nabla \vec{v} = -\nabla p + \mu \nabla^2 \vec{v} \tag{2.2} \]

\[ \vec{v} \cdot \nabla c_i = D \nabla^2 c_i \tag{2.3} \]

where \( p \) is pressure, \( \vec{v} \) is velocity vector, \( \rho \) is density, \( \mu \) is viscosity, \( D \) is diffusivity and \( c_i \) is a scalar representing the concentration of fluorescent.

The diffusivity of the fluorescent dye \( D \) was set as \( 5 \times 10^{-10} \) m\(^2\)/s with constant diluting assumption. Density and viscosity were set to be same as the properties of water. Zero pressure condition was imposed on outlet while no-slip condition was applied for solid wall. Similarly, zero flux condition across channel walls and convection flux across the outlet were imposed on the species transport equation.

The RTD analysis was carried out by injecting an inert tracer at certain time \( t=0 \) and then measuring the tracer concentration \( C \) at the sampling point as a function of time. It should be pointed out that the tracer should have physical properties similar to the reaction mixture and be completely soluble in the mixture; in addition, it should be non-reactive[55]. Thus Au ion was selected as the tracer. Two most frequently used injecting methods are pulse input and step input. In pulse input, which was adopted in this work, an amount of tracer is suddenly injected by one shot into the reactor in as short a time as possible. The residence time distribution function \( E(t) \), describing how much time difference fluid elements have spent in the reactor, is defined as \( C(t)/ \int_0^\infty C(t) dt \).
The flow field is governed by Eq. (2.1) and (2.2) while the transient mass transport of tracer is described by a dynamic species transport equation (2.4). The value of diffusivity of tracer was set as $10^{-9}$ m$^2$/s in the model.[56]

$$\frac{\partial}{\partial t} c_i + \vec{v} \cdot \nabla c_i = D \nabla^2 c_i \quad (2.4)$$

where $t$ stands for time and $c_i$ is the concentration of tracer.

The mean residence time $t_m$, indicating the average time that species spend in the reactor, was calculated by Eq. (2.5). The width of the distribution[57] $\Delta \tau$ was employed to describe the spread of residence time. The width of the distribution was defined as the time required for fraction $\alpha$ of total injected volume of tracer to travel to the sampling point, and it could be determined by Eq. (2.6) and (2.7), where $t(\alpha)$ stands for the time that $\alpha$ fraction of elements emerge at the sampling point, and $t(\beta)$ stands for the time that the elements begin to appear at the sampling point. In this study, $\alpha$ is set as 0.99.

$$t_m = \int_0^{\infty} t E(t) \, dt / \int_0^{\infty} E(t) \, dt \quad (2.5)$$

$$\alpha = \int_{t(\beta)}^{t(\alpha)} E(t) \, dt \quad (2.6)$$

$$\Delta \tau = t(\alpha) - t(\beta) \quad (2.7)$$

All the numerical simulations were carried out in a two-dimensional domain. Comsol Multiphysics 3.5a was adopted as the numerical solver.

2.4 Results and discussion

Typical TEM images of the nanoparticles obtained from location 1, location 2 and the outlet at flow rates 2ml/hr, 6ml/hr and 10ml/hr are shown in Figure 2.3. The mean particle diameter and distribution are listed in Table 2.1. The histogram of the particle size distribution
Figure 2.3 TEM results of Au nanoclusters obtained at (a) 10mL/h, location 1–B11 (b) 10mL/h, location 2–B12 (c) 10mL/h, outlet (d) 6mL/h, location 1–B21 (e) 6mL/h, location 2–B22 (f) 6mL/h, outlet (g) 2mL/h, location 1–B31 (h) 2mL/h, location 2–B21 (i) 2mL/h, outlet. (* Bar at the bottom of each picture is 5nm to scale except for d which is 2nm.)

Table 2.1 Mean residence time, width of residence time distribution and particle size at different locations and at different flow rates.

<table>
<thead>
<tr>
<th>Flow rate, mL/h</th>
<th>Mean Residence Time, s and Particle size, nm</th>
<th>Width of distribution, s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Location 1</td>
<td>Location 2</td>
</tr>
<tr>
<td>2</td>
<td>48.88</td>
<td>76.11</td>
</tr>
<tr>
<td></td>
<td>3.19 ± 0.55</td>
<td>3.34 ± 0.61</td>
</tr>
<tr>
<td>6</td>
<td>17.60</td>
<td>26.88</td>
</tr>
<tr>
<td></td>
<td>2.73 ± 0.64</td>
<td>2.80 ± 0.48</td>
</tr>
<tr>
<td>10</td>
<td>11.04</td>
<td>16.79</td>
</tr>
<tr>
<td></td>
<td>2.36 ± 0.52</td>
<td>2.80 ± 0.69</td>
</tr>
</tbody>
</table>
obtained at these locations at the corresponding flow rates are shown in Figure B1 in the Appendix. The results indicate that for any particular flow rate, the average particle size increases due to surface growth as reagents flow through channels. The broadest size distribution was seen at the outlet, which was found to be the case for all the three different flow rates (2, 6, 10 mL/h). It is also to be noted that with the increase in particle size there is also tendency for particles to agglomerate leading to further increase in particle size distribution, which is believed to be the reason for large nanoparticles obtained from the outlet at 2 mL/h. One can see relatively better control over size and size distribution at a high flow rate of 10mL/h at location 1.

It is not difficult to understand the reason for increasing particle sizes as well as size distributions in the direction of the flow if one can understand the flow environment inside the millifluidic reactor. The fluorescent dilution process illustrated the particle formation process. As the two reagents are injected into the millifluidic reactor, they flow in parallel with same speed. Mixing between these two reagents are dominant by molecular diffusion, thus a mixing zone is formed across the interface. Supersaturated solute formation, nucleation and particle growth are all proceeding inside the mixing zone. The dilution experiments aims to visualize the spreading of fluorescence along the millifluidic channel using a microscope and a video camera.[46] The normalized fluorescent intensity profiles were plotted across the cross section of the millifluidic channel at 2mL/h and 5 mL/h in Figure 2.4(A). This mixing process was also modeled as mixing two streams (of concentration of 0 and 1) at steady state. The good agreements of simulation results with experimental observations validate the accuracy of the simulation model.

The region where intensity/concentration increases from 0 to 1 indicates the mixing zone inside microfluidic channel. If compared two flow rates at same location, high flow rate leads to confined mixing zone due to less dispersion time. Since molecular diffusion is a random
movement, larger mixing zone is expected to produce poly dispersed particles. At a flow rate of 10 mL/h, the mixing zone is confined so that the concentration change between the two fluids behaves almost as a step change, and more uniform particles are expected.

Figure 2.4 (A) Normalized dye intensity profile at location 1 from experimental and simulation studies. (B) RTD analysis of 10 mL/h at different locations. (C) RTD analysis of 2 mL/h, 6 mL/h and 10 mL/h at outlet. (D) Comparative analysis of residence time dependent particle size and size distribution of Au nanoparticles from batch and millifluidic reactors.

The disadvantage associated with single phase synthesis is the possibility for large residence time distributions (RTD) due to velocity distribution. From Figure B2 in the Appendix, we know that a parabolic velocity profile with maximum velocity in the center and zero velocity at the wall is established over the channel cross-sections under the hydrodynamic pressure driven conditions. This means that a reaction mixture sampled after the initiation of the mixing is
formed from an ensemble of volume elements that have spent varying time inside the reactor.\[58\] As shown in Figure 2.4(B) and (C), the residence time distribution of the reagents exhibits a non-Gaussian distribution. The motion inside the reactor is dominated by two effects: convection and diffusion. If the process is purely driven by diffusion, a Gaussian distribution is expected. On the other hand, if only convection occurs, the RTD curve behaves like a sharp pulse with long tails, which is similar as the E curve of 10 mL/h. From Figure 2.4(B) and (C), long tails in RTD curve are observed at high flow rate (6mL/h and 10mL/h), indicating a convection-dominant process. At 2 mL/h, the strong effect of diffusion leads to a shape of E-curve similar to Gaussian distribution. Table 2.1 lists the residence time and width of residence time distribution of different flow rates and locations.

RTD analysis can qualitatively predict the spread of particle size distribution (PSD) since the varying residence time determines the varying particle sizes. The data from the Table 2.1 indicates that the size and size distribution increase as the fluid moves from location 1 towards the outlet at the same flow rate, which is consistent with the residence time distribution. The size distribution in the outlet at 2 mL/h, 6 mL/h and 10 mL/h is also consistent with the residence time distribution. If one compares the particle size at different locations that have approximately same residence time, for example location 2 at 10 mL/h and location 1 at 6 mL/h (highlighted in blue) or outlet at 6 mL/h and location 1 at 2mL/h (highlighted in orange) or location 2 at 6ml/h and outlet at 10 ml/h (highlighted in green), one can see a good correlation of particle size and size distribution with the corresponding residence times. However, the correlation in the dispersion between the numerically obtained RTD and the experimentally obtained PSD is not one-to-one because of a number of reasons: (a) the numerically obtained RTD simulates only the included growth time of the particles while the experimentally obtained PSD also includes the
effects of nucleation and growth kinetics; (b) The experimental procedures, particularly nucleation, are subject to stochastic fluctuations and such features are not present in numerical simulations of the mixing process. While the measured sizes are consistent with the RTD, the dispersion in the measured sizes is subject to random variations. In addition, the variations in sampling time to arrest the reaction on the TEM grid could also cause variations in the dispersion of the sizes. One needs to notice that the particle size depends on two factors: growth time which is controlled by residence time and growth rate which is controlled by kinetics. The RTD analysis provides a key part of particle growth time, but actual capture of particle size needs kinetic information of particle growth rate. This is the long term goal since no kinetic data for this reaction has been revealed in literature.

Based on the results shown in Table 2.1, one may hypothesize that nanoparticles of smaller size and narrower size distribution may be produced if further increase the flow rate. Although no quantitative information on nucleation and reaction kinetics are available at this stage, the nucleation process is expected to be a rapid process indeed so that the particle size grows to 2 nm as soon as the two reagents are mixed. Therefore, additional experiments were conducted at a higher flow rate of 40 mL/h where the residence time on the outlet was calculated to be only 3.53 s. The average particle size obtained was 2.53 nm, which supports the expectation. The TEM images of sampling location 1, 2 and outlet are shown in Figure 2.5. Surprisingly, a fourfold increase in the flow rate did not result in either decrease in the particles size or narrowing in size distribution compared to the flow rate of 10 ml/hr. It appears that the nucleation time for the reaction under consideration is probably smaller than 3.53 s, which is the smallest possible residence time in location 1 at the total flow rate of 40 mL/h. Our arguments are strengthened by the recent insitu SAXS investigation of Ag nanoparticle formation where results show that silver nanoparticles are formed via three distinct periods within 6 ms. [59]
In order to test the ability of the millifluidic reactor on controlling the synthesis process, samples were taken from batch reactor at the time approximately similar to the investigated residence times within the millifluidic channels. Figure B3 in the Appendix shows the TEM images and the particle size histograms for the particles obtained at different time intervals. Clearly, the increasing particle size with time is seen in the case of the flask process as well. Additionally, the size distribution of the particles was also found to be broad.

Figure 2.4(D) compares the particle growth process of Au nanoparticles obtained from the batch and the millifluidic reactor. Clearly, the batch reactor results in larger size distributions than millifluidic reactor for the same reaction\growth time. One can also see that the size distribution of particles from the millifluidic process is tending narrower as the residence time decreases. In contrast, the size distribution continues to broaden with time in the flask reactor. It is also to be noted from the literature that similar situation is encountered even within a microfluidic reactor where when the residence times are adequately small, further increase in flow rates have smaller effects in reducing the particle size distribution.[49] The reason for this is that the particle size distribution depends on both the residence time effect as well as the growth
dynamics of the particles. Krishnadasan[58] revealed that the growth rate decreases with increase of particle size, and small particles catch up with large particles which results in narrowing the size distribution over time. What is also noticeable is that the particle size within the millifluidic reactor remains constant up to the residence time of about 40 sec and then there is a gradual increase in the size as well as size distribution. Combining this information with the fact that even at the smallest possible residence time (3.53 s) in location 1 at the total flow rate of 40 mL/h, we do not obtain either smaller or narrower size distribution compared to the flow rate of 10 ml/hr. It is, therefore, likely that the nucleation time for the particular gold reduction reaction we examined is smaller than 3.53 s. One can also conclude that there could be three different phases’ reduction & nucleation, coalescence of nuclei to form the particles and growth of the particles to the gold nanoparticle formation within the millifluidic channels; similar to the case of microfluidic channels. This conjecture is supported by recent observations based on in situ small X-ray scattering investigations on nucleation and growth of gold nanoparticles.[59, 60] In principle, one can take advantage of these differences to arrive at conditions for the preparation of monodisperse gold nanoparticles utilizing the millifluidic reactors.

2.5 Conclusion

In conclusion, we have developed a novel approach to study the time resolved growth of nanoparticles at different locations utilizing TEM of samples obtained through dissection of the millifluidic chip at specific locations. Taking advantage of the possibility to convert spatially resolved information from the millifluidic channel into time resolved information, we have been able to map the growth of gold nanoparticles within the channel. The time resolved formation of gold nanoparticles was also found to be dependent on the flow rates and therefore on the residence time. In addition to the residence time, kinetics of the reaction appears to be critical in
controlling the size and size distribution of the particles. We have also demonstrated that numerical simulations can be used to predict the flow rate dependent properties of nanoparticles formed within millifluidic channels. While the experimental results obtained so far do not demonstrate formation of monodisperse gold nanoparticles, the approach presented here has a great potential to lead to identification of experimental conditions based on numerical simulations for such a result. Similar to the case of microchannels, our work demonstrate that there are potential opportunities for millifluidic reactors to separate nucleation and growth phases and in general, higher flow rates could result in smaller size distributions and normally smaller nanoparticles provided kinetics of the reaction are appropriate.[61] Although the surface area of the geometry (where the fluid is in contact with the solid) is vastly different in milli and microfluidic reactors, it is the interfacial area between the two reacting fluids that important in governing the initiation and propagation of the reactions. The reactions occur where the two reagents flow in parallel with an interface in the middle of the channel. Any nucleation that is triggered at the solid fluid interface must be small as it is only a line segment on the top and bottom of the channel. (The reaction interface is right in the middle of the channel intersection the top and bottom cover plates at a line). So we expect similar size and PSD in milli and micro systems, only the throughput will be higher in the milli system because of the larger interfacial area between the reactants.

We hope that the experimental results coupled with numerical simulation results reported here will form the basis for future studies towards optimization of millifluidic reactor systems with parameters such as shorter mixing times, narrower residence time distributions and smaller separation times in order to enable better control over nanoparticle size and size distribution. Our results also demonstrate that in addition to the residence times, reaction kinetics involved in
nanoparticle formation need to be taken into consideration for developing the millifluidic synthesis process for nanoparticles.
Chapter 3 Geometric Optimization of a Flow-focusing Millifluidic Device†

3.1 Introduction

As seen in Chapter 2, traditional microfluidic/millifluidic reactors manipulated with single-phase flow are associated with large residence time distribution due to the intrinsic laminar flow behavior. Consequently, large residence time distribution results in nanomaterial with broad size distribution, leading trouble to the cases where size, size distribution and shape control is extremely important. Therefore, investigation of multiphase flows in microfluidic devices has been gaining much attention recently as a solution to improve the performances of single-phase flows[40, 62].

Multiphase flow systems introduce a second immiscible flow to enhance mixing and transverse channel transport.[39] The resulting flows have various forms such as stratified flow, slug flow or jetting flows, depending on the interactions among surface tension force, inertia force and viscous forces. [63, 64] Among these flow patterns, the slug flow takes advantage of the large interfacial area, fast heat and mass transfer and reduced axial dispersion; therefore, it has been used in various applications, [65, 66] especially in chemical synthesis.[30, 42, 67] Multiphase flows in microfluidics are generally carried out either by gas-liquid flow or liquid-liquid flow. Since we have been interested in utilizing multiphase flows for the controlled synthesis of nanomaterial, liquid–liquid flow is desirable as the thin film of carrier fluid, usually developed on the channel wall, prevents surface growth of the nanomaterial. As most of the microfluidic devices are fabricated using polymers, the weak sealing limits the flow to be

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manipulated at low Reynolds number (Re) and Capillary number (Ca) regimes. The flow pattern in this regime usually exhibits a slug flow.

Many designs on multiphase microfluidic devices have been reported to generate slug flows and these can be categorized into flow–focusing devices, [68-72] co-flowing devices, [73-75] T- junction devices,[76-81] Uniform bubbles or slugs can be generated in these devices; however, the formation mechanics especially in liquid-liquid slug flows is still not well understood. Several researchers point out that the bubble size depends mainly on the ratio of the gas flow rate and liquid flow rate in flow-focusing devices, [69, 82] and is independent of Ca for both low and high Re flows[83]. For nanoparticle synthesis, liquid slugs usually serve as the batch reactors; Tice et al. points out that mixing efficiency inside slugs depends on the length of slugs, [35] thus designs producing uniformly small slugs are desired to produce nanoparticles with narrow size distribution.

