Dynamic and Stimuli-Responsive Multi-Phase Emulsion Droplets for Optical Components

by

Sara Nagelberg

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S.M. Massachusetts Institute of Technology (2015)

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Signature of Author

Department of Mechanical Engineering
January 15, 2020

Certified by

Mathias Kolle
Associate Professor Of Mechanical Engineering
Thesis Supervisor

Accepted by

Nicolas Hadjiconstantinou
Graduate Officer

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ABSTRACT

Dynamic micro-optical components have revolutionized imaging, sensing, and display technologies. Multi-phase emulsions are micro-scale droplets formed from multiple immiscible material components suspended in a fluid medium. An interesting aspect of these droplets is that by tailoring the chemistry of the surrounding medium it is possible to control the droplet morphology or to render the droplets responsive to stimuli in the environment, including light, heat, specific molecules, or even bacteria.

This thesis explores the optical characteristics of multi-phase droplets, including their refractive, emissive, and reflective properties. This work focuses predominantly on bi-phase droplets formed from two immiscible oils in water, which form double emulsions or Janus droplets. As tunable refractive components, these droplets form dynamic compound micro-lenses with adjustable focal length that is continuously variable from converging lenses to diverging lenses. Macroscopically these refractive droplets can appear nearly transparent or strongly scattering, depending on their configurations. When a fluorescent dye is dispersed within the higher refractive index phase, a portion of the light emitted will undergo total internal reflection. This results in a strong morphology-dependent angular emission profile, which can be used in molecular sensing for chemicals or pathogens. In reflection, the droplets produce striking iridescent colors. This is due to the interference light being totally internally reflected at the internal interface along distinct optical paths, leading to color.

These optical characteristics are analyzed both experimentally and theoretically. Finite Difference Time Domain simulations were used to model wave-optical effects and phenomena that could be treated using geometrical optics were calculated using a custom-built ray tracing algorithm. Additionally, a theoretical model was developed to explain the iridescent colors, under a geometric approximation that takes into account interference effects. Experimentally the droplets were characterized using several different custom-built microscope setups. Beyond the optical characteristics, we used these setups to investigate the effects of thermal Marangoni flows within the droplets, which cause the droplets to re-orient towards a heat source.

This work sets the foundation of understanding the refractive, reflective, and emissive properties of multi-phase droplets, which could form the basis of dynamically controllable or stimuli-responsive micro-scale optical components.

Thesis Supervisor: Mathias Kolle

Title: Associate Professor of Mechanical Engineering

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Chapter 1

Introduction

1.1 Overview

1.1.1 Background

Micro-scale optical components have contributed to significant advances in imaging, sensing, and display technologies, as well as to the miniaturization of devices. Dynamically switchable, reflective micro-optics, such as liquid crystals and digital micro-mirror devices, have enabled advances in optical technology ranging from high-resolution displays to structured illumination microscopy, holographic optical tweezers, and wavefront-shapers [1, 2]. Refractive elements, such as static micro-lenses, are important components of 3D displays [3, 4, 5], endoscopes, and integral imaging systems [4, 6, 7].

Optofluidic elements can serve as versatile, reconfigurable, optical components. On length scales smaller than the capillary length, in which interfacial tension is the dominant force, liquids form smooth [8] spherical interfaces between fluid volumes, appropriate for optical interfaces. The liquid nature of these interfaces means that they can be adjusted and reconfigured dynamically [9], and designed to be responsive to environmental stimuli.

Microscale liquid spheres are responsible for a variety of interesting optical phenomena. Optical material dispersion and internal reflections from water droplets in the atmosphere cause rainbows. Interference from scattered waves from atmospheric droplets causes the optical phenomena known as a “glory” [10, 11]. Scattering from emulsions (suspensions of small droplets) of oil in water give food products such as milk and mayonnaise their white appearance [12]. Complex emulsions, or dispersed droplets formed with multiple distinct material components in a single droplet, are important in a number of industries, including pharmaceuticals, diagnostics, food, cosmetics and optics [13].

This thesis focuses on the optical properties of multi-phase, particularly bi-phase, emulsion droplets. These droplets are formed from immiscible oils in an aqueous medium and can be reconfigured in various morphologies as shown in Figure 1.1. The morphology of the droplets is determined by the interfacial tension between the droplet phases and the surrounding medium and thus can be controlled by adjusting those interfacial tension, for example by changing the chemistry of the surrounding medium [14].

Figure 1.1: Bi-phase droplet morphology. Side-view optical micrographs of bi-phase droplets comprised of heptane (dyed red with Sudan Red 7B) and Fluorinert FC770. By modifying interfacial tension by adjusting surfactant concentration (here Sodium Dodecyl Sulfate and Zonyl), curvature of internal interface can be varied.

In particular, this thesis focuses on understanding some of the interesting optical properties that these droplets exhibit as micro-optical components. In the correct configurations they can act as tunable micro-lenses with variable focal length [15]. Adding a dye to the higher refractive index phase leads to a morphology dependent emission profile that can be used

for bacteria sensing [16]. In specific droplet configurations, total internal reflection along the internal interface leads to striking color separation in reflection that is highly morphology-dependent[17]. Besides the optical properties of the droplets, the thesis will also explore one of the numerous tuning mechanisms: manipulation of the bi-phase droplets using thermal gradients.

1.1.2 Thesis Outline

This first chapter provides an overview of the multi-phase droplets that are studied; what determines their morphology and how it can be controlled, as well as how they are fabricated. It also introduces the optical modeling environments and experiments that are relevant throughout this thesis.

Chapter 2 discusses multi-phase droplets as tunable compound micro-lenses. Ray tracing and Finite Difference Time Domain simulations are used to predict lensing behaviour. The lenses' characteristics are demonstrated by assessing their capability to transfer images, as well as by experimentally measuring their Point Spread Function (PSF) and Modulation Transfer Function (MTF). The macroscopic appearance in transmission is also discussed; Janus droplets appear transparent when viewed along the optical axis, while double emulsions scatter light strongly and appear opaque.

Fluorescent emission-based droplet sensors are presented in Chapter 3. When an fluorescent dye is dispersed within one of the phases of the droplets, the angular emission profile will depend on the droplet morphology. Our collaborators used this morphology-dependent emission as an optical transduction mechanism in a sensing scheme targeting detection of bacterial pathogens and specific chemistries, wherein, binding of a pathogen leads to changes in the droplet configurations. Ray tracing calculations are presented here, which relate these configuration changes to changes in the droplets' emission profile. These results can be used to optimize the system to increase the morphology-dependence of the emission profile and

by doing so increase the sensitivity of the emission-based droplet sensors.

Chapter 4 discusses how light interference within the droplets leads to iridescent color. A mathematical model that explains the color generation within the droplets is developed. The model extends beyond the droplets; any system in which total internal reflection occurs along a microscale concave interface could display this form of structural color.

Chapter 5 discusses how bi-phase emulsion droplets orient in thermal gradients. Marangoni flows occur when gradients in interfacial tension, caused by thermal or chemical gradients, cause a net force along an interface between fluids. In the case of bi-phase emulsions, these forces cause the droplets to rotate and move in a thermal gradient.

Figure 1.2: Optical responses of bi-phase droplets. a) The dynamic nature of the internal interface allows the droplets to behave as adjustable compound microlenses with varying focal length. b) An emissive dye in one of the droplet phases results in morphology dependent emission profiles. c) Interference within each droplet results in structural color.

1.2 Bi-Phase Emulsion Droplets

1.2.1 Fabrication

Multi-phase droplets can be fabricated in a number of ways including co-flow [18], flow focus, and T-junction microfluidics [19, 20, 21], and phase separation techniques [22, 14, 23]. The droplets that are the focus of this thesis are primarily fabricated by the phase separation method

presented by Zarzar et al [14]. This method makes use of the immiscibility of hydrocarbon and fluorocarbon oils that have relatively low mixing temperatures. Bi-phase droplets can be fabricated by heating two oils above their mixing temperature, emulsifying, and then cooling them to induce phase separation. To create poly-disperse droplets, the emulsification step is as simple as shaking or vortexing a vial with the mixed hydrocarbon-fluorocarbon solution in an aqueous surfactant medium.