Microfluidic devices in general and those for droplet based applications have certain disadvantages that hinder their applications. For example, their fabrication usually requires expensive and time-consuming techniques such as lithography and etching in a clean room. In addition, there remain a number of issues related to reaction control and process scale up in order to meet the requirements for practical applications. [50] Yet another drawback is the difficulty to withstand high pressures associated with high flow rates and small residence times, which is often required for controlled synthesis of uniform nanomaterial. [84-87]

Scaling up of microfluidic devices into millifluidic ones presents some considerable advantages over microfluidics while retaining similar flow characteristics.[10] One is the low cost for fabrication of millifluidic devices. They can be produced by using precision micromachining to fabricate metal mold inserts, injection molding for cost-effective chip
replication, and lamination for adequate sealing of the devices/chips. Since the connecting capillary tubes and the various modules of the system can assemble and disassemble easily, the modular setup can be designed on demand in a short time.[11] These advantages have attracted many research interests recently. Droplet-based microfluidics have been applied to investigate polymerization reactions [88], to microbiology analysis [89] and screening. [90] The use of millifluidic device has also been reported to offer the potential to produce multiple emulsions. [12] We have recently demonstrated the utility of millifluidic reactors in single phase synthesis of ultrasmall nanoclusters [91, 92] and also as a tool for probing the time resolved growth of nanoparticles. 23a To the best of our knowledge a millifluidic device for segmented flow applications in general and for nanomaterials synthesis in particular has not been developed to date.

While several experimental investigations were carried out to study the effects of flow rates of multiphases, fluid properties (viscosity and surface tension), and channel geometry on liquid-liquid flow regimes within micro systems, [35, 76] a detailed understanding of the effects of operational and design parameters on the hydrodynamics within millifluidic systems has not been carried out. Recent development in computational fluid dynamics (CFD) modeling has provided a new approach to study slug flows. Several numerical methods, such as the volume of fluid method (VOF), [93-95] level-set method, [96-98] lattice-Boltzmann method [72, 79, 99-101] and phase field method [80, 102] have been used to study the hydrodynamics of slug flow, and they are able to capture the slug formation hydrodynamics. Numerical simulation can provide insight in slug breaking mechanics that are difficult to observe in experiments. They are also relatively simple and time-saving to carry out so that intensive experimental studies may be avoided. Many researchers have utilized two dimensional (2D) numerical simulations to study
droplet formation process. Compare to 3D simulations, it assumes that the channel is infinite long in the third dimension to reduce the computational effort; however, the third dimension plays an important role in droplet formation process especially when the aspect ratio (depth/width of the channel) is large[103, 104]. In this study, we adopted VOF method in a three-dimensional (3D) domain to study the slug formation process inside the flow-focusing millifluidic devices.

Our previous investigations were focused on a single phase snake mixer type millifluidic device, 17 and here we report our studies on the slug flow of two immiscible fluids within a ‘hydrodynamic focused’ polymeric millifluidic reactor at the squeezing regime (Ca < 0.002) by varying a number of process parameters in order to control the generation of periodical, and uniform slugs. Based on the literature, prior investigations suggest that the slug length can be tuned by varying the flow rates of each phase inside microfluidic devices. [35, 76, 94] Especially in squeezing regime, the slug lengths were found to depend only on the flow rate of the two phases[76, 80]. In order to investigate the possibility to create controlled slugs within a flow focusing millifluidic chip, we carried out experiments under various flow rates. The chip showed the similar ability, as that of microfluidics, in controlling slug lengths except that the slug lengths were very long. Uniform copper nanoparticles are also obtained inside the millifluidic chip, indicating its similar capability in nanomaterial synthesis as microfluidic reactors.

Since the geometric dimensions in microfluidic flow focusing devices play important roles in droplet formation process, [105, 106] we hypothesized that the internal geometry of the focusing region also plays an important role on slug size other than the flow ratio; therefore, we investigated the evolution of the slug formation within two modified geometries. The results discussed below validate our hypothesis and lead us to propose alternate millifluidic designs to
produce slugs with smaller sizes. In addition, we demonstrate for the first time that the slugs generated within the millifluidic reactors are suitable for controlled synthesis of copper nanoparticles.

3.2 Experiments

3.2.1 Chemicals and reagents

Methylene blue, rhodamine B, tetradecane (purity: 99.0%) and silicon oil (viscosity: 10 cSt) Copper(II) nitrate hydrate (99.999%), sodium borohydride (≥ 98.0%), Sodium hydroxide pellets (99.998%) and O-[2-(3-Mercaptopropionylamino)ethyl]-O’-methylpolyethylene glycol (Mw 5000) [MPEG], Tetradecane were obtained from Sigma-Aldrich. All chemicals were used as received without further purification. Water was supplied by a Barnstead Water Purifier Nanopure water system (18.3 MΩ cm).

3.2.2 Fabrication of flow focusing millifluidic chip

Polymethyl methacrylate (PMMA) based millifluidic chips (Figure 3.1(a) and (b)) were replicated from a micromachined brass mold insert [107, 108] using a HEX 2 hot embossing machine (Jenoptik, Jena, Germany). The brass insert (Figure 3.1(c)) contained the inverse fluidic chip design and was patterned at the KERN Micro CNC machining center (Kern, Eschenlohe, Germany) using cutting tools with 50μm smallest diameter. The brass insert containing the chip design as well as the cover slide was precisely transferred into PMMA sheet material at elevated temperature (150-160°C).[109] Subsequently, the chips were separated by sawing and thoroughly cleaned with IPA and DI water, and dehydrated at 60°C for 1hr in a convection oven. The unstructured PMMA cover slides of ~1mm thickness were thermally welded onto the fluidic chips [110] using the fixture shown in Figure 3.1(d). Thermal welding was performed in a
Figure 3.1  (a) Millfluidic chip and cover slide hot embossed into PMMA at 150-160°C. (b) Millifluidic chip and cover slide after separation and cleaning. (c) Mold insert made from brass with inverted pattern of the millifluidic chip. (d) Spring-loaded clamping fixture for thermal welding of cover slides onto millifluidic chips. (e) Sealed chip after fly-cutting ready for testing. (f) Microplumber manifolds with clamped millifluidic chip ready for experiments.
convection oven using spring clamp fixture and a total force of ~100KN for the 3”x1” chip area. The maximum temperature of ~110˚C was kept for 1.5hrs followed by a slow cool down ramp of several hours to room temperature. In the final step, fly-cutting completed the fabrication process leading to the opening of the inlet and outlet holes (Figure 3.1(e)) that connect the millimeter fluidic channels to the manifold as shown in Figure 3.1(f).

3.2.3 Slug formation and its control

The experimental set-up for the slug formation is shown in Figure 3.2. In this setup, the PMMA flow focusing chip was mounted on a manifold (Model: 6 way manifold, MicroPlumbers microsciences LLC). Silicon oil was used as continuous phase and was pumped through the two outermost channels. The aqueous solutions of 0.1 mM rhodamine B and 0.1 mM methylene blue were used as a dispersed phase and were pumped through the two middle channels. The flow rate of each channel was controlled by high precision syringe pumps (NEMESYS, Cetoni). The generated slugs were recorded by the use of a handheld digital camera (Model: 44302, Celestron) which took pictures at a frequency of 30 frames per second. When setting a new flow rate, the system was run for at least 2 minutes to reach a steady state prior to taking the images. The slug sizes were averaged by taking more than 20 observed stable slugs.

![Figure 3.2 Schematics of the experimental setup for plug formation](image-url)
3.3 Numerical simulations

The VOF method was used to investigate the hydrodynamics of liquid–liquid slug formation between the aqueous solution (dispersed phase) and silicone oil (continuous phase) inside the millifluidic channels. It can be used to model two or more immiscible fluids by solving a single set of continuity and momentum equations and tracking the volume fraction of each fluid inside the computational domain. It is naturally conservative and relatively simple in tracking topological changes of the interface.[111] In addition to fast convergence, the other advantages are reasonably accuracy, relative simplicity and the ability to solve complex free surface flows. Its extensive application in modeling multiphase flows, including gas-liquid [93, 112, 113] and liquid-liquid slug flows [94, 95, 114] in microchannels is well documented.

The flows were manipulated in typical laminar flow regime (Re<1) and both fluids were modeled as incompressible Newtonian fluids. The VOF solver in commercial CFD software ANSYS Flunet 12 was adopted in this study.

Only a single set of continuity [Eq.(3.1)] and momentum equation [Eq.(3.2)] were solved continuously throughout the computational domain.

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0 \tag{3.1}
\]

\[
\frac{\partial (\rho \vec{v})}{\partial t} + \nabla \cdot (\rho \vec{v} \vec{v}) = -\nabla P + \nabla \cdot [\mu (\nabla \vec{v} + \nabla \vec{v}^T)] + \vec{F} \tag{3.2}
\]

of which \( \rho \) and \( \mu \) are the volume – averaged density and viscosity, which are defined as (3.3) and (3.4) respectively :

\[
\rho = \alpha_q \rho_q + (1 - \alpha_q) \rho_p \tag{3.3}
\]

\[
\mu = \alpha_q \mu_q + (1 - \alpha_q) \mu_p \tag{3.4}
\]
The VOF method used the geometric reconstruction scheme which based on piecewise linear interpolation [115] led to reconstructed interfaces. The interface was tracked by solving an additional advection equation [Eq.(3.5)], which yielded the volume fraction $\alpha_q$ of each fluid.

$$\frac{\partial (\alpha_q \rho_q)}{\partial t} + \nabla \cdot \left( \alpha_q \rho_q \vec{v}_q \right) = 0 \quad (3.5)$$

The body force term in Eq. (2) was computed using the continuum surface force (CSF) model [116] as shown in Eq. (3.6).

$$\vec{F} = \sigma \left[ \frac{\rho \kappa \hat{n}}{\sqrt{\rho_p + \rho_p}} \right] \quad (3.6)$$

where $\sigma$ was the surface tension coefficient, and $\hat{n}$ was the unit surface normal vector, and $\kappa$ was the local surface curvature, which are defined by Eq. (3.7) to Eq. (3.9).

$$n = \nabla \cdot \alpha_q \quad (3.7)$$

$$\hat{n} = \frac{n}{|n|} \quad (3.8)$$

$$\kappa = \nabla \cdot \hat{n} \quad (3.9)$$

The wall adhesion force was also taken into account by specifying contact angle as a boundary condition. We assumed that the contact line maintained a constant value and was independent of the velocity and the direction of contact line, thus a constant contact angle $\theta_w$ was used for all the operation conditions. The interface normal in the cells near the wall was calculated by Eq. (3.10):

$$\hat{n} = \hat{n}_w \cos \theta_w + \hat{t}_w \sin \theta_w \quad (3.10)$$
where $\hat{n}_w$ and $\hat{t}_w$ were the unit vectors normal and tangential to the wall. The calculated surface normal in one cell away from the wall was used to tune the local curvature $\kappa$, and this curvature was used to calculate the body force term in Eq. (3.6).

For solution methods, a transient explicit solver was used along with the implicit body force formulation. The PISO (pressure-implicit with splitting of operators) scheme was used for pressure-velocity coupling of the momentum equation and continuity equation. For spatial discretization, Green-Gauss node-based method was used for gradients, the PRESTO! (pressure staggering options) scheme was used for pressure interpolation, and the second-order up-wind differencing scheme was used for the momentum equation.

The internal structure of the focusing region of the millifluidic chip is shown in Figure 3.3(a). As the corners inside the millifluidic channels were rounded during fabrication, the internal structure in the focusing region was read into Image J to measure and use it to mimic the shape for numerical simulations. The three-dimensional computational setup of the millifluidic chip, as shown in Figure 3.3(b), has four inlets and one outlet. Aqueous solution ($\rho_d = 1000 \text{ kg/m}^3, \mu_d = 0.001 \text{ Pa} \cdot \text{s}$) was injected into the chip from the central inlets (inlet B and C) while silicone oil ($\rho_c = 963 \text{ kg/m}^3, \mu_c = 0.0093 \text{ Pa} \cdot \text{s}$) was injected through the side inlets (inlet A and D). The interfacial tension ($\sigma$) between the two solutions was assumed to have a constant value of 0.0365 N/m. [76, 94] The four inlets were all modeled as velocity inlets, and the outlet was modeled as outflow. No-slip boundary condition was imposed on the channel walls. Raj et al. have carried out similar numerical simulations of water-silicone oil slug flow in a T-junction microfluidic channel and found that the value of the contact angle was crucial in determining the flow pattern but only marginally affected the slug lengths. [94] The suitable contact angle ($\theta_w$) was in the range of 120 to 180 degrees. Our preliminary simulations showed
that stable slugs were obtained if the value of $\theta_w$ was larger than 120 degree, and slug lengths were insensitive to the value of contact angles. Therefore, in this study, $\theta_w$ was set as 120 degree. Same boundary conditions were also applied to the other designs.

Figure 3.3 (a) The internal structure of focusing region inside the millifluidic chip. The width of the straight channel is 0.5 mm. The chip has uniform depth of 1 mm. (b) Geometry of the flow focusing millifluidic chip used in three dimensional numerical simulations. The computational grids show one layer in z direction and focus on the flow focusing region. The computational domain consists of 180,400 hexahedral elements, of which the grids in the focusing region and in the straight channels are refined to capture the gradient in these regions. The four inlets and the outlet have the same dimensions as 1 mm depth and 0.5 mm in width.

The numerical simulations were carried out in a three-dimensional domain to quantitatively capture the slug formation process. The computational mesh was generated by ANSYS ICEM (ANSYS INc.). Hexahedral elements were generated with the mapped meshing scheme. The grids near the wall were refined to ensure good quality of gradient calculation. The lengths of the inlet channels were truncated so as to reduce the computational cost; however, the necessary length was chosen to ensure complete laminar flow development prior to the focusing
The slug formation was studied at two sets of flow rates: for the first set, the flow rate of the aqueous solution \( (Q_a) \) in each inlet was varied from 50 µL/min, 25 µL/min and 10 µL/min while the flow rate of silicone oil \( (Q_c) \) remained at 50 µL/min. In the second set, the flow rate of the aqueous solution in each inlet was varied from 25 µL/min, 10 µL/min and 5 µL/min while the flow rate of silicone oil remained at 100 µL/min. The maximum Ca calculated from the total flow rate of continuous phase inside the straight channel \( (Q_c = 200 \ \mu\text{L/min}) \) was 0.0017.

Three meshes with different grid resolutions were prepared to investigate grid resolution on the slug lengths. The slug length to the corresponding coarse mesh (44,980 elements), medium mesh (180,400 elements) and finer mesh (588,039 elements) were 6.15 mm, 6.02 mm, and 5.98 mm respectively. Therefore, the slug lengths were found to be independent from grid resolution in medium mesh. Similar mesh method was also adopted in other geometries.

The time steps during the simulations were selected appropriately to keep the maximum Courant number \( (Cr) \) less than 0.25. The numerical runs were performed remotely with 8 processors on cluster Philip the HPC (High Performance HPC) facility located at Louisiana State University.

### 3.4 Copper nanoparticle synthesis using slugs generated within the millifluidic reactor

Copper nanoclusters were synthesized using the new PMMA based four channeled millifluidic reactors as described connected with pressure pumps (Mitos P-pumps, Dolomite). Each slug formed within the millifluidic reactor, by two immiscible fluidic flows (tetradecane and water), acted as a mini-reactor for reagent combination and reaction. Tetradecane was used as a non-solvent carrier fluid injected through two outer inlet channels of the millifluidic reactor. The two aqueous based reagent streams were delivered through the two center inlet channels under nitrogen at room temperature. One of the centered inlets contained solutions of copper
nitrate and polymeric surfactant (MPEG) as stabilizer while the other contained the solution of sodium borohydride and sodium hydroxide in water. The concentration of each inlet solution is accurately prepared as described previously. Copper nanoparticle formation took place within the individual fused slug as it traversed along the switchback channel. The copper nanoparticles were collected under nitrogen and characterized using Transmission Electron Microscopy (TEM).