Single-phase mono-disperse are straightforward to fabricate using microfluidics. There are several ways of doing this including single junction co-flowing, flow focus, and T-junction microfluidics [24]. In our lab, we used co-flow glass capillary microfluidic devices that consisted of an outer square capillary, and an inner cylindrical capillary, which was pulled to form a small, roughly 30 μ m-wide tip. The whole system was held above the mixing temperature of the two oils, and syringe pumps were used to inject the homogenous mixture of fluorocarbon and hydrocarbon into the inner capillary and aqueous surfactant solution into the outer capillary. The temperature of the microfluidic device and syringe pumps was maintained by a heat lamp, while the droplets were formed, and the droplets were then cooled below the critical mixing temperature to induce phase separation. We closely followed the procedures reported by Zarzar et al. [14]. Droplets studied in this thesis were also fabricated by the Swager Group and Zarzar Group, using other methods including commercial microfluidic chips; a Telos High Throughput Droplet System, Telos 2 Reagent Chip (100 μ m) and a Dolomite flow focusing four-channel glass hydrophilic microfluidic chip (100 μ m).

Figure 1.3: Bi-phase droplet fabrication. Two immiscible oils are heated above their mixing temperature and then emulsified in a similarly heated aqueous solution containing surfactant. The droplets are then cooled back down and phase separate such that each droplet has the same volume ratio of the two oils. Graphic recreated with permission from [14].

1.2.2 Bi-phase Droplet Morphology

The morphology of multi-phase emulsion droplets is set by the interfacial tensions between each of the constituents as well as with the surrounding medium. When one of the droplet oils is hydrophilic and the other hydrophobic, double emulsions will form, with the hydrophilic oil completely encapsulating the hydrophobic oil. When the interfacial tension between the two oils is too high, then the droplets will separate into droplets of each of the oils individually. When the interfacial tension between the two oils and each of the oils with the medium are of similar magnitude, a variety of dumbbell type shapes can form. In the case where the interfacial tension between the two oils is very low as compared to each of the oils with the surrounding medium, then the overall droplet shape will be spherical [20], as shown in Figure 1.4. These spherical droplets formed from two oils are known as Janus droplets, named for the two-faced roman god [25]. The exact morphology of the bi-phase droplets can be predicted based on the contact angles between the liquids and the volumes of each of the liquids. This can be thought of as an energy minimization problem combined with volume conservation.

The droplets studied here are assumed to fall into the categories of Janus droplets and double emulsions, where the overall droplet shape is spherical. This is an appropriate approximation

Figure 1.4: Bi-phase droplet morphologies. Depending on the balance of interfacial tension, bi-phase droplets can take on a variety of different morphologies, including dumbbell shapes, double emulsion and Janus droplets. Figure recreated with permission from [20].

when the interfacial tension between the droplet phases (γ_{FH}) is much smaller than the interfacial tensions between the droplet constituents and the aqueous medium (γ_F and γ_H) [20].

All of the internal and external interfaces were assumed to be spherical based on the following argument: interfaces between liquids can be considered to be spherical when the ratio of gravitational forces to surface tension forces is small. This ratio is given by the Bond number $B_o = \frac{\Delta\rho g L^2}{\gamma}$, where $\Delta\rho$ is the difference in density of the two droplet phases, g the gravitational acceleration and L the droplet diameter [26]. For a material system similar to the one used here, such as the hexane-perfluorohexane bi-phase droplets with a diameter less than $100\mu m$, constituent densities of $\rho_H = 0.66g/cm^3$ and $\rho_{FH} = 1.68g/cm^3$ and a surface tension $\gamma_{FH} = 0.4mN/m$ [26], the Bond number is around 0.25. While a Bond number of around 0.1 is usually considered to be an upper limit for assuming spherical curvature of a liquid-liquid interface [27], images of our complex droplets show that the interface of the droplets obtained can be approximated reasonably well with a spherical fit

The curvature of the internal interface formed between the immiscible phases can be adjusted

using surfactants that modify the relative interfacial tensions between the droplet phases and water (γ_F and γ_H). Surfactant-mediated modification of interfacial tensions results in a variation of the contact angles at the triple-phase contact line. This determines the radius of curvature of the lenses' internal interface, which in turn affects the optical properties of the droplets.

Figure 1.5: Janus droplet morphology. The contact angles between the droplet phases is set by the balance of interfacial tensions γ_F , γ_H and γ_{FH} . These set the relationship between the internal radius of curvature (R_i), the overall droplet radius (R_d), the distance (d) from the center of the droplet to the center of curvature of the internal interface, and the volume ratio $v_r = \frac{V_H}{V_F}$.

In order to predict the optical properties of the droplets, we need to first understand mathematically the shape of the droplets. During the fabrication process, the volume ratio of the two liquids is set. We define the volume ratio v_r as the ratio of the hydrocarbon phase to the fluorocarbon phase $v_r = \frac{V_H}{V_F}$. The parameters we use to define the droplet shape for optical characterization are R_d , radius of the drop, R_i , internal radius of curvature, and d , the distance from the center of curvature of the internal interface to the center of the droplet. A diagram of these parameters can be seen in Figure 1.5.

Under the assumption that the overall droplet shape is spherical, these parameters are constrained by the relation:

$$(d + R_d - R_i)^2(d^2 + 2d(R_i - R_d) - 3(R_d + R_i)^2) + 16d\frac{R_d^3}{1 + v_r} = 0, \quad (1.1)$$

which is derived from volume conservation in detail in Appendix A.1. The internal radius of curvature, R_i , is set by the balance of interfacial tensions at the triple-phase contact line given by

$$\frac{\gamma_H - \gamma_F}{\gamma_{FH}} = \frac{R_d^2 + R_i^2 - d^2}{2R_d R_i}. \quad (1.2)$$

These two equations together define the droplets morphology as a function of interfacial tensions.

1.3 Computational Tools

In order to predict the optical characteristics of the droplets, several types of optical calculations were utilized. The bi-phase emulsion droplets sit at an interesting length scale for optical modeling. They can vary from a few micrometers in size, where wave-optical phenomena are important, up to several hundred micrometers, where wave-optics becomes extremely computationally expensive and generally geometric optical techniques are used. In the cases where wave-optical effects are important, the droplets were modeled with Finite Difference Time Domain (FDTD) simulations using the open-source software MIT Electromagnetic Equation Propagation (MEEP) [28]. In many cases the droplets are large enough to be described using geometric optics, so ray tracing is a key tool in understanding how the droplets interact with light.

1.3.1 Ray Tracing

Ray tracing is a versatile and powerful technique for predicting how light interacts with an object. Primarily it is used in the limit where geometric optics applies, but can be extended as an approximation in the wave optics regime as well [29]. While there are a number of commercial ray tracing programs available, I wrote a custom ray tracer in MATLAB for the multi-phase droplet system. Besides being economically advantageous and a good learning opportunity, having a custom built ray tracer allowed us to be more flexible with the types of effects that were handled in the ray tracer, including approximating continuous volume emission and interference effects.

The ray tracer was implemented using MATLAB's object-oriented programming. Each ray object is defined by its location, direction, amplitude, and polarization. Droplets are defined by their location, volume ratio, and internal and external radii of curvature. Locations of ray-droplet intersections are calculated analytically and the amplitude of refracted and reflected rays are calculated with the Fresnel equations. Because the ray tracer handles the full 3D geometry of the droplets, the direction of refracted rays are determined with the vector version of Snell's law. For each ray-droplet intersection, the algorithm is called recursively and a bundle of rays is returned, allowing the raytracer to handle a high number of reflection/transmission events, including total internal reflection. For a detailed description of the ray tracing algorithm, see Appendix B.

There are a few limitations to raytracing. One is in the case when a continuum of light needs to be approximated, in this case a very high number of rays needs to be used and the exiting rays need to be binned, which can result in numerical errors, and high computation times. The bigger limitation is that ray tracing techniques fail when wave optics effects become important. While to some extent interference can be approximated with ray tracing, diffraction cannot. Nor can evanescent coupling such as in the case of frustrated total internal reflection.

1.3.2 Finite Difference Time Domain Simulations

There are a number of ways to model wave-optical effects. For periodic structures, optical properties can be calculated in the frequency domain with eigensolvers that compute the band diagram and eigenmodes of the system [30], or with semi-analytical techniques using the sum of spatial harmonics, such as rigorous coupled-wave analysis [31]. Similarly, for systems with spherical symmetry Mie scattering (spherical multi-pole expansion) can be used. Finite Difference Time Domain (FDTD) techniques are often used when none of these symmetries are present. FDTD is a numerical technique in which Maxwell's equations are discretized and solved in a leapfrog manner over a Yee lattice. In order to model wave-optical effects in the droplets, FDTD simulations were done using the open source software package MIT Electromagnetic Equation Propagation (MEEP) [28]. Both the C++ and Python interfaces were used at various points throughout this work for setting up the simulations, and the resulting fields were then analyzed in MATLAB.