3.5 Results and discussion

3.5.1 Slug formation process in fabricated flow-focusing millifluidic chip

The slug formation process in the fabricated millifluidic chip can be described to proceed through five different stages: (1) the two streams of dispersed phase (aqueous solution) penetrates the continuous phase into the focusing region [Figure 3.4 (a)]. (2) The two streams merge together; meanwhile, the dispersed phase grows and effectively blocks the focusing region [Figure 3.4 (b)]. During this stage, the dispersed phase expands with a parabolic shape before it reaches the edge of the straight channel. As the continuous phase flows faster inside the gap between the tip of the dispersed phase and the channel wall in order to maintain the flow rate, a high pressure drop is built from each inlet to the interface of two phases [Figure 3.4 (c)]. (3) Due to the shear force and the pressure exerted by the continuous phase, the continuous phase drives the thread in its axial direction, and a visible neck forms while the dispersed phase is squeezed into the straight channel [Figure 3.4 (d)]. (4) The neck of the dispersed phase breaks asymmetrically adjacent to the channel wall in the junction region [Figure 3.4 (e)]. (5) Finally, a slug is pinched off from the dispersed phase and pushed into the
Figure 3.4 Left: Predicted slug formation process in the fabricated millifluidic chip from numerical simulation. Right: Observed slug formation process by experiments. The flow rate of the continuous phase in each inlet is 100 µL/min while the flow rate of the dispersed phase is 25 µL/min.
straight channel [Figure 3.4 (f)]. A good agreement of slug formation process between the experimental observation and numerical prediction indicates that our numerical model is able to capture the slug formation hydrodynamics.

3.5.2 Slug size as a function of flow ratio

Many reports show that the slug size obtained from liquid-liquid slug flow inside microfluidic chips can be easily tuned by adjusting the flow ratio of oil phase to water phase. The slug length was reported to increase with the volumetric ratio of water phase to oil phase based on both experimental observations\(^{35, 76, 114}\) and numerical simulations.\(^{80, 94}\) In this study, the effects of the flow rates (\(Q_c\) and \(Q_d\)) on slug lengths were investigated using numerical simulations supported by experiments. The obtained slug lengths under explored flow rates are shown in Figure 3.5.

Due to the irregular motion of syringe pumps, pressure fluctuations were induced to \(Q_c\) and \(Q_d\); therefore, fluctuations in slug lengths were observed. The fluctuations of flow rates became especially noticeable when \(Q_c\) and \(Q_d\) varied significantly, which was also observed by Tice et al. during their investigation of liquid-liquid slug flow inside microfluidic channels.\(^{35}\) The slug flow could be considered as nearly monodispersed as the maximum fluctuation of slug lengths was found to be less than 20%. The predicted slug lengths from numerical simulations agreed fairly well with the observed average slug lengths from the experiment. They both indicated that the slug lengths decreased with the flow ratio of the continuous phase to dispersed phase (\(Q_c/Q_d\)), suggesting that in this millifluidic channel the slug lengths can be tuned by adjusting the flow ratio. In the squeezing region, the slug length was reported previously as a function of the ratio of the flow rate of the two phases. Garstecki et al.\(^{11}\) proposed, based on their
Figure 3.5 Observed and predicted slug length under various flow ratios. The flow rates of the continuous phases are set as 50 µL/min and 100 µL/min respectively. The curves are the fitting results of the scaling law $L/W_c = \epsilon + \omega Q_d/Q_c$. The spread of the slug lengths in experiments is shown by the error bar.

observations of slug flow inside a T-junction microfluidic device, a linear scaling law in squeezing region as shown in Eq. (3.11):

$$L/W_c = 1 + \omega (Q_d/Q_c)$$  \hspace{1cm} (3.11)

where $L$ is the slug length, $W_c$ is the inlet width of the continuous phase, $\omega$ is the fitting constant related to the thinning width, and $Q_d/Q_c$ is the flow ratio of dispersed phase to continuous phase which is inverse to the x axis of Figure 3.5. The scaling law showed that the slug lengths in squeezing regime was independent of Ca and viscosities and depended only on the flow ratio. Their experimental results agreed well with the scaling law when $\omega$ was unity. Xu et al.,$^{[117]}$
compared their work with other experimental data and modified the linear scaling law to Eq. (3.12), suggesting that the channel geometry also played a role in controlling the slug lengths

\[ \frac{L}{w_c} = 1 + \omega Q \]  

(3.12)

where \( W_c \) is the width of inlet channel of continuous phase, \( \varepsilon \) and \( \omega \) are two fitting constants depending on the channel geometry.

In this study, the linear scaling law shown in Eq. (3.12) was adopted to show the effect of geometric dimensions on slug lengths, and \( W_c \) is selected as 0.5 mm. The obtained slug lengths from both experiments and numerical simulations can be fitted well. The linear relationship confirmed that the millifluidic reactor may provide similar control as microfluidic reactors, and the slug sizes can be manipulated inside this millifluidic chip easily by adjusting the flow ratios.

3.5.3 Synthesis of copper nanoparticles using the slugs generated within the millifluidic reactor

In order to test the capability of this millifluidic reactor, we carried out copper nanoparticle synthesis at two different flow ratios: a lower flow ratio (\( Q_c:Q_d = 1:1 \), slug length = 7.13 mm) and a higher flow ratio (\( Q_c:Q_d = 4:1 \), slug length = 4.35 mm). Each slug formed within the millifluidic reactor by the two immiscible fluidic flows (tetradecane and water) acted as a mini-reactor for reagent combination and reaction. Tetradecane was used as a non-solvent carrier fluid injected through two outer inlet channels of the millifluidic reactor. The two aqueous based reagent streams were delivered through the two center inlet channels under nitrogen at room temperature. One of the centered inlets contained solution of copper nitrate and polymeric surfactant, \( O-[2-(3-{\text{Mercaptopropionylamino}})_{\text{ethyl}}]-O'-\text{methylpolyethylene glycol (Mw 5000)}} [\text{MPEG}] \), while the other contained the solution of sodium borohydride and sodium hydroxide in water. We have previously demonstrated the utility of MPEG in a single phase millifluidic
synthesis to provide stable metal cluster colloids due to better coordination with metals, steric stabilization and superior colloidal stability.\textsuperscript{23b} In the current situation where copper nanoparticle formation took place within a slug, the surfactant was able to provide similar advantages due to better chelation with copper surface through bi-dentate ligands present at the terminal. Copper nanoparticle formation took place as each individual fused slug traversed the long switchback channel. The copper nanoparticles formed were collected under inert atmospheric conditions (nitrogen flow) at two different flow rates. As seen from the Transmission Electron Microscopy (TEM) images in Figure 3.6, lower flow ratio led to the formation of bigger (14.09 nm $\sigma = 3.41$) but less uniform particles compared to those (5.99 nm $\sigma = 1.14$) formed at a higher flow rate. In comparison with copper nanoparticles formed within the slug versus a single phase in a millifluidic reactor one could delineate some distinct differences on the characteristics of the copper nanoparticles formed. Both the snake mixer type millifluidic device previously used for single phase synthesis \textsuperscript{23b} as well as the current segmented flow focused millifluidic devices provided size controlled copper nanoparticles while retaining the spherical shape of the particles. At lower flow rate in the segmented flow millifluidic device yielded much bigger sized nanoparticle (14.09 nm $\sigma = 3.41$) while the single phase flow synthesis at a comparable flow rate of 6.8 ml/h flow rate resulted in obtaining copper nanoparticles of average diameter 3 nm with broader size distribution. \textsuperscript{23b} At a higher flow rate (850 $\mu$L/min ~ 51 ml/h) both types of millifluidic devices yielded very small copper nano particles of comparable size (2-3 nm). The results indicate that the shorter slugs yield more uniform nanoparticles. This is likely to be due to better mixing and reduced axial dispersion inside the shorter slugs. Tice et al., have studied the mixing performances of aqueous slugs inside a T-junction microfluidic device, and they concluded that the shorter slugs have better mixing due the relatively small amount of fluid.
However, in our case where millifluidic channels have been used, the larger dimensions resulted in longer slugs. This could be one of the reasons for the inability to produce uniform nanoparticles under the selected flow conditions. Therefore, both geometry as well as flow conditions need to be further optimized in order to arrive at optimum millifluidic design necessary to produce more uniform nanoparticles.

Figure 3.6 Copper nanoparticles synthesized at two different flow rates (a) 50 mbar pressure (150 µL/min) and (b) 200 mbar (850 µL/min)
3.5.4 Geometric optimization through CFD simulations

3.5.4.1 The effect of flow rate on slug size

A good understanding of how the geometry and operating conditions affect the slug length is necessary before starting geometric optimization. Based on the previous discussion on droplet formation, the volume of the slug can therefore be divided into two parts: the blockage volume ($V_{\text{block}}$) and the squeezing volume ($V_{\text{squeeze}}$). $V_{\text{squeeze}}$ may be expressed as the volume of aqueous solution squeezed into the straight channel during the squeezing stage (stage (4)); therefore, it is proportional to $Q_d$ and the time that the continuous phase takes to squeeze the dispersed phase ($V_{\text{squeeze}} \propto Q_d \cdot \tau_{\text{squeeze}}$). However, $V_{\text{block}}$ is fairly complicated to express as a function of $Q_d$; nevertheless, it may be considered as the accumulated volume of the aqueous solution inside the focusing region during the expanding stage (stage (2) ~ stage (3)).

In order to qualitatively understand the effect of $Q_c$ and $Q_d$ on slug breaking, the evolution of the neck width ($W_n$) was plotted as shown in Figure 3.7(b). As illustrated in Figure 3.7(a), $W_n$ was measured at the center line connecting the two inlets of the continuous phase. The $t=0$ was selected at the point when the dispersed phase first emerged at the line. $W_n$ first increased as the dispersed phase expanded in the junction region. When the dispersed phase reached the straight channel, $W_n$ grew to its maximum value; when squeezing occurs, $W_n$ started to decrease until one neck broke in the junction region. Due to the asymmetric breaking, $W_n$ maintained constant value till the second neck broke. As the slug separated from the dispersed phase, its tail slug formed a large sphere inside the junction region due to the surface tension force. As shown in Figure 3.7(c), this phenomenon was referred as “tailing”; which was not observed experimentally due to the fast process. When the tail passed through the center line, $W_n$
Figure 3.7 The scheme of the flow–focusing region and the liquid–liquid interface. For the analysis of the breakup, we track the width of neck of the dispersed phase \( W_n \) at the center line. (b) The predicted evolution of the neck width of the dispersed phase \( W_n \) from numerical simulation under various flow rates. The time \( t=0 \) is selected when the dispersed phase approached the line connecting the center of the two inlets of continuous phase. (c) The “tailing” phenomenon observed in numerical simulation.

first increased and then decreased. The evolution ended when the tail of the slug left the center line. From Figure 3.7(b), one can find that maximum \( W_n \) remained approximately constant \( (W_n \sim 1.4 \text{ mm}) \) under all the three flow rates. This suggested that the flow rates of the two phases \( (Q_c \text{ and } Q_d) \) had marginal effect on \( V_{\text{block}} \); \( V_{\text{block}} \) depends only on the geometry of the focusing region. As seen in Eq. (12), the slug lengths were determined by a geometry-controlled parameter \( \varepsilon \), which was controlled by \( V_{\text{block}} \). On the other hand, if \( Q_c \) was fixed \( (Q_c=50 \mu \text{L/min while } Q_d=50 \text{ and } 25 \mu \text{L/min respectively}) \), the squeezing rate or the squeezing time was almost the same (as we can see from the slope in the squeezing stage). This indicated that \( \tau_{\text{squeeze}} \) was a function of \( Q_c \) only, and high \( Q_d \) resulted in large slug size.
As $Q_c$ increased ($Q_n=25 \, \mu L/min$ while $Q_c=50$ and $100 \, \mu L/min$ respectively), $\tau_{\text{squeeze}}$ decreased dramatically; this meant that increasing $Q_c$ can reduce $V_{\text{squeeze}}$ so as to reduce the total volume of the slug. However, $Q_c$ was usually limited by the material and sealing of the chip during fabrication; the high pressure drop resulting from the high flow rate might cause leaking or damage. Another way to reduce the slug length, as an alternate to increasing the flow ratio, is to reduce $V_{\text{block}}$ by optimizing the geometry.

3.5.4.2 The effect of channel depth

The internal structural mainly affects $V_{\text{block}}$; which can be defined as the fluid volume enclosed by the parabolic surface in 3D as shown in Figure 3.7(a). $V_{\text{block}}$ is influenced by two parameters: the depth of the channel $h$ and the width of the shoulder in the focusing regime $W_{J}$. For the fabricated millifluidic channel, $W_{J}$ is approximately 2 mm and $h$ is 1 mm.

Gupta and Kumar have studied the effect of $h$ on slug length within a T-junction[118], and Liu et al. have also studied the effect of geometry on slug lengths in a cross-junction through numerical simulation[72]. They both indicated that reducing the channel depth may shorten slug lengths.

In order to investigate the influence of channel height on slug lengths within this millifluidic reactor, two channels of same planner geometry but different depths ($h = 0.5 \, \text{mm}$ and $0.25 \, \text{mm}$ respectively) are simulated at various flow ratios. Although reducing channel width lead to an increase in $Ca$, the influence is insignificant and the slug formation processes were still dominated by squeezing mechanism.

From the Figure 3.8 one can see that by reducing the channel height one may obtain smaller slugs to an extent. The corresponding $\epsilon$ values for $h = 1 \, \text{mm}$, $0.5 \, \text{mm}$ and $0.25 \, \text{mm}$ are
6.98, 5.89 and 4.84 respectively, which indicated that reducing channel height lead to a decrease in $V_{\text{block}}$. One can also conclude that by further reduction in channel height leads to a very small aspect ratio (channel depth / channel width). This may lead to even smaller slug formation albeit may not be practical from the stand point of view of fabrication as it may lead to collapse of the channel walls during fabrication.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.8.png}
\caption{Predicted slug lengths of the millifluidic reactor under various channel height, h. The flow rates of the continuous phases are set as the same as the explored flow ratios. The curves are the fitting results of the scaling law $L/W_c = \varepsilon + \omega Q_d/Q_c$.}
\end{figure}
3.5.4.3 The effect of $W_j$

In order to study the effect of $W_j$, we proposed two extra designs with optimized focusing region as shown in Figure 3.9. Compared to the fabricated chip, the optimized design 1 (Figure 3.9(a)) shrank the focusing region by directly connecting the four channels without rounded transitional channels; the width of the shoulder ($W_j$) was 1 mm. The optimized design 2 (Figure 3.9(b)) further reduced the $W_j$ to 0.5 mm. The depth of both channels was 1 mm.

In the optimized design 1, the slug formation process also underwent expansion (Figure 3.10 (b)~(c)) and squeezing (Figure 3.10 (d)~(e)) stages. The evolutions of $W_n$ at three flow rates were plotted in Figure 3.11, and they exhibited similar shapes as in the fabricated chip. In this design, the breaking points were inside the focusing region adjacent to the inlets of dispersed phase; therefore, “tailing” phenomenon was also observed for all the explored flow rates. Due to

Figure 3.9 Geometry and computational grid of two optimized millifluidic chip. (a) Optimized design 1 with 121,600 hexahedral elements in the computational domain. (b) Optimized design 2 with 90,000 hexahedral elements in the computational domain. The four inlets and the outlet of both designs have the same dimensions as 1 mm depth and 0.5 mm in width. The grids in the focusing region and near channel walls are refined to capture the gradient in these regions.
Figure 3.10 The predicted slug formation process from numerical simulation in optimized design 1. The formation process is shown at $Q_c = 100 \, \mu\text{L/min}$ and $Q_d = 25 \, \mu\text{L/min}$.

Figure 3.11 The predicted evolution of the dispersed phase neck width. The time starts when the dispersed phase first approached the line connecting the center of the two inlets of continuous phase.
the reduced shoulder \((W_j)\), the maximum neck width at the expanding stage decreased to approximately 0.95 mm. Therefore, \(V_{\text{block}}\) was significantly reduced, as one can also see from the significant reduction in \(\varepsilon\) (\(\varepsilon=3.07\) for this design compared to \(\varepsilon=6.98\) for the fabricated chip). Meanwhile, \(\tau_{\text{squeeze}}\) was also shortened because of the smaller neck width. As seen from Figure 3.12, much smaller slugs were obtained in all the explored flow rates in comparison with those in the fabricated chip.

![Figure 3.12 Predicted slug lengths of the two optimized designs under various flow ratios. The flow rates of the continuous phases are set as 50 \(\mu\)L/min and 100 \(\mu\)L/min respectively. The curves are the fitting results of the scaling law \(L/W_c = \varepsilon + \omega Q_d/Q_c\).](image)

Different from the fabricated millifluidic chip and optimized design 1, the optimized design 2 showed different breaking mechanism. The slug formation process shown in Figure 3.13 proceeded thorough expanding ((a)~(c)), squeezing with oscillations ((d)~(f)) and pinch-off stages ((g)~(i)). The breaking point moved downstream to the vicinity of the center line.
Figure 3.13 Predicted slug formation process from numerical simulation in optimized design 2. The formation process is shown at $Q_c = 100 \mu$L/min and $Q_d = 25 \mu$L/min.

connecting the two continuous phase inlets. As we had carried out mesh dependence studies with two grid resolutions (mesh 1 had 63,000 elements and mesh 2 had 90,000 elements), same oscillations were observed in both meshes; therefore, the numerical errors were likely eliminated. We concluded that the flow region had moved away from the squeezing regime described previously; it was in the transition from squeezing to dripping regime. Although the inlet flow
rates were maintained same as in previous chips, the local Ca was increased due to the smaller focusing region; therefore, the viscous force played more effect in this design. De Menech et al. mentioned that in this flow regime, the use of only Ca calculated for continuous phase to describe the dynamics of break up is not sufficient; one needs to take account an effective Ca calculated on the basis of both phases. Since our goal here is to obtain small slugs through optimizing geometries, we did not focus on the flow behaviors of the dripping regime in detail.

The maximum neck width at the expanding stage for design 2 was reduced to approximately 0.63 mm, leading to a significant reduced V_{block}. Therefore, smaller slugs were observed for all the explored flow ratios than design 1, as seen from Figure 3.12. Compared to the other geometries, changing the flow ratio inside the optimized design 2 did not lead to noticeable differences in slug length, which gives us another support that the slug breaking mechanism is in the transition from squeezing to dripping regime.

Since the breaking points propagated downstream in optimized design 2, the internal structure above the breaking points had less effect on V_{block} compared to the other two geometries; therefore, we may expect that further reducing W_j could not lead to a noticeable reduction in slug sizes. Other approaches that may produce smaller slugs in dripping regime should be adopted.

3.6 Conclusions

We have carried out experiments and numerical simulations of volume of fluid (VOF) method to investigate the liquid-liquid slug flows in a fabricated flow-focusing millifluidic device. The millifluidic device showed similar controllability on producing monodispersed slug lengths and also on nanoparticle synthesis as in the case of microfluidic devices. The slug
formation process was found to experience expanding and squeezing stages; therefore, the slug volume was expressed as the volume accumulated during these two stages. Through numerical simulation, we found that while manipulating flow rates can control the slug volume during squeezing stage, the blockage volume accumulated during the expanding stage depended only on the internal structure of the focusing region. Reducing the channel height does not significantly shorten the slug lengths. Further optimization of the geometry suggested two designs with better focusing region to reduce blockage volume; which produced slugs with smaller sizes. When the focusing region was reduced to certain value (as seen in the case of optimized design 2), the flow pattern shifted to the dripping region where the effect of the continuous phase was not significant. Although further reduction of the focusing region could reduce the blockage volume, the effect of reducing the slug lengths would be marginal. Preliminary investigations confirm the utility of slugs generated within the millifluidics for flow controlled synthesis of copper nanoparticles and the possibility to produce smaller sizes of particles at high flow rates. With recent advances reported in the synthesis of complex materials using segmented flow based microfluidics, our investigations reported here are anticipated to catalyze the development of future of lab-on-a-chip devices based on millifluidics.

3.7 Notations

A  cross sectional area (m$^2$)
Q  volumetric flow rate (µL/min)
F  body force
W  neck width of the dispersed phase or the width of channel (mm)
n  normal of the two fluid interface
h  channel height (m)
t  time (ms)
U  superficial velocity (=Q/A, m/s)
D  hydraulic diameter (m)

Greek letters

α  volume fraction in each computational cell
ρ  density (kg/m$^3$)
µ  dynamic viscosity (Pa*s)
u  velocity (m/s)
θ  contact angle (degree)
k  curvature of the two fluid interface
σ  liquid – liquid interface tension (N/m)
ω  geometric fitting coefficient of flow ratio
ε  geometric fitting coefficient

Subscript

c  continuous phase
d  dispersed phase
n  neck of the dispersed phase
w  wall
t  total

Dimensionless numbers

Re  = $\frac{\rho U t D}{\mu}$  Reynolds number (inertial forces vs. viscous forces)
Ca  = $\frac{\mu_e U_c}{\sigma}$  Capillary number (viscous force vs. interfacial forces)
Chapter 4 Numerical Investigations of Mixing Performances inside Slugs

4.1 Introduction

The previous chapter has discussed the slug formation process inside a flow-focusing millifluidic reactor where long slugs were observed due to the large internal area in the focusing region. The synthesized Cu nanoparticles did not show a significant improvement over those from single phase millifluidic reactors as expected. We attributed the reason to the poor mixing inside long slugs. In this chapter, numerical simulations are adopted to study mixing performances inside slugs at various operating conditions.

One advantage associated with slug flows is the rapid mixing inside slugs[33] driven by the strong convection. When slugs are travelling inside channels, the shear force exerted from the channel wall creates vortices: the fluid elements in the center have large velocity while those near wall have small velocity; the center fluid elements are forced to circulate along the wall as they cannot penetrate the two-phase interface, creating two parallel layers of vortices. Based on their experimental observations, Tice et al.[35] reported that mixing efficiency inside slugs is critically determined by the initial distribution of the reagents. Ideally, there are two types of initial distribution: axial and radial distribution as shown in Figure 4.1(a). Axial distribution leads to rapid mixing because the strong convection of the vortex can efficiently mix the reagents. In contrast, if the reagents are initially distributed in radial direction, mixing is dominated by molecular diffusion between these two layers, resulting in a slow mixing process. The initial distribution in reality is complicated because “twirling” effect redistributes the reagent into different part of the slugs. As the dispersed phase is injected into the immiscible continuous phase, the shear force between the two phases creates an eddy, which is referred as “twirling
effect” by Tice et al.[35] as shown in Figure 4.1(b). Twirling effect not only accelerates mixing before the slugs are separated from the dispersed phase but also distributes the reagents in axially direction. After slugs are separated, the recirculation mixes the reagents efficiently as they are on the path of the vortex.

![Image of twirling effect](image)

Figure 4.1 (a) Two ideal initial distributions of reagents. Top: axial distribution; Bottom: radial distribution. (b) Schematic illustration of “twirling” effect. Reproduced from reference 26a with copyright permission from 2003 American Chemical Society.

Experimental studies can give qualitative information about mixing, but the quantitative information is limited due to the complexity in measuring mixing efficiency. CFD simulations can provide the insightful knowledge without conducting experiments. In this work, CFD simulations are carried out to study the slug formation process and mixing performance inside slugs in a T-junction microfluidic reactor. The accuracy of the model is verified by comparing the data of slug formation dynamics with the experimental from Tice et al.[35] The work provides insights in mixing performances in various operation conditions.

**4.2 Numerical models**

VOF method, as discussed in section 2.5, is applied to study the slug formation process. In the dispersed phase, two aqueous streams are injected into the system. Dye solution is
modeled with concentration of 1 while water solution has concentration of 0. The species transport equation is used to study the transport of dye into water solution as shown in Eq. (4.1):

\[
\frac{\partial}{\partial t} C_i + \vec{v} \cdot \nabla C_i = D \nabla^2 C_i
\]  

(4.1)
of which \( C_i \) is defined as the concentration of dye solution, \( \vec{v} \) is the velocity filed that solved by Eq. (3.1) and Eq. (3.2), and \( D \) is the diffusion coefficient of dye in water. Assuming constant dilution approximation, the diffusivity of dye is set as \( 10^{-11} \text{m}^2/\text{s} \). In this work, mixing occurs only inside slugs, and the reagent does not transport to the continuous phase.

The mixing efficiency index \( \eta \) is employed to quantify the mixing performance as shown in Eq. (4.2), which evaluates the deviation from perfectly mixed state.

\[
\eta = \left[ 1 - \frac{\frac{1}{N} \sum^N_i (\bar{C}_s - \bar{C}_s^\star)^2}{\frac{1}{N} \sum^N_i (\bar{C}_s^0 - \bar{C}_s^\star)^2} \right]
\]

(4.2)

In this equation, \( N \) is the total number of cells inside the slugs used for estimation of the mixing index. The variable \( \bar{C}_s \) represents the scaled concentration value in each cell, while \( \bar{C}_s^0 \) and \( \bar{C}_s^\star \) are the scaled concentration values if the solutions are unmixed or perfectly mixed respectively. It should be noted that \( \bar{C}_s^0 \) has a value either 0 or 1. Based on Eq. (4.2), the theoretical limit for \( \eta \) is between 0 and 1. A user defined function is used to exact the position, the phase value and concentration data out from the computation domain. The perfect mixing condition is calculated by Eq. (4.3)

\[
\bar{C}_s^\star = \left( \sum^N_i \alpha_i V \bar{C}_s \right) / \left( \sum^N_i \alpha_i V \right)
\]

(4.3)

where \( V \) is the volume of the computational cell, and \( \alpha_i \) is the volume fraction of aqueous phase.
The commercial CFD solver ANSYS Fluent 12.1 (ANSYS Inc., USA) is adopted for the numerical simulations. A transient explicit solver is used along with the implicit body force formulation and the PISO (pressure – implicit with splitting of operators) scheme is used for pressure – velocity coupling of the momentum equation and continuity equation. For spatial discretization, Green – Gauss node – based method is used for gradients, the PRESTO! (pressure staggering options) scheme is used for pressure interpolation, and the second – order up – wind differencing scheme is used for the momentum equation.

The computational domain consists of uniform hexahedral elements, which are generated with the mapped meshing scheme in ICEM CFD software (ANSYS Inc., USA). The geometric setup of the microfluidic T-junction is shown in Figure 4.2. The width and depth of the entire channel is 50 µm[33], and the length of the channel after junction region is set as 1000 µm which ensures to hold at least two slugs. The lengths of the inlet channels are reduced so as to reduce the computational cost; however, proper values are assigned to ensure that fully laminar flows are developed prior to the junction. Velocity inlets are specified for these two inlets, and the outlet is modeled as outflow. No-slip boundary condition is imposed on the channel walls associated with constant contact angles. The time step is selected appropriately to keep the maximum Courant number (Cr) under 0.25. Numerical runs are performed remotely with 8 processors on cluster Philip – the HPC (High Performance HPC) facility located at Louisiana State University.

The properties of the fluids in this work follows the experimental values of Tice et al.[35]: the PFD solution is a 10:1 mixture of perfluorodecalin (PFD) and 1H, 1H, 2H, 2H – perfluoroocatanol. The density and viscosity are 1893 and 5.1 cp respectively. The aqueous phase contains dye and transparent water solution. The properties of these two solutions are close
to water solution: the densities of both solutions are 1000 kg/m$^3$ while the viscosities are set as 1.08 and 1.05 cp respectively. The interfacial tension between two phases has a constant value of 14 mN/m[35].

![Figure 4.2 Geometric dimensions of the microfluidic T-junction](image)

**4.3 Results and discussion**

In the present study, the slug formation dynamics are validated with the experimental observations by two factors: slug length and slug frequency. Since the slug formation process is fast, Tice et al.[35] adopted a length variable- “period” to avoid measuring the short slug formation time directly. Period is defined as the center-to-center distance between two adjacent slugs. The operating conditions are controlled by two parameters: water fraction (wf, the ratio of volumetric flow rate of aqueous phase to total flow rate) and total velocity ($U_{\text{total}}$). The effects of these two parameters on slug formations are investigated through numerical simulations.
4.3.1 Mesh dependence study

In order to eliminate the effect of grid resolution on simulation results, mesh dependence study is carried out at $U_{total} = 50$ mm/s and $w_f = 0.40$. The simulations are performed at three structured grids with different resolutions: a coarse grid (edge length = 5 µm), a medium grid (edge length = 2 µm) and a fine grid (edge length = 1 µm). The averaged slug length and period predicted from these grids are shown in Table 4.1. The slug length and period are believed to be converged with medium and fine grid resolution.

Table 4.1 Dependence of slug formation dynamics on grid resolution

<table>
<thead>
<tr>
<th>Slug formation dynamics</th>
<th>Grid resolution</th>
<th>Experimental observation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coarse</td>
<td>Medium</td>
</tr>
<tr>
<td>Slug length (µm)</td>
<td>100</td>
<td>114</td>
</tr>
<tr>
<td>Period (µm)</td>
<td>241</td>
<td>230</td>
</tr>
</tbody>
</table>

At high flow rates, the interface of the two phases propagates fast downstream; since VOF method uses geometric reconstruction to capture the two-phase interfaces inside each computational cell, low grid resolution might lose accuracy in capturing the interfaces at high moving velocity. The capability of the medium and fine grid resolutions to handle high flow rates ($U_{total} = 150$ mm/s) is studied at $w_f = 0.52$. The corresponding slug lengths for medium and fine grid resolutions are 102 and 100 µm while the periods are 144 µm and 142 µm respectively. Since the predicted slug lengths and periods may be regarded to be independent from the grid
resolutions, the medium mesh is believed to be capable to handle the highest flow velocity in this study. Therefore, the medium grid resolution is used for the following numerical simulations.

4.3.2 Four steps of slug formation process

Garstecki et al. postulated that the dynamics of slug break-up is dominated by the balance of pressures in the continuous phase and dispersed phase at the junction[76, 80]. Three types of forces are exerted at the tip of dispersed phase during breakup: surface tension force, shear stress force and the force arising from the increased velocity of continuous phase around the tip (take as resistance force for short). The surface tension force stabilizes the interface while the other two forces act as destabilizing forces. The interaction of the three forces changes the pressure between two phases at the junction region and breaks the slugs from dispersed phase. The slug formation process may be disrobed as four steps as shown Figure 4.3: (A) The tip of dispersed

![Figure 4.3](A) (B) (C) (D)

Figure 4.3 Four steps of slug formation process

phase (water) penetrates into continues phase (oil phase), and the slug begins to grow in the junction region. (B) As the tip of the dispersed phase grows downstream, it blocks the cross-section of the channel. The velocity of the oil phase is accelerated; the high velocity builds up a pressure drop from the inlet of oil phase. The shear stress force and resistance force squeeze the neck that connects the slug to the dispersed phase. (C) As the aqueous phase elongates and grows
downstream, and the neck is further squeezed and pushed towards the upper corner in the junction. (D) Finally, the neck breaks, and the slug with well–defined shape separates from the dispersed phase and travels downstream. Garstecki et al. have provided detail information on the relative magnitude of the three forces during break-up process[76, 80]. As it is not the key point in this study, we do not discuss them in detail here.

4.3.3 The effect of water fraction on slug formation

The effect of water fraction on slug length and period is studied by varying wf while $U_{\text{total}}$ remains constant at 50 mm/s. Tice et al.[35] reported that short slugs formed when the flow rate of the aqueous stream was lower than that of the PFD stream, and long slugs formed when the flow rate of the aqueous stream was high than that of the PFD stream. Similar phenomena were also observed in silicone-water[76], and kerosene-water[114] systems, which suggest that the slug length could be easily controlled by varying the relative ratio of aqueous phase to carrier fluid[35].

Numerical simulations were performed to study the effect of water fraction at $U_{\text{total}} = 50$ mm/s while $wf$ varies from 0.14 to 0.84. The contact angle is set as $140^\circ$. A comparison of predicted slug lengths and periods from simulations and measured from experiments are shown in Figure 4.4 (a). The predicted slug lengths and periods agree quantitatively with the experimental values except at $wf=0.84$. If the contact angle is set as $150^\circ$, the predicted slug length and period agrees with the experimental results better. The sensitivity of slug lengths and periods on contact angle is discussed in section 4.3.6.

Clearly from Figure 4.4(a), the curve of slug length consists of two regimes. At low $wf$ region ($wf = 0.14-0.40$), the slug lengths increase slowly with $wf$; however, at $wf = 0.60 – 0.84$, the slug lengths increase faster. As mentioned before, slug breaking process is the interaction of
Figure 4.4 (a) The slug length and period as a function of various water fraction. The experimental values are obtained from Tice et al., 2003. (b) Contour of slug formation at various wfs. The contact angle is set as $140^\circ$ for $wf=0.14-0.73$ while for $wf = 0.84$ the contact angle is $150^\circ$. 
shear stress force, resistance force and surface tension force. Garstecki postulated that the viscous force plays an important role in slug formation dynamics if Ca of the continuous phase is above an approximate critical value of 0.01\cite{76,80}. At low wf (wf=0.14-0.40), the breaking mechanism is governed by dripping that shear force dominates the breaking process. As shown in Figure 4.4(b), slugs are separated from the dispersed phase quickly as before the dispersed phase effectively blocks the entire width of the channel, thus short slugs are obtained. At high wf region (wf=0.60-0.84), the shear stress force is not significant; resistance force takes major effect in slug breaking. The slugs do not separate in the junction region immediately after the dispersed phase blocks the entire channel; instead, it propagates downstream and forms a segment before slugs separate from the dispersed phase. As a result, long slugs are produced, and the slug lengths are linearly proportional to water fraction. Numerical simulations are also performed to investigate the effect of $U_{\text{total}}$ ($U_{\text{total}} = 20, 50, 100$ and $150$ mm/s) on slug formation dynamics. The simulations are carried out at constant wf (wf =0.52) and contact angle of $140^\circ$.