The spatial distribution of monochromatic light could be modeled using a continuous source and running the simulation to reach steady state. Spectral content could be modeled with a temporal pulse containing all frequencies in the desired range. In both cases, the far-field diffraction pattern could be calculated by applying Fraunhofer diffraction to the reflected or transmitted field.

1.4 Experimental Characterization

Throughout the work in this thesis the primary experimental technique used is optical microscopy. Several bench-top and commercial microscope systems were used for the optical characterization of the droplets. Custom image transfer microscopes were used to assess the lensing capabilities of the droplets (discussed in Section 2.3.2). Commercial upright microscopes were used to image emission and reflection color from the droplets (Chapters 3 and 4). Side view micrographs were taken in order to determine the droplet morphology for a

given surfactant concentration.

1.4.1 Microscopy

A number of custom-built microscopes were used throughout this work, though they each had the same basic components; an objective lens, a Thorlabs tube lens (effective focal length = 200 mm) and a digital sensor (usually a Thorlabs USB3 CMOS or Allied Vision ProSilica GT3300C camera). Other components, such as lasers, filters, and lights, could be added as needed.

Figure 1.6: Diagram of side-view microscope setup. In order to image droplets that are gravity aligned, a custom side-view microscope was built. This allows for bright-field and fluorescent imaging. The sample was mounted on a three axis translation stage. In this diagram, gravity is acting in the $-z$ direction.

Because of density differences between the droplet components, the emulsions would orient with the optical axis aligned with gravity. In order to determine the morphology of the droplets, a side-view microscope was necessary. A diagram of this setup can be seen in Figure 1.6. This setup included a cube for a dichroic mirror so that a laser could be coupled

in (see Chapter 5), as well as a port for a filter cube so that fluorescent imaging could be done (Chapters 3 and 5). For bright-field imaging, a white screen was placed behind the sample, and the sample was illuminated from the side using a goose-neck lamp.

1.4.2 Droplet Geometry Measurements

The side-view micrographs are used for determining the contact angle between the constituent droplet fluids. In order to be able to see the full droplet morphology without being hindered by reflections and shadows of the surface that droplets were sitting on, we used a hydrogel substrate that was index-matched to the aqueous medium in order to minimize light scatter.

Figure 1.7: Measurement of droplet contact angle. a) Diagram of sideview imaging to determine droplet morphology. The droplet size, the contact angle between the phases and the volume ratio of the two phases completely define the droplet morphology. To determine the contact angle the droplets are imaged while sitting on a hydrogel substrate to minimize scatter from the surface. b) Image of the a droplet with circles fit. This type of fitting was done manually using imageJ/FIJI[32] and c) diagram showing relation between contact angles and fitted circles which can be calculated using Equation 1.4.

The contact angle between the phases can be determined from fitting circles to the interfaces in these images as shown in Figure 1.7. When the interface between the two liquids is imaged through the outer phase of the droplet, the image of the interface is magnified (or in the case of a lower refractive index outer phase de-magnified). In order to correct for the

magnification, the paraxial approximation was used, resulting in a correction factor of

$$h_{\text{real}} = \frac{n_{\text{medium}}}{n_{\text{outer}}} h_{\text{image}} \quad (1.3)$$

This correction was applied to the curvature R_i and the position of the interface. A detailed derivation of this correction is discussed in Appendix A.2. From the two circles that define the inner and outer interfaces of the droplets, the contact angle can be determined using the law of cosines:

$$\cos(\theta_F) = \frac{R_i^2 + R_d^2 - d^2}{2R_i R_d}. \quad (1.4)$$

These side-view measurements of the droplets geometry, the contact angles and volume ratios, are used throughout the thesis.

Chapter 2

Multi-Phase Droplets as Dynamic Compound Micro-Lenses

2.1 Introduction

The advancement of micrometre-scale optical elements have contributed significantly to the miniaturization of a variety of devices and instrumentation. Static micrometre-sized lenses are key components in integral imaging and 3D displays [3, 4, 5] synthetic aperture imaging [7], endoscopes [33], plenoptic cameras [6] and solar concentrators [34]. Dynamically switchable reflective (digital micro-mirror displays [35]) and absorptive (liquid crystal displays) micro-optics have enabled advances in optical technology ranging from high-resolution displays to structured illumination microscopy, holographic optical tweezers and wavefront-shapers [2, 1].

Morphological reconfiguration of micro-scale refractive components to enhance optical performance has been observed in the context of biological vision systems, such as rod photoreceptor cell nuclei of mammals. Photoreceptor nuclei of nocturnal mammals concentrate the highly refractive heterochromatin in the nuclear center, while diurnal mammalian retina

cells locate heterochromatin material towards their periphery. The nucleus geometry with the higher refractive index material concentrated at the nucleus center focuses light, while an inversion of this nucleic geometry leads to strong light scattering. This structure helps guide light towards the rods' light sensing segments, thereby increasing the signal to noise ratio of retinal transmitted images [36, 37, 38].

Similarly, man-made, refractive micro-elements with reconfigurable morphology, enabling in-situ tunable optical properties are poised to complement and extend the capabilities of present micro-optical devices [39, 40, 41, 42]. In particular, tunable micro-lens designs employed as responsive in-line, phase-modulating, intensity-preserving components will extend the light manipulation capabilities of optical systems [2].

To this end, optofluidic devices using dynamic fluid lens materials represent an ideal platform to create versatile, reconfigurable, refractive optical components [42, 43].

Droplets smaller than the capillary length, wherein surface tension is the dominant force, create curved interfaces between fluid volumes [44] and display intrinsic lensing behaviour. In addition, liquids have minimal surface roughness, on the order of nanometers, even if the interfacial tension is very low [45, 8]. Dynamic lensing materials based on hydrogels and liquids can be reshaped through various external stimuli after the optical element is formed, which is ideal for adaptive optics, imaging devices or sensors [39, 46, 47, 48].

For example, reconfigurable liquid lenses have been demonstrated by taking advantage of electro-wetting [49, 50, 51, 52, 53, 54, 55, 56] and the integration of microfluidics with MEMS technology [41]. Adjustable focal length lenses have been realized using microfluidics, by varying the amount of liquid in a reservoir behind an elastic membrane [57, 58, 59, 60, 61]. Alternatively, the controlled flow of liquids within microfluidic channels can be used to create micro-lenses with variable focus [62, 46]. Micrometre-sized solid-liquid doublet lenses that allow for minimization of optical aberrations have also been fabricated [58]. Tunable fluid micro-lenses, as individual components or arranged in arrays, have found applications in

miniaturized optical components with variable working distances and optics-based biosensing devices [63, 64]. Incorporation of dyes into the liquids allows for droplets that serve as both lenses and optical filters [65]. In particular, the incorporation of laser dyes in micro-fluidic droplets enables lasing-based sensing approaches with high sensitivity and throughput [66].

This chapter explores the optical characteristics of bi-phase emulsion droplet based compound micro-lenses. While such droplets could be fabricated with a variety of materials, this chapter predominantly focuses on emulsions of FC770 and heptane in water. The refractive index contrast at each material interface as well as the curvature of each interface contributes to the focusing power of the lens (see lens maker's equation [67]) The low refractive index of the fluorocarbon and high refractive index of the hydrocarbon (relative to the surrounding water) enables switching between converging or diverging lens geometries (Figure 2.1). Most importantly, such complex droplets can be dynamically reconfigured between double emulsion and Janus (two-sided) morphologies through application of external stimuli, which makes these droplets very promising as highly tunable compound lenses. This chapter demonstrates the adjustability in focal length of the lenses, as well as their microscopic and macroscopic light manipulation characteristics, though both optical modeling and experimental verification.

Figure 2.1: Dynamic micro-lens concept. a) Droplet morphology set by balance of interfacial tensions. b) When the high index hydrocarbon forms the internal droplet phase the droplets will focus light. Similarly, when the low index fluorocarbon forms the internal phase, they will cause light to diverge