4.3.4 Effect of total velocity on slug formation

Tice et al. has reported that the total flow velocity and water fraction are the two important parameters that decide the flow patterns\cite{119}. Under low Ca numbers, the usual flow patterns are slug and stratified flow. If Ca increases to certain threshold, the dispersed phase forms a short segment and the separation point is beyond the junction. At high Ca, the flow shifts to jetting regime. The segment propagates further downstream and its length fluctuates. The slug sizes also decrease noticeably. At the explored velocities in the experimental work, the flow patterns were reported to belong to slug flow regime, and the slug length and period were reported to be virtually dependent of the total flow rate\cite{35}. The simulations agree well with experimental observations at 20 mm/s and 50 mm/s as shown in Figure 4.5 (a) and (b). Slugs
separate from dispersed phase inside the junction region, and the lengths of slugs and periods are marginally changed by flow velocities.

<table>
<thead>
<tr>
<th>$U_{total}$ (mm/s)</th>
<th>20</th>
<th>50</th>
<th>100</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ca$</td>
<td>0.0035</td>
<td>0.0087</td>
<td>0.018</td>
<td>0.026</td>
</tr>
</tbody>
</table>

Figure 4.5 (a) Comparison of slug length and period length at various velocities. The experimental values are obtained from Tice et al., 2003. (b) Contours of slug formation at various velocities.

However, the predictions of high total velocities deviate from the experimental observations. As $U_{total}$ increase to 100 mm/s, the flow pattern shifts to jetting regime. A segment forms near the junction region and the slug length and period decrease noticeably. Further increase of velocity to 150 mm/s leads to a longer laminar segment; meanwhile, the period decreases significantly while the slug length is marginally influenced. One possible reason for the deviation might due to failure modeling of wall adhesion force at high velocities. In this study, constant static contact angle is specified; in reality, dynamic contact angles are formed when the flows are moving along the wall. At low flow velocities, the difference between static contact angle and dynamic contact angle might be ignored; however, at high velocities, the difference between them might be significant. The sensitivity of slug formation dynamics is discussed in the following section.
4.3.5 Sensitivity of contact angle

The effect of wall adhesion on slug formation is taken into account by specifying a constant contact angle near wall. Other researchers have reported that the contact angle has a significant effect on determining the flow patterns (stratified flow or slug flow) while the slug lengths are marginally influenced by contact angle\[94, 114, 120\]. In reality, because a thin film of oil phase is developed on the wall (wetting by oil phase), other researchers suggested to use a quasi-non-wetting condition that set the contact angle of dispersed phase as $180^\circ$\[121\]. However, due to the poor near-wall grid resolution, the thin film cannot be observed\[113\]; therefore, a small contact angle is assigned to tune the slug size.

The slug formation at various \(\text{wf} (\text{wf} = 0.14 \sim 0.84)\) are investigated \(\text{U}_{\text{total}} = 50 \text{ mm/s}\) with two different contact angles ($140^\circ$ and $180^\circ$). As shown in Figure 4.6, the different of predicted slug length and period is small at low \(\text{wf} (\text{wf}=0.14\sim0.40)\); however, at high \(\text{wf} (\text{wf}=0.60\sim0.84)\), they start to differ from each other significantly. The large deviation is due to the different wall adhesion force resulting from the contact angle that exerted on the dispersed phase before slug separation. At low \(\text{wf}\), because the slug are separated before the dispersed phase block the channel, the difference of adhesion force that exerted on the dispersed phase is small; therefore, the slug length and period have approximate same value. At high \(\text{wf}\), the dispersed phase forms a long segment before separation; thus different contact angle leads to large difference in wall adhesion force, thus in turn different slug length. Longer segment gives larger difference; thus a significant difference in slug length is observed at \(\text{wf}=0.84\). Among the explored contact angles, the slug length predicted by contact angle of $150^\circ$ matches the experimental results best; thus in the following study, the contact angle is set as $150^\circ$ for \(\text{wf}=0.84\). As discussed in section 4.3.5, the predicted slug formation dynamics at high velocities deviate from experimental observations.
Figure 4.6 Comparison of slug length and period at various Wfs if the contact angles are set as 140° and 180° (b) Slug lengths and periods at different contact angles
The reason might be the dynamic contact angles are different from the statistic contact angle at high velocities. Therefore, the contact angles are varied to see if the slug formation dynamics at high velocities can be predicted. As shown in Figure 4.6 (b), increasing contact angle marginally affects the slug length and period. The observed slug formation dynamics at high velocities (100 mm/s and 150 mm/s) cannot be observed at the explored contact angles.

In a short conclusion, the VOF model with static contact angle can predicate the slug formation dynamics well at low flow velocities (20 mm/s and 50 mm/s). At high velocities, it fails to capture the breaking mechanisms and dynamic contact angle model is needed. Thus the following studies about mixing inside slugs are carried out at low flow velocities.

4.3.6 Mixing efficiency as a function of water fraction

Tice et al. reported that mixing efficiency is virtually dependent on slug length, and mixing inside long slugs is not as good as inside short slugs. However, quantitative comparison of mixing efficiency inside slugs is more difficult to obtain from experiments than numerical simulation. In this section, numerical simulations on mixing inside slugs are carried out at $U_{\text{total}} = 50$ mm/s while $w_f$ varies from 0.14 to 0.84. The predicted mixing performances as shown in Figure 4.7(b) agree well with the experimental observations in Figure 4.7 (a).

A qualitative conclusion can be made from Figure 4.7 that mixing inside short slugs is better than it in long slugs. Two factors mainly influence mixing inside slugs: twirling effect and slug size. When the dispersed phase penetrates the carrier fluid, the shear force between the immiscible phases creates an eddy that mixes dye and water before the separation of slug as well as redistributes these two reagents into axial direction of the slugs. As indicated from both experiments and simulations, twirling occurs before the tip of the dispersed phase made contact
Figure 4.7 (A) Experimental observation of mixing at different water fraction reported by Tice et al. (B) Contour of dye centration predicted by numerical simulations
with the low channel wall. Two effects may influence twirling: twirling time and twirling strength. Twirling time is controlled by the flow rate of the dispersed phase: the smaller the flow rate is, the longer time twirling has to redistribute the reagents. Tice et al. argued that twirling strength is the amount of carrier fluid (oil phase) that flows past the tip of dispersed phase; in other words, twirling length can be regarded as the shear force between two phases. However, direct evidences were not provided in their experiments.

Slug size plays an important role in mixing for two aspects. Long slugs have large amounts of dye to be twirled to axial direction; therefore, twirling effect on long slugs is not as significant as in short slugs in distributing the initial reagents in axial direction when the twirling time is same. The other aspect is that long slugs have long circulation path, thus the recirculation period is longer.

In order to qualitatively understand the relatively importance of these factors on mixing, the mixing efficiency indices of slugs obtained under various \( \text{wt} \) were plotted with residence time as shown in Figure 4.8. The starting time \( (t=0) \) is adopted as the moment as the second slug is separated from the dispersed phase. The residence time ends at the time this slug approaches near the outlet of the channel. Clearly there are two regimes: convection dominated and diffusion dominated regime. In the convection dominated regime, the mixing efficiency increases rapidly with residence time; recirculation mixes the reagents inside the two parts efficiently as dye is distributed in axial direction; after the concentrations of the two layers become uniform, mixing is controlled by diffusion between these two layers. The lines in diffusion dominated regime have approximately same slopes, indicating that the difference of the circulation length marginally affected mixing in this regime. As soon as the reagents diffuse to the other part (dye or water intensive zone), they are mixed by recirculation effectively.
Figure 4.8 mixing efficiency index inside slugs as a function of residence time of the slug

With the increase of \( w_f \), the mixing efficiency is noticeably dampened in the convection dominated regime. The initial mixing resulting from twirling effect drops down dramatically because of the large amount of reagents to be twirled. There are three possible reasons: first one is with the \( w_f \) increases, the velocity of dispersed increase, thus the reagents have less twirling time. The other reason is that as the \( w_f \) increase, the slug length increase, thus the amounts of reagents inside the slugs are large, thus twirling effect is not significant to redistribute such large amounts of dye. The third reason is that with \( w_f \) increases, the flow rate of the continuous phase decreases; therefore, twirling strength is decreased. In this stage, one can know that which reason is dominant. The question is answered by varying \( U_{\text{total}} \).
4.3.7 The effect of total velocity on mixing

As discussed in the above section, the twirling effect is a vortex induced by the shear force between the two phases. Since the mixing of dye and water solutions inside long slugs is not efficient, one may ask if the mixing efficiencies in long slugs can be improved by using high total velocity \( U_{\text{total}} \). When \( U_{\text{total}} \) is increased, the shear force exerted by the continuous phase is strengthened, which consequently enhances the twirling effect as well as the recirculating flow inside slugs. To understand the impact of \( U_{\text{total}} \) on mixing, additional simulations were carried out with \( U_{\text{total}} = 20 \) and 50 mm/s and \( \omega f = 0.20 \) and 0.52. As discussed in section 3.3, the slug sizes are almost identical for a particular \( \omega f \) value; therefore, the effect of the amount of fluid on mixing is eliminated by comparing the slugs with same \( \omega f \) but different values of \( U_{\text{total}} \).

The contour plots of the dye concentration shown in Figure 4.9(A) indicate that the mixing efficiencies in small slugs (\( \omega f = 0.20 \)) cannot be improved significantly by increasing \( U_{\text{total}} \). When \( U_{\text{total}} = 20 \) mm/s is used, the long twirling time results in a good initial mixing but “over–twirling” phenomenon as well. As shown in Figure 4.9(B), if \( U_{\text{total}} \) is increased to 50 mm/s, the initial mixing index decreases approximately 5% than that of \( U_{\text{total}} = 20 \) mm/s because of the reduced twirling time; however, as the twirling effect is strengthened by increasing \( U_{\text{total}} \), the solutions are distributed more effectively in the front and rear parts of the slugs. After the slugs is separated, the enhanced recirculating flow can mix the solutions rapidly in the upper and lower parts, which is evident by the large slope of the mixing efficiency curve of \( U_{\text{total}} = 50 \) mm/s in the convection dominated regime. When the slugs approaches the outlet of the channel, the mixing indices increase about 3% higher than that of \( U_{\text{total}} = 20 \) mm/s. On the other hand, the enhanced twirling effect results in “over–twirling” as well. As seen in Figure 4.9(A), the majority of the
Figure 4.9 (A) Contours of the dye concentration for $U_{\text{total}} = 20$ and $50$ mm/s with $wf = 0.2$ and $0.52$. The plane is taken from the middle of the microfluidic T-junction in z direction. (B) The mixing efficiency inside slugs with respect to residence time for $U_{\text{total}} = 20$ and $50$ mm/s with $wf = 0.2$ and $0.52$
dye solution is distributed in the upper part of the slug; consequently, the mixing efficiency is undermined by enhanced twirling strength to some extent.

If \( wf \) is increased to 0.52, the obtained slug size is close to two times than that of \( wf=0.20 \). As seen from Figure 4.9(B), mixing is not improved by increasing \( U_{\text{total}} \). Compared to the large amount of fluid inside the slug, the amount that can be distributed by twirling is still small even though the twirling effect is strengthened. The mixing indices corresponding to \( U_{\text{total}} = 20 \text{ mm/s} \) and 50 mm/s are close to each other when the slugs reach the outlet.

Based on these results, one may conclude that mixing inside slugs cannot be improved significantly by increasing \( U_{\text{total}} \). Since the short slugs already have efficient mixing performance because of their small sizes, increasing the shear force has limited effect on improving mixing. On the other hand, long slugs have relatively large amounts of fluid to be distributed through the twirling effect. Even though the twirling strength is enhanced by increasing \( U_{\text{total}} \), the impact on mixing is still insufficient compared to the large amount of fluid inside slugs. Therefore, it is more effective to reduce the slug sizes than increasing the total velocities in terms of improving the mixing performance inside slugs.

4.4 Conclusion

In this work, we have adopted the VOF method coupled with the species transport model to quantitatively investigate the dynamic mixing process of dye and water solutions inside slugs generated by a microfluidic T–junction. After eliminating the potential errors resulting from the grid resolution of the computational mesh and the entrance lengths of the channel inlets, we have validated the numerical model by comparing the obtained slug lengths and periods with the experimental data reported by Tice et al.\textsuperscript{22} at various operating conditions. The simulation results
have shown that the VOF method can capture the slug formation dynamics and the internal velocity fields inside the slugs successfully. The mixing indices of slugs have been employed to understand the evolutions of mixing efficiencies inside the microfluidic channels. When the dispersed phase enters the junction region, the shear effect exerted by the continuous phase induces the twirling effect, which distributes the solutions transversely to the front and rear parts of the slugs. After the slugs are detached from the dispersed phase, the recirculating flow inside the slugs can mix the solutions efficiently. The twirling effect is noticeably influenced by the slug sizes. For long slugs, the twirling effect cannot distribute effectively because of the large amount of fluid contained in the slugs. In contrast, the twirling effect appears to be very effective for short slugs as the amount of fluid is small, even though long twirling time in certain operating conditions may cause “over–twirling” phenomenon that undermines the mixing. Although one can enhance the twirling strength by increasing the total velocity, its impact on improving mixing is not as effective as reducing slug sizes. This study provides fluid mechanical insights to the design and operation of droplet–based microfluidics where efficient mixing inside slugs is essential in such cases as nanomaterial synthesis, studies of in–situ reaction kinetics, cell activation in cryopreserved cells and protein crystallization.
Chapter 5 Numerical Study of the Viscous Droplet Breakup Process inside a Microfluidic Device Controlled by External Static Electric Field

5.1 Introduction

Droplet-based microfluidics has attracted extensive research interests due to its superior control over fluid flow in the microfluidic devices[39, 40]. By introducing another fluid to the system, the reagent fluid is encapsulated inside discrete droplets or slugs of micro–liter volume[20]. Compared to the traditional microfluidic systems using single–phase flow, droplet–based microfluidics provides several unique advantages such as rapid mixing, reduced dispersion and minimized surface fouling[20, 35]. These advantages have ensured droplet–based microfluidics numerous applications on DNA analysis, protein crystallization, chemical synthesis and other fields[13, 122].

For most of these mentioned applications, it is critical to generate droplets of controlled sizes. Most of the droplet–generating techniques in literature are based on passive methods which utilize device geometry and the fluid flow. According to the types of fluid flow inside the devices, the passive droplet–generating devices can be generally categorized as co–flow, cross–flow and hydrodynamic flow–focusing[105]. In all of these mentioned devices, the flow rates of the continuous and dispersed phases are manipulated to generate droplets of desire sizes. By tuning the flow ratios of the two phases (the flow rate of the continuous phase to the dispersed phase), the relative magnitudes of inertial, viscous and surface tension forces are altered which in turn results in different breakup patterns. Based on the relative importance of these forces, the droplet breakup process can be classified into the squeezing, dripping and jetting regimes [105]. Previous studies in literature have shown that the droplets generated by passive methods usually have sizes comparable to the device dimensions. For example, the diameter of the droplets
produced in the dripping regime using the hydrodynamic flow–focusing devices (HFFD) usually approximates to the orifice size [68]. If droplets of small sizes are required, the HFFD have to be operated in the dripping regime with very high flow ratios. However, this approach is not effective for particular circumstances, i.e., if the dispersed phase is more viscous than the continuous phase. For example, Nie et al. have used silicone oil of different viscosity values as the dispersed phase and aqueous solutions as the continuous phase to study the droplet breakup process in a HFFD. If the viscosity values of the dispersed and continuous phases were 50 cp and 1 cp respectively, the obtained droplets remained large sizes for a broad range of operating ratios. They concluded that the droplet sizes are marginally affected by increasing the flow ratios when the dispersed phase has larger viscosity values than the continuous phase [123]. In these circumstances, active droplet–based microfluidic devices can provide better control over droplet sizes compared to the passive devices. The active techniques utilize external actuators, such as deflected membranes[124], pressure chambers[125], acoustic waves [126, 127] and electric fields [128, 129] to provide better control over droplets inside the microfluidic devices. Link et al. has presented their study on manipulating droplets by introducing external static electric field to the conventional microfluidic devices. They have developed modules that were able to precisely control the droplet motions involving breakup, coalescence, sorting, etc. [129].

The idea of employing electric field to control the droplet breakup in microfluidic devices is imported from the electrospray or electro-hydrodynamic atomization (EDHA) technique, which has been used for the fabrication of mono–dispersed polymeric particles[130, 131]. In EDHA, the droplet breakup from the disperse phase is primarily controlled by the electric field while the continuous phase is usually static. In microfluidic devices incorporated with the electric field, the conventional microfluidic devices, i.e., microfluidic HFFDs, are embedded
with electrodes that are attached to a high voltage direct current (DC) power supply. Because of
the difference of the electrical properties existed between the two phases, i.e., the electric
permittivity and conductivity, surface charges including polarization charges and free charges are
induced by the electric field. The interaction of the electric field and the surface charges results
in additional electrical forces on the fluid interface known as Maxwell stress. With appropriate
distributions of the electric field in the microfluidic devices, Maxwell stress provides an
additional handle to break the droplet from the disperse phase. Hence the droplet size can be
controlled by both the flow ratio and the electric field strength. Link et al. have studied the effect
of the electric field strength on droplet sizes in a microfluidic HFFD coupled with an external
static electric field; they reported that the droplet size decreased remarkably when the applied
voltage exceeded the threshold value[129]. Kim et al. have also explored the dependence of
droplet sizes on the electric field strengths, and they reported similar results as those from Link.
They demonstrated that tiny water–in–oil less than 1 μm could be generated in their microfluidic
HFFD with the aid of very high electric field [132].

Despite the experimental explorations, the fundamentals of the droplet breakup process in
the microfluidic devices controlled by external electric field have not been fully understood yet.
Many parameters are playing roles in the droplet breakup process, i.e., the flow rates of both the
continuous and dispersed phases, the fluid properties, the electrical properties and etc., which
makes the breakup process very complicated. Numerical simulations provide an effective way to
investigate the droplet breakup process. Herein, we present our work of using numerical
simulations to study the effect of the external static electric field on controlling the breakup of
viscous oil droplets inside a microfluidic HFFD. The dispersed phase used by this study is
silicone oil of large viscosity values, and the continuous phase is an aqueous solution that is
much less viscous compared to the dispersed phase. In the numerical model, the motion of the interface between the two phases was tracked by the conservative level – set method (LSM). A body force term describing the electric force was added to the Navier–Stokes equations in order to take account of the effect of the electric field on the droplet breakup dynamics. The distributions of the electric field were estimated by the electric static equation simplified with the perfect dielectric assumption. The accuracy of the LSM was validated by comparing the predicated droplet sizes from the simulations with the experimental observations reported by Nie et al. in 2008[123]. The electrostatic model was validated by the classic droplet deformation problem [133]. After the numerical model had been validated, we applied various electric voltages to the microfluidic systems to study the resultant droplet breakup process. This work would benefit the understanding of the droplet breakup dynamics controlled by the electric field and may provide help to design and operate the droplet–generating devices.

5.2 Numerical methods

5.2.1 Governing equations for electric field

The electric field is governed by Poisson’s equation:

\[ \nabla \cdot (\varepsilon \nabla V) = \rho_f \]  \hspace{1cm} (5.1)

where \( \varepsilon = \varepsilon_0 \varepsilon_r \) is the permittivity of the medium (unit: C/(V*m)), \( \varepsilon_0 = 8.854 \times 10^{-12} \) C/(V*m) is the vacuum permittivity, \( V \) is the electric potential (unit: V) and \( \rho_f \) is the volumetric free charge density (unit: C/m\(^3\)). The electric field \( \vec{E} \) (unit: V/m) is related to the electric potential through the equation:

\[ \vec{E} = -\nabla V \]  \hspace{1cm} (5.2)
In this study, the electric permittivity of the two phases are different, thus $\varepsilon$ varies across the fluid interface. Consequently, the electric field changes not only in the strength but also in its direction as it crosses the fluid interface. The permittivity value is weighted according to the volume fraction of each phases or the level–set function $\phi$ as seen in Eq. (5.3):

$$\varepsilon = \varepsilon_c + (\varepsilon_d - \varepsilon_c)\phi$$

(5.3)

of which the subscripts $c$ and $d$ denote the continuous and disperse phases; $\varepsilon_c$ and $\varepsilon_d$ are the permittivity values of the pure fluid; $\phi$ is the level–set function.

5.2.2 Governing equations for the fluid flow

The interface between the two phases is tracked by the conservative level–set method (LSM). The LSM was introduced by Osher and Sethain in 1988 [134] and was further developed by Sussman, Smereka, and Osher in 1994 [98]. It has now emerged as a popular method to simulate the multiphase flow problems. Besides being robust, LSM does not require geometric constructions thus can accurately represent the interfacial variables such as the interfacial normal and curvature. As the level–set function transits across the interface smoothly, the standard discretization of the interfacial variables using the level–set function can achieve high order accuracy, i.e., the secondary–order or higher order accuracy. Such advantage is especially important for this study. As a thin filament is formed inside the orifice of the microfluidic HFFD, accurate predictions of the surface normal and curvature are critical to estimate the surface tension force, electric body force and other quantities. One drawback associated with the LSM is the large computational cost compared to other methods such as the volume of fluid (VOF) method. The other is the non–conservation of mass which is commonly found in the traditional LSM, which can be avoided by using the conservative LSM.
Olsson and Kresis have proposed a conservative form of LSM in 2005, and this method has been demonstrated to be able to solve the mass conservation issue [96]. Their level–set equation is expressed as

$$\frac{\partial \phi}{\partial t} + \bar{u} \cdot \nabla \phi = \gamma \nabla \cdot \left( \epsilon \nabla \phi - \phi (1 - \phi) \frac{\nabla \phi}{|\nabla \phi|} \right)$$

(5.3)

where the level–set function $\phi$ is a smooth step function between 0 and 1; $\bar{u}$ is the velocity field predicted by the Navier–Stokes equations. If $\phi = 0$, it corresponds to the continuous phase; if $\phi = 1$, it stands for the dispersed phase. Across the interface, $\phi$ transits smoothly from 0 to 1. The left–hand side of Eq. (5.3) is an advection equation; since it is numerically unstable, the terms on the right–hand side are necessary for numerical stability. The parameter $\epsilon$ determines the thickness of the interface where $\phi$ goes smoothly from 0 to 1. It is on the same order as the computational mesh size of those elements where the fluid interface propagates through. The parameter $\gamma$ determines the amount of reinitialization or stabilization of the level–set function. A suitable value for $\gamma$ is the maximum magnitude of the velocity field. These two parameters are tuned accordingly during the simulations.

The interfacial variables such as the unit normal of the interface $\hat{n}$ and the curvature $\kappa$ are calculated based on $\phi$ as seen in Eq. (5.4) and Eq. (5.5):

$$\hat{n} = \nabla \phi / |\nabla \phi|$$

(5.4)

$$\kappa = -\nabla \cdot \hat{n}|_{\phi=0.5}$$

(5.5)

The interfacial tension force acting on the interface is then estimated by

$$\overline{F}_{sf} = \sigma \kappa \delta \hat{n}$$

(5.6)
of which $\sigma$ is the interfacial tension coefficient (unit: N/m); $\delta$ is a Dirac delta function indicating the location of the interface, which is approximated by a smooth function shown in Eq. (5.7):

$$\delta = 6|\nabla \phi||\phi(1 - \phi)|$$

In this study, the LSM solves one–set of the Navier–Stokes equations with the assumption that the both phases are incompressible fluid. The governing equations for the fluid flow are

$$\frac{\partial}{\partial t} \rho + \nabla \cdot (\rho \vec{u}) = 0$$

$$\frac{\partial}{\partial t} (\rho \vec{u}) + \nabla \cdot (\rho \vec{u}\vec{u}) = -\nabla P + \nabla \cdot [\mu(\nabla \vec{u} + \nabla \vec{u}^T)] + \vec{F}_{sf} + \vec{F}_{ef}$$

where $\rho$ and $\mu$ are the weighted density and viscosity across the interface, $\vec{F}_{sf}$ is the surface tension force formulated by Eq.(6) and $\vec{F}_{ef}$ is the volumetric electric body force. Since the density difference between the two phases is small, the gravitational force is neglected in this study.

The fluid properties used by the Navier–Stokes equations are weighted by $\phi$ across the interface:

$$\rho = \rho_c + (\rho_d - \rho_c)\phi$$

$$\mu = \mu_c + (\mu_d - \mu_c)\phi$$

in which $\rho_c$ and $\rho_d$ are the density values of the continuous phase and the dispersed phase; $\mu_c$ and $\mu_d$ are the viscosity values of the two phases respectively.

The electric body force $\vec{F}_{ef}$ is computed by taking the divergence of Maxwell stress tensor ($\vec{T}_{MW}$) with the assumption of incompressible fluid:
\[ F_{ef} = \nabla \cdot T_{MW} = -\frac{1}{2} (E \cdot E) \nabla \varepsilon + \rho_f E \]  

(5.10)

of which the first term \(-\frac{1}{2} (E \cdot E) \nabla \varepsilon\) estimates the component of the electric force contributed by the polarization charges induced by the varying electric permittivity across the interface. The direction of this force component is determined by \( \nabla \varepsilon \). The second term \( \rho_f E \) takes account of the component contributed by the interaction of the free charges and the electric field. The direction of this force component is same as that of the electric field.

5.2.3 Perfect dielectric model

In order to estimate the free charge density \( \rho_f \) on the interface, the transport of the ionic species has to be taken into account. The governing equation that describes the transport of the free electric charges inside electric field is the charge conservation equation shown as following:

\[ \frac{\partial}{\partial t} \rho_{f,i} + \nabla \cdot \vec{J}_i = 0 \]  

(5.11)

where \( \rho_{f,i} \) is the free charge density of \( i^{th} \) ionic species; The ionic flux of the \( i^{th} \) ionic species \( \vec{J}_i \) is governed by the Nernst–Planck equation as shown in Eq. (5.12):

\[ \vec{J}_i = \rho_{f,i} \vec{u} - D_i \nabla \rho_{f,i} - \frac{z_i F \rho_{f,i} D_i}{RT} \nabla \psi \]  

(5.12)

in which the three terms correspond to the ion transport due to convection, diffusion and migration respectively; \( D_i \) is the diffusion coefficient of the \( i^{th} \) ionic species (unit: m\(^2\)/s); \( z_i \) is the valence of the \( i^{th} \) ionic species; \( F \) is the Faraday constant (\( F = 9.649 \times 10^4 \) C/mol); \( R \) is the ideal gas constant (\( R = 8.3145 \) V*C/(K*mol)); \( T \) is temperature (unit: K).

Although the transport equation of the ionic species shown in Eq. (5.11) and (5.12) seems adequate to describe the free charge density on the fluid interface, there are difficulties in solving
these equations. The key issues are related to the definition of the electrostatic boundary condition on the fluid interface [135]. The relationship of the individual ionic species concentrations between the two phases is still not clear, which requires detailed chemistry of the system to invoke[133, 135]. Usually the transport equations of the ionic species are simplified by making suitable assumptions. Currently, three simplified models have been reported in literature. Namely, they are the perfect conductor model [136], the perfect dielectric model [137, 138] and the leaky dielectric model[139].

In this study, the perfect dielectric model is adopted based on the assumption that both the continuous phase and the dispersed phase can be regarded as dielectric. The concentration of the free charges on the interface is negligible compared to that of the polarization charges. The governing equation of the electrostatics shown in Eq. (5.1) is then simplified to the Laplace equation:

\[
\nabla \cdot (\varepsilon \nabla V) = 0
\]

(5.13)

Accordingly, the electric body force \( \vec{F}_{ef} \) shown in Eq. (5.10) contains the component contributed by the polarization charges only:

\[
\vec{F}_{ef} = -\frac{1}{2} (\vec{E} \cdot \vec{E}) \nabla \varepsilon
\]

(5.14)

The boundary conditions for the electrostatic problems on the fluid interface are:

\[
V_c = V_d
\]

(5.15)

\[
\varepsilon_c \vec{E}_c \cdot \vec{n}_c + \varepsilon_d \vec{E}_d \cdot \vec{n}_d = 0
\]

(5.16)

of which \( V_c \) and \( V_d \) stands for the electric potential measured from the sides of the continuous phase and dispersed phase respectively; \( \vec{n}_c \) and \( \vec{n}_d \) are the normal of the fluid interface on the
sides of the respective two phases. The Eq. (5.15) and (5.16) represents the continuity of the electric potential and displacement on the fluid interface.

5.2.4 Simulation setup

In this study, the geometry of the microfluidic device, the fluid properties and the operating flow rates follow those been reported by Nie et al. in 2008[123]. A conventional microfluidic hydrodynamic flow–focusing device (HFFD) was selected to investigate the droplet breakup process. The dimensions of the geometry are shown in Figure 5.1. The microfluidic channels have uniform depth as 86 μm. The continuous phase, which is an aqueous solution with the density and viscosity values close to water, is injected from the two side inlets with identical flow rates as \( \frac{1}{2} Q_c \). The dispersed phase, which is silicone oil of large viscosity values, is injected from the center channel with a total flow rate as \( Q_d \). The two phases meet each other in the flow–focusing region and flow through an orifice of confined spaces together. The dispersed phase is squeezed by the continuous phase in the orifice region. After the droplets are pinched off from the dispersed phase, they travel through the expanding channel and leave this microfluidic device.

The numerical simulations were carried out in a two–dimensional domain. The commercial simulation software Comsol Multiphysics 4.2 was adopted to solve the governing equations. For the fluid domain, all the inlets were specified with constant flow rates while the outlet was specified as a pressure outlet without viscous stress. All the wall boundaries were specified as the wetting wall conditions with a contact angle of 145°. After several computational grids with different resolutions were tested, a computational mesh consisting of 16 nodes across the orifice and 13,160 elements totally in the entire domain was selected for the following numerical investigations. In the first part of this study, no electric field was applied to the microfluidic system. The dispersed phase remained a constant flow rate with \( Q_d = 0.04 \text{ mL/h} \)
Figure 5.1 The geometry and dimensions of the microfluidic flow–focusing device used in this study. The channels have uniform depths as 86 μm. The width and length of the orifice are 80 μm and 150 μm respectively. The blue lines indicate the computational mesh by the simulations.

while $Q_c$ was varied to investigate the effect of increasing the flow ratio on droplet sizes. In the second part of the study, $Q_d$ and $Q_c$ maintained constant flow rates as 0.04 mL/h and 2 mL/h respectively for all the cases. External electric field was applied to the system by specifying the left side inlet with electric potential as $V_0$, which was varied from 10 V to 660 V. The right side inlet was specified with electric potential as 0 V. The other boundaries were specified with zero free charge condition which is expressed as

$$\bar{n} \cdot (\varepsilon \bar{E}) = 0$$

(5.17)

of which $\bar{n}$ is the normal of the boundary; $\varepsilon$ is the electric permittivity of the fluid close to the boundary.
The simulations were performed with 8 processors on the Philip high performance computer located in Louisiana State University. For each case, the simulation endured until at least three droplets had been separated from the dispersed phase. The properties of the two phases used by the simulations are listed in Table 5.1. The types of silicone oil with $\mu_d = 50$ and 100 cp were used by the dispersed phase. The interfacial tension coefficient between the two phases was assumed to maintain a constant value as $\sigma = 4.8 \text{ mN/m}$ for all the investigated cases. The small variations of the density and interfacial tension between the two types of silicone oil were neglected.

Table 5.1 Properties of the two phases used by the simulations

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Continuous phase</th>
<th>Dispersed phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/m$^3$)</td>
<td>1000</td>
<td>960</td>
</tr>
<tr>
<td>Viscosity (mPa*s)</td>
<td>1</td>
<td>50/100</td>
</tr>
<tr>
<td>Relative permittivity</td>
<td>78.5</td>
<td>2.8</td>
</tr>
</tbody>
</table>

5.3 Results and discussion

5.3.1 Validation of the numerical model

In order to validate the accuracy of the conservative level–set model, numerical simulations were carried out to preliminarily study the droplet breakup process solely governed by the fluid flow. The experiments have been performed by Nie et al. in 2008 [123]. In their work, they remained a constant flow rate of the dispersed phase ($Q_d = 0.04 \text{ mL/h}$) while varying the flow ratio of the continuous phase to the dispersed phase ($Q_c/Q_d$). For a particular operating
condition with $Q_c/Q_d = 20$, the corresponding capillary number is 0.0067 ($Ca = \mu_c U_c/\sigma$, $U_c$ is the mean velocity of the continuous phase in the orifice, which is determined as the flow rate of the continuous phase divided by the cross-sectional area of the orifice), indicating that the breaking mechanism is dominated by “squeezing” mechanism or referred as “dripping regime–model 1” by Nie [123]. As seen in Figure 5.2, the snapshots of the droplet breakup process predicted by the simulations agree with the observations from the experiments qualitatively. The two cases shown in Figure 5.2 have same operating conditions ($Q_c$, $Q_d$, $\mu_c$) but different viscosity values in the dispersed phase ($\mu_d$). Nie et al. have pointed out that $\mu_d$ has a significant effect on determining the droplet breakup modes although it does not appear in the classic expression of $Ca$. They have observed the mono–dispersed breakup mode if $\mu_d = 20$ cp was used. As seen in

Figure 5.2 Snapshots of the droplet breakup process with different viscosity values of the dispersed phase: (a) $\mu_d = 20$ cp (b) $\mu_d = 100$ cp. The flow rate of the dispersed phase is $Q_d = 0.04$ mL/h, and the flow ratio $Q_c/Q_d$ is 20. The corresponding $Ca$ is to 0.0067. The upper pictures are the snapshots cited from the experiments performed by Nie et al.[123]. The scale bars indicated as the black lines are 100 μm. The lower pictures are provided by the numerical simulations.
Figure 5.2(A), the pendant growing on the front tip of the dispersed phase blocks the entire exit of the orifice. While the continuous phase squeezes the dispersed phase, a visible “neck” shape is formed inside the orifice. For this case, only one droplet is pinched off from the dispersed phase. In contrast, the dispersed phase with \( \mu_d = 100 \) cp results in poly-dispersed breakup mode. As shown in Figure 5.2(B), the dispersed phase does not block the orifice exit completely in this case, and the dispersed phase forms a thin filament inside the orifice. After the primary droplet is pinched off, several secondary droplets with much smaller sizes are generated from the filament. The numerical simulations have predicted these two breakup modes successfully.

The numerical simulations have also achieved quantitative agreements with the experimental results in terms of primary droplet sizes. We have studied the droplet breakup process with two viscosity values of dispersed phase, \( \mu_d = 50 \) cp and 100 cp, respectively. The diameters of the droplets predicted by the numerical simulations as well as those reported by Nie et al. are plotted in Figure 5.3 as a function of \( Q_c/Q_d \). As seen in Figure 5.3, the primary droplet sizes predicted by the simulations are close to the experimental results. One may notice that the primary droplet sizes do not decrease noticeably by increasing the flow ratio, which suggests that the conventional approach to manipulate droplet sizes by tuning the flow ratio is not effective in these circumstances. Other approaches are necessary in order to reduce the droplet size.
Figure 5.3 The diameters of the droplets as a function of flow ratio $Q_c/Q_d$: (a) $\mu_d = 50$ cp (b) $\mu_d = 100$ cp. For all the explored cases, $Q_d$ is 0.04 mL/h while $Q_c/Q_d$ is varied from 10 to 100. The filled symbols correspond to the primary droplets while the open symbols stand for the secondary droplets produced by the poly-dispersed breakup mode. If multiple secondary droplets are obtained, only two of them are plotted for the purpose of showing the general size range. The experimental results are cited from Nie’s work [123].
5.3.2 Droplet breakup process without electric field

The investigations in this study were focused on the dripping regime where the droplets were generated by the mono-dispersed breakup mode. In this section, we demonstrate the droplet formation process solely governed by the hydrodynamics. A typical droplet breakup process with $\mu_d = 50$ cp, $Q_d = 0.04$ mL/h and $Q_c/Q_d = 50$ is plotted in Figure 5.4. The corresponding $Ca$ is 0.017, indicating that the breakup process is governed by the “dripping regime”. Absent of other external forces, three forces play roles in the breakup process: the surface tension force, the viscous shear force and the inertial force. Due to the complexity of the dynamic breakup process, the magnitude of each force was difficult to be quantified; instead, the evolutions of the pressure values in the upstream of the orifice, which are shortened as upstream pressure evolutions in the following text, were measured from the two phases and plotted versus

![Figure 5.4 Droplet formation process in the dripping regime with the operating condition: $\mu_d = 50$ cp, $Q_d = 0.04$ mL/h and $Q_c/Q_d = 50$. The corresponding $Ca$ for this droplet breakup process is 0.017. The diamond and circle indicate the sampling locations where the upstream pressure values are measured.](image)
time in Figure 5.5. The sampling locations in the continuous phase and the dispersed phase are indicated by the circle and diamond symbols as seen in Figure 5.4.

![Figure 5.5 Upstream pressure evolutions of the continuous phase and dispersed phases during the droplet breakup process with $\mu_d = 50$ cp, $Q_d = 0.04$ mL/h and $Q_c/Q_d = 50$. No external electric field is applied to this system. The (a) ~ (f) corresponds to the six steps shown in Figure 5.4. The dash lines indicate the locations of the corresponding steps on the curves for the visualization purpose. Generally, the droplet breakup process consists of two stages: the blocking stage and the squeezing stage. The detailed procedures of the droplet breakup process can be summarized as six steps: (a) the dispersed phase is injected towards the orifice from the center inlet. As the dispersed phase has to penetrate the continuous phase, it maintains a higher pressure in its

98
upstream than that of the continuous phase, which is evident in Figure 5.5. When the dispersed phase enters the flow–focusing region, it gradually blocks the flowing channel of the continuous phase. In order to maintain its constant flow rate, the continuous phase has to increase its velocity, which requires an elevation in its upstream pressure.

The upstream pressure in the dispersed phase increases accordingly as well so as to maintain the flow rate. Thus the upstream pressure values in both phases increase slowly from step (a) to (b) with higher pressure values in the dispersed phase. When the tip of the dispersed phase reaches the orifice entrance, the interface maintains a conical shape which is usually referred as the “Taylor cone”. (c) As soon as the dispersed phase enters the orifice, the squeezing stage starts. The pressure values of the both phases shoot up quickly as a result of the confined flowing area inside the orifice. Since this stage, the pressure value of the continuous phase exceeds that of the dispersed phase. When the tip of the dispersed phase reaches the orifice exit, the pressure curves of both phases reach their peaks. As a result of the pressure difference, the continuous phase squeezes the fluid interface, forming a visible neck inside the orifice. (d) When the tip of the dispersed phase leaves the orifice exit and enters the expanding channel, the pressure values in both phases declined suddenly because of the expanded flowing area. As the continuous phase continues squeezing the interface, the neck in the orifice is compressed into a thin filament. A pendant is growing in the expanding channel close to the orifice exit, with its tail attached to the dispersed phase by the filament. (e) As the continuous phase keeps exerting the compression effect, the width of the filament is reduced relatively slowly. Because of the slowly increased flowing area inside the orifice, the upstream pressure values in both phases decrease accordingly as well. (f) When the width of the filament is squeezed to a critical value, the surface tension force snaps off the pendant from the dispersed phase and brings the interface out of the
flow–focusing region. Consequently, a droplet of well–defined spherical size is generated in the expanding channel. The pressure values in both phases rapidly drop to those required by the initial step (a), with larger pressure in the dispersed phase than that in the continuous phase. A new cycle starts to repeat.

5.3.3 The effect of increasing the flow ratios on droplet sizes

For most of the applications using passive droplet–based microfluidics, manipulation of the flow ratio is the primary approach to control the droplet sizes. However, the droplet diameters versus flow ratios shown in Figure 5.3 have already indicated that increasing the flow ratios cannot lead to a noticeable reduction in the droplet sizes. In order to understand the effect of flow ratios on the breakup process, the neck width evolution analyses were performed on two cases of identical $Q_d$ ($Q_d = 0.04 \text{ mL/h}$) and $\mu_d$ ($\mu_d = 50 \text{ cp}$) but different flow ratios ($Q_c/Q_d=50$ and 100 respectively). The neck width $W_n$ was measured at the orifice entrance with respect to time during the simulations, of which the sampling location is indicated as the red dot line shown in Figure 5.4(a). The obtained evolution curves of $W_n$ are shown in Figure 5.6.

Taking the case with $Q_c/Q_d=50$ as an example, $W_n$ is initially 0 during one cycle of the droplet breakup process. It reaches its maximum value at the end of the blocking stage when the dispersed phase enters the orifice (as shown in Figure 5.4(b)). Because of the large squeezing rate caused by the significant pressure difference between the two phases, it drops rapidly from step (b) to (c). After the tip of the dispersed phase enters the expanding channel, the squeezing rate from step (c) to (e) is slowed down, resulting in the long tails of the evolution curves. Finally, it returns to 0 when the droplet is pinched off (as shown in Figure 5.4(e)). As seen in Figure 5.6, if the flow ratio is doubled from 50 to 100, the maximum $W_n$ is slightly reduced, and the tail length is shortened as well. However, the squeezing rates, which can be indicated as the slope of
the curve from step (b) to (d), are marginally influenced by the increased flow ratio. Consequently, the droplet sizes obtained from these two flow ratios are almost same, revealing that the acceleration of the squeezing rate from step (b) to (d) is the key to reduce the droplet sizes. Since the manipulation of the flow ratio turns out to be ineffective, the electric force is employed to help compressing the filament.

Figure 5.6 The evolutions of neck width $W_n$ with different flow ratios $Q_c/Q_d=50$ and 100. The other operating conditions of these two cases are identical: $\mu_d = 50$ cp, $Q_d = 0.04$ mL/h. The symbols (b) ~ (e) indicate the corresponding steps of the droplet breakup process shown in Figure 5.4.
5.3.4 Validation of the perfect dielectric model by the classic drop deformation

Before utilizing the electric field to control the droplet breakup process, we simulated one case of the classic droplet deformation problem for the purpose of validating the LSM coupled with the perfect dielectric model. It is well known that a fluid droplet suspended inside another immiscible fluid would deform with the presence of external electric field\[133\]. The resultant deformation is a function of the interfacial tension, fluid properties of the both phase (such as viscosity, permittivity and conductivity), and the magnitude of the applied electric field. O’Konski and Thacher have derived the analytical expression that can predict the steady–state deformation of a dielectric droplet in another dielectric media \[140\]:

$$d_\infty = \frac{R_0 \varepsilon_c}{\sigma} |E_0|^2 \frac{9(S-1)^2}{16(S+2)^2}$$  \hspace{1cm} (18)

In our case, $d_\infty$ is the deformation in steady state; $R_0=1$ mm is the non–deformed droplet diameter; $\varepsilon_c = \varepsilon_0$ is the dielectric permittivity of the suspending medium; $\sigma = 0.0032$ N/m is the interfacial tension coefficient; $E_0 = 1.5 \times 10^5$ V/m is the magnitude of the electric field far from the droplet; the parameter $S$ represents the ratio of the dielectric permittivity of the droplet ($\varepsilon_d = 10 \varepsilon_0$) to that of the suspending medium: $S = \varepsilon_d / \varepsilon_c$, of which $\varepsilon_0$ is the vacuum permittivity. If these parameters are provided to the analytical expression, the deformation of the droplet in steady state is $d_\infty = 0.023$.

The same parameters were also adopted by the numerical simulations. When the electric field is absent, the droplet preserves its spherical shape as seen in Figure 5.7(b). After the deformation reaches steady state in the electric field, the deformed shape of the droplet is shown in Figure 5.7(c). The corresponding deformation value predicted by the simulation is 0.02, which agrees well with the analytical solution. In addition, the dynamic response curve of the
deformation shown in Figure 5.7(a) has a similar shape as that reported by Supeene et al [133]. Therefore, the numerical model using LSM coupled with the perfect dielectric model is regarded as sufficiently reliable to study the droplet breakup process in the following sections.

Figure 5.7 (a) The dynamic response curve of the droplet deformation caused by the external electric field. (b) The shape of the droplet used by the numerical simulation prior to the deformation. (c) The shape of the droplet when the deformation reaches its steady state.
5.3.5 Overview of the electric field on droplet breakup

As seen in Figure 5.8(a), the external electric field is applied to the microfluidic system in such a way that the left side inlet is attached to a DC power supply while the right side inlet is connected to the ground. This kind of configuration induces polarization charges on the fluid interface and generates electric field inside both phases. As suggested by the continuity of the electric displacement shown in Eq. (11), the magnitude of the electric field in the dispersed phase is larger than that in the continuous phase since \( \varepsilon_d \) is less than \( \varepsilon_c \). The numerical simulations have captured such phenomenon. The contour plot of the electric field strength shown in Figure 5.8(a) reveals that the electric field with large magnitudes exists in the front tip of the dispersed phase. Because of the interaction between the electric field and the polarization charges, the electric force is induced on the fluid interface, of which the distributions are plotted as the white arrows shown in Figure 5.8(b). As the direction of the electric force is determined by the gradient of the permittivity values (\( \nabla \varepsilon \)), the flow configuration such that \( \varepsilon_d \) is less than \( \varepsilon_c \) results in the electric force always pointing from the continuous phase to the dispersed phase. If the force vectors are decomposed along x and y directions, one may notice that the force component on x direction exerts a compression effect to the dispersed phase; consequently, it helps to squeeze the neck of the dispersed phase during the drop breakup process. On the other hand, the force component along the y direction is pointing opposite to the moving direction of the dispersed phase, thus it retards the traveling of the interface to the orifice. In order to understand the effect of electric field strength on the resultant droplet sizes, the droplet breakup processes with two types of dispersed phase (\( \mu_d = 50 \) and 100 cp) were studied with constant flow rates of the two phases (\( Q_d = 0.04 \) mL/h and \( Q_c/Q_d = 50 \)) but varying values of the applied voltage \( V_0 \). The predicted droplet sizes and droplet periods from the numerical simulations are shown in Figure 5.9(a) and (b).
Figure 5.8 (a) Contour plot of the electric field strength at one time step during the droplet formation with $\mu_d=50$ cp, $Q_d=0.04$ mL/h and $Q_c/Q_d = 50$. The black lines indicate the electric field lines. A high potential $V_0 = 240$ V is applied on the left inlet channel of the continuous phase while the right inlet channel is connected to the ground. The color map indicates the magnitude of the electric field strength. (b) Contour plot of the volume fraction of the dispersed phase in the regions enclosed by the red dash curves shown in (a). The white arrows indicate the vectors of the electric body force induced on the fluid interface.
Figure 5.9 Droplet diameters and periods as functions of the applied voltages $V_0$ with $Q_d = 0.04$ mL/h and $Q_c/Q_d = 50$. (a) Averaged droplet diameters versus applied voltages $V_0$. (b) Averaged droplet periods versus applied voltages $V_0$. 
Interesting, the curves of the droplet sizes versus $V_0$ exhibit the descending–ascending–descending shapes instead of the monotonously descending shape. The droplet period, which is defined as the droplet formation time between two adjacent droplets, follows the similar trend as that of the droplet size. According to the shape of the curves shown in Figure 5.9, the droplet breakup process controlled by the electric field of various strengths is divided into three distinct regimes. In Regime 1 where $V_0$ ranges between 0 V and 300 V, the droplet sizes and periods decrease almost linearly with the increasing values of $V_0$. Similar relationships of the droplet sizes and applied voltages have also been reported by Link [129] and Kim [132] individually based on their experiments on aqueous droplet–in–oil systems. If $V_0$ is between 300 V and 480 V, the droplet breakup process is governed by Regime 2 where the droplet sizes and periods grow with the increasing $V_0$. In Regime 3 where $V_0$ exceeds 500 V, the droplet sizes and periods decrease almost linearly with $V_0$ again. Such breakup patterns are resulted from the interactions of the electric force and the fluid flow in the microfluidic system. In the following sections, the droplet breakup processes in these individual regimes are discussed one by one.

5.3.6 Droplet breakup process in Regime 1

In Regime 1, the droplet sizes and periods decrease almost linearly with the increment of the applied voltage $V_0$. The contour plots of the droplet breakup process of two cases in this regime are shown in Figure 5.10. These two cases have identical operating conditions, i.e., $Q_d=0.04$ mL/h and $Q_c/Q_d=50$, but the applied $V_0$ are 60 V and 240 V respectively. By comparing (b1) and (b2), one may notice that the dispersed phase deforms inside the flow–focusing region noticeably if $V_0$ increases to 240 V. Such deformation is resulted from the $y$ component of the electric force, which retards the movement of the dispersed phase by exerting the force opposite to the flow direction. Besides of the deformation, the dispersed phase has to spend more time during the blocking stage if $V_0$ is increased, which is evident by comparing the time interval between (a1), (b1) and (a2), (b2). On the other hand, the component of the electric force along the $x$ direction helps to squeeze the dispersed phase, resulting in the enhanced squeezing rate during the squeezing stage.
Figure 5.10 Two examples of the droplet breakup process in Regime 1 with identical operating conditions of $\mu_d=50$ cp, $Q_d=0.04$ mL/h and $Q_c/Q_d=50$ but different $V_0$. (a1)–(e1): the applied voltage $V_0=60$ V; (a2)–(e2): the applied voltage $V_0=240$ V.

Compared to the breakup process without electric field shown in Figure 5.4, the squeezing time from step (b) to (e) is reduced from 20 ms to 12 ms if $V_0=60$ V is applied to the system. As the droplet growing time is shortened by applying the electric field, the averaged
droplet size is consequently reduced from 141.28 μm to 126.26 μm. If \( V_0 \) is further increased to 240 V, the time interval required by the squeezing stage is shortened to 8 ms, which eventually leads to averaged droplet sizes as 106.72 μm.

Since the dispersed phase has to overcome the retardation effect exerted by the \( y \) component of the electric force, a high pressure value has to be built up in its upstream so as to maintain the constant flow rate. By comparing the upstream pressure evolutions of the two phases shown in Figure 5.11(a) with those in Figure 5.5, one may notice that the pressure values in the dispersed phase have increased noticeably as \( V_0 = 60 \) V is applied. Meanwhile, the pressure values in the continuous phase are marginally influenced by the electric field. As a result of the increased pressure in the dispersed phase, the squeezing effect contributed by the hydrodynamics is undermined; in other words, the squeezing effect dominated by the pressure difference between the continuous and dispersed phases since the pressure difference is reduced. If \( V_0 \) is further increased to 240 V, the pressure values in the dispersed phase have increased significantly as seen in Figure 5.11(b). The pressure difference between the two phases from step (c) to (e) is so small that the squeezing effect contributed by the hydrodynamics is negligible compared to that contributed by the electric force. One may expect that the squeezing effect depends solely on the electric force if \( V_0 \) exceeds 240 V.

5.3.7 Droplet breakup process in Regime 2

When the applied voltage \( V_0 \) ranges between 300 V and 480 V, the droplet breakup process is governed by Regime 2 where the droplet sizes increase with \( V_0 \). A typical droplet breakup process in this Regime is plotted in Figure 5.12 while the corresponding upstream pressure evolution curves of the two phases are plotted in Figure 5.13.
Figure 5.11 Upstream pressure evolutions of the continuous and dispersed phases during the droplet breakup process with the operating conditions: $\mu_d = 50$ cp, $Q_d = 0.04$ mL/h and $Q_c/Q_d = 50$. (a) $V_0 = 60$ V; (b) $V_0 = 240$ V. (b1) ~ (e1) and (b2) ~ (e2) correspond to the droplet breakup steps shown in Figure 5.9. The blue dot lines indicate the location of corresponding steps shown on the curves.
Figure 5.12 Droplet breakup process in Regime 2 with $\mu_d = 50$ cp, $Q_d = 0.04$ mL/h and $Q_c/Q_d = 50$. The applied voltage $V_0$ is 480 V.

Figure 5.13 Upstream pressure evolutions of the continuous and dispersed phases during the droplet breakup process with the operating conditions: $\mu_d = 50$ cp, $Q_d = 0.04$ mL/h and $Q_c/Q_d = 50$. The applied voltage $V_0 = 480$ V. (b) ~ (e) correspond to the droplet breakup steps shown in Figure 5.11. The blue dot lines indicate the location of corresponding steps shown on the curves.
Because of the excessive retardation effect exerted by the electric field, the dispersed phase deforms considerably in the flow–focusing region during the blocking stage as seen in Figure 5.11(b). Such deformation of the dielectric fluid resulted from the electric field is coincide with the classic drop deformation theory; similar deformed shape of the silicone oil has also been observed by Zhang et al. in their experiments [141]. In order to overcome the retardation effect, the upstream pressure in the dispersed phase elevates significantly; meanwhile, the pressure in the continuous phase increase slowly. Consequently, the pressure in the dispersed phase overwhelms that in the continuous phase for the entire droplet breakup process as evident in Figure 5.13.

During the squeezing stage (from step (c) to (e) shown in Figure 5.12) of the breakup process, two mechanisms are competing. One is the squeezing mechanism solely contributed by the electric force. The other is the stabilization mechanism. The high pressure in the dispersed phase expands the interface outward thus resists the squeezing effect. Because of such stabilization effect, the squeezing time interval from stage (c) to (e) in the case with \( V_0 = 480 \text{ V} \) is prolonged compared to the one in the case with \( V_0 = 240 \text{ V} \), resulting in larger droplet sizes as seen in Figure 5.10 and Figure 5.12. The neck evolution curves measured at the orifice entrance provide the same evidence. As shown in Figure 5.14, the slope of the right half of the neck evolution curves, which can be regarded as the squeezing rate, is increased when \( V_0 \) is raised from 12 V to 360 V; as a result, the squeezing time interval is reduced from 12 ms to 6 ms. However, if \( V_0 \) is further increased to 480 V, the slope of the curve decreases because of the stabilization effect, which consequently prolongs the squeezing time interval to 9 ms. Similar stabilization effect has also been observed in other systems with the utilization of strong electric field. Kim et al. have applied the electric field to control the droplet breakup process of water.
(dispersed phase) in oil (continuous phase). They found that the electric field had the effect to reduce the droplet size if the applied voltage was less than certain value, i.e., 1200 V in the case $Q_c/Q_d = 350/60$. If the applied voltage increased to 1300 V, no droplets were pinched off from the dispersed phase; the dispersed phase formed a stable jet and propagated downstream without into droplets in the orifice region [132].

![Figure 5.14 The evolution curves of neck width $W_n$ measured from the orifice entrance from the cases with the operating conditions: $\mu_d=50$ cp, $Q_d=0.04$ mL/h and $Q_c/Q_d = 50$. The applied voltage $V_0$ is varied in these cases. The sampling location is marked by the red dash line shown in Figure 5.12(a).](image-url)
5.3.8 Droplet breakup process in Regime 3

If the microfluidic system is applied with very high voltages, i.e., $V_0 > 500$ V, the droplet breakup process is governed by Regime 3 where the droplet sizes decrease with the $V_0$ values. A typical droplet breakup process with $V_0 = 600$ V in this regime is shown in Figure 5.15, and the corresponding upstream pressure evolution curves are shown in Figure 5.16. Because of the significant retardation effect exerted by the large electric force, the pressure in the dispersed phase overwhelms that in the continuous phase, which leads to a broad deformation of the dispersed phase as shown in Figure 5.15(b).

\[ V_0 = 600 \text{ V} \]

![Figure 5.15](image)

Figure 5.15 Droplet breakup process in Regime 3 with the operating conditions $\mu_d =50$ cp, $Q_d =25$ mL/h and $Q_c/Q_d =50$. The applied voltage $V_0$ is 600 V.

During the squeezing stage, a thin jet evolves from the apex of the dispersed phase and is elongated inside the orifice as seen in Figure 5.15(c) and (d). The jet predicted by the numerical simulations is similar to that been observed by Zhang et al. in their experiments. Zhang et al. have investigated the flow behavior of silicone oil in an electric field, and they observed the formation of oil jets when the flow was governed by dripping regime and the applied electric
voltage exceeded 9 kV. They pointed out these jets were unsteady and were initiated by the large electric field strength [141].

Figure 5.16 Upstream pressure evolutions of the continuous and dispersed phases during the droplet breakup process with the operating conditions: \( \mu_d = 50 \) cp, \( Q_d = 0.04 \) mL/h and \( Q_c/Q_d=50 \). The applied voltage \( V_0 = 600 \) V. (b) ~ (e) correspond to the droplet breakup steps shown in Figure 5.15. The blue dot lines indicate the location of corresponding steps shown on the curves.

Due to the significant deformation, most of the flowing channel in the flow–focusing region close to the orifice entrance is occupied by the dispersed phase. Similar to what occurs in Regime 2, the large pressure in the dispersed phase tends to stabilize the interface; therefore, the squeezing rate is slowed down in this regime, which is evident from the slope of the corresponding neck evolution curve shown in Figure 5.14. However, the squeezing time interval
required by the case with $V_0 = 600$ V is less than that with $V_0 = 480$ V; consequently, the resultant droplet sizes with $V_0 = 600$ are smaller as well. Such differences are resulted from the thin width of the jet. Compared to that in the case with $V_0 = 480$ V, the maximum $W_n$ of the jet is smaller; therefore, the amount of fluid that can be injected into the droplet is confined by the small width of the jet. In addition, the reduced jet width requires less time to be squeezed to the critical neck width that the surface tension force can snap off the jet from the dispersed phase. As evident in Figure 5.14, the total squeezing time required by the case with $V_0 = 600$ V is about 2.5 ms less than that with $V_0 = 480$ V. Because of these two reasons, the droplets formed in this regime are smaller compared to those obtained in Regime 2.

The simulations indicate that the squeezing effect contributed by the continuous phase is vanished because of the overwhelmed pressure in the dispersed phase; therefore, the advantage of the hydrodynamic flow–focusing over flow control does not exist in these two regimes. We suggest applying relatively low voltages to the microfluidic system so that the breakup process is governed by Regime 1, where the advantages of the hydrodynamic flow–focusing still preserve.

5.4 Conclusion

In this study, we have adopted the conservative level–set method coupled with the perfect dielectric model to study the breakup process of viscous oil droplets inside an aqueous solution. When the viscosity in the dispersed phase is much higher than that in the continuous phase, the resultant droplets from a conventional microfluidic hydrodynamic flow–focusing device remain large sizes for a long range of flow ratios, indicating that the common operating approach that uses high flow ratios cannot increase the squeezing rate effectively during the squeezing stage of the droplet breakup process. In such circumstance, the active droplet–based microfluidics that incorporates the conventional microfluidics with external actuators, i.e., electric field, has shown
its unique ability in controlling the droplet breakup process. As a result of the difference of the electric properties such as the permittivity and conductivity between the two phases, the external electric field induces electric charges on the fluid interface. With appropriate configurations of the electric field, the electric force generated by the interaction of the electric field and electric charges exerts a compression effect on the fluid interface. If the electric force is decomposed along x and y coordinates, its component along the x direction clearly shows its role in squeezing the dispersed phase. As this component accelerates the squeezing rate, it consequently produces droplets of reduced sizes. On the other hand, the component on the y direction is pointing opposite to the flow direction of the dispersed phase; therefore, it exerts a retardation effect to the dispersed phase.

With the assumption that both the continuous and dispersed phases can be regarded as dielectric fluids, the simulations in this study considers only the electric force resulted from the interaction of the electric field and polarization charges. When the flow in the microfluidic device is in dripping regime and the applied voltage is increased from 0 V to 660 V, the droplet breakup process experiences three distinct regimes. In Regime 1 where the applied voltage is relatively low, the electric force assists the hydrodynamic forces to squeeze the dispersed phase, thus the obtained droplet sizes decrease linearly with the growth of the applied voltages. Because of the retardation effect resulted from the electric force, the pressure in the dispersed phase increases accordingly with the growth of the applied voltage; meanwhile, the pressure in the continuous phase is marginally influenced by the applied voltage. As a result, the squeezing effect contributed by the hydrodynamic forces is weakened by the increment of the applied voltage. In Regime 2 where moderate voltages are applied, the squeezing effect is dominated by the electric force. The large retardation effect exerted by the electric force increases the pressure
in the dispersed phase significantly. Such large pressure not only causes a considerable
deformation of the dispersed phase in the flow–focusing region but also stabilizes the fluid
interface during the squeezing stage. The competition between the squeezing and retardation
effects prolongs the squeezing time; consequently, the resultant droplet sizes increases with the
growth of the applied voltages in this regime. If the applied voltage is further increased to
Regime 3, the dispersed phase deforms significantly with a ball–cone shape and takes up most of
the flowing channels in the flow–focusing region. Unsteady jets involve from the tip of the cone
and are quickly pinched off from the dispersed phase because of its small width. In this regime,
the resultant droplet sizes decrease with the applied voltages again. As the advantages of
hydrodynamic flow–focusing technique is undermined in Regime 2 and Regime 3, the
microfluidic devices incorporated with external electric field are suggested to be operated with
suitable applied voltages in order to limit the droplet breakup process in Regime 1.
Chapter 6 Summary and Conclusion

Computational fluid dynamics (CFD) simulations incorporated with experiments were applied to study the fluid flow and associated transported phenomena inside microfluidic and millifluidic systems. A millifluidic reactor with a snake shape was applied to synthesize gold nanoparticles by traditional wet–synthesis using single – phase flow. Although the millifluidic reactor have shown better control than conventional batch reactors in the aspect of reagent addition, resultant particle size distributions and etc., it confronted same challenges as the other conventional microfluidic and millifluidic reactors did. The parabolic velocity profile resulted in significant reagent dispersion: the reagents used by the chemical reactions had wide residence time distributions (RTDs) inside the reactor; consequently, the produced gold nanoparticles also had broad particle size distributions. The RTD analyses performed by numerical simulations indicated that the reagent dispersion could be suppressed by increasing the flow ratio; as a result, the particle size distributions were reduced as well. However, this approach was usually limited by the material and binding strength of millifluidic or microfluidic chips. It could not eliminate the reagent dispersion completely.

Droplet–based microfluidics was proposed to address the reagent dispersion as well as the other challenges such as slow mixing and reactor fouling found in conventional microfluidics. This technology introduces another immiscible fluid to encapsulate the reagents inside discrete slugs or droplets. We had fabricated a millifluidic reactor and used this reactor to synthesize copper nanoparticles at Center for Advanced Microstructures and Devices (CAMD). The reactor was able to generate stable slug flow in squeezing regime, but the slug sizes were excessively long. The TEM analyses indicated that the nanoparticles synthesized inside short slugs had narrower size distributions than those inside long slugs, which suggested the necessity of
generating short slugs. The numerical simulations using volume of fluid (VOF) method had achieved both qualitative and quantitative agreement with the experimental observations in terms of slug formation dynamics. The simulation results revealed that the dispersed phase occupied the entire flow–focusing region during the blocking stage, and reducing the flow – focusing region was the key to minimize the slug lengths. Two designs with reduced “shoulder” length in the flow–focusing region were tested by numerical simulations. They had demonstrated the ability to reduce the resultant slug lengths more effectively than reducing the channel depths.

Since rapid mixing inside the slugs is the key to obtain uniform nanoparticles, numerical simulations were continued to investigate the mixing process inside slugs. The VOF method coupled with species transport model was applied to study the dynamic mixing process inside slugs. The mixing efficiency was quantified by mixing efficiency indices. The twirling effect, which occurred during the slug formation process, played a critical role in the mixing process. It distributed the reagent to the front tip of the slugs. After the slugs were detached from the dispersed phase, the recirculating flow inside slugs could mix the reagents efficiently as the reagents were on the flow path. If the droplet-based microfluidic devices were operated with large flow rate of the dispersed phase, long slugs with large amount of fluid were generated; these slugs had poor mixing as the twirling effect was not able to distribute such large amount of fluid inside slugs. The mixing process of long slugs depended on the slow diffusion process. In contrast, using low flow rate of the dispersed phase resulted in short slugs. Since the twirling effect can effectively distribute the small amount of fluid inside short slugs, the mixing efficiency curves exhibited fast mixing regime dominated by convection. Although the twirling effect can be strengthened by increasing the operating flow rates, the resultant mixing process
cannot be improved noticeably. The study suggested that reducing the slug sizes was more effective in improving mixing than increasing the operating flow rates.

For many applications using droplet-based microfluidics, it is now a trend to combine other physics with the microfluidic devices so as to obtain better control over the droplet breakup, movement and etc. Especially in these circumstances when the dispersed phase had a large viscosity value, the droplet sizes maintained constant values for a wide range of operating ratios, indicating that the conventional controlling scheme that manipulates flow rates was incapable of controlling droplet sizes. One solution was to apply external electric field to control the droplet breakup process. We had studied the droplet breakup process controlled by electric field via numerical simulations. The interaction of the electric force and hydrodynamic forces resulted in three distinct breakup regimes. One component of the electric field could provide the squeezing effect while the other retarded the movement of the dispersed phase. In order to overcome the retardation effect, the dispersed phase elevated its upstream pressure. If the applied voltage was in center range, the high pressure stabilized the interface thus elongated the squeezing time; therefore, for a particular operating flow rate, the obtained droplet sizes from various applied voltages demonstrated a decrease-increase-decrease profile.

For all these projects, the numerical simulations have assisted us to understand the flow behavior in microfluidic systems, especially in the droplet-based microfluidics of which the flow was complicated because of the involvement of multiple forces. They have provided guidance in the aspect of designing and operating microfluidic devices properly.
References


advances in the design and the use of miniaturized droplet-based continuous process: Applications in chemistry and high-pressure microflows, Lab on a Chip, 11 (2011) 779-787.


Appendix A Letters of Permission


![License Agreement](image1.png)

Figure A1 The approval letter of rewriting Chapter 2 by a published research paper in *ChemPhysChem*
The Chapter 3 is reproduced with permission from the research paper published on Chemical Engineering Journal: Li, Y.; Yamane, D. G.; Li, S.; Biswas, S.; Reddy, R. K.; Goettert, J. S.; Nandakumar, K.; Kumar, C. S. S. R., Geometric optimization of liquid-liquid slug flow in a flow-focusing millifluidic device for synthesis of nanomaterials. Chem. Eng. J. 2012, accepted. The licensed copyright belongs to Elsevier. The approval letter is shown as Figure A2:

Figure A2 The approval letter of rewriting Chapter 3 by a published research paper in Chemical Engineering Journal.
Figure B1 Histograms of size distribution of Au nanoparticles obtained in milli-fluidic reactor at different flow rates and different locations. The first index (1, 2 and 3) represents the flow rate of 10, 6, and 2 respectively while the second index (1 and 2) represents the sampling location marked in Figure S1(b).
Figure B2 Velocity profile across the width of the channel

Figure B3 TEM images and histograms of size distribution of Au nanoparticles obtained at different times during the flask reaction. T10, T20, T75 and T90 stand for the sampling time at 10 s, 20 s, 75 s, and 90 s respectively.
Vita

Yuehao Li was born in 1985 in Huai’an, Jiangsu Province, China. He completed his high school in Jiangsu Huai’an High School in 2005 and at the same year joined East China University of Science and Technology (ECUST). From August, 2008 to May, 2009, he spent one year in Lamar University, Beaumont, Texas as an exchange student between ECUST and Lamar University. He received his Bachelor’s degree in Chemical Engineering from ECUST in July 2009. In 2012, he received his Master’s degree in Chemical Engineering from Louisiana State University. From 2012 to 2014, he continued his research project related to the numerical modeling on multiphase flow under the supervision of Prof. K. Nandakumar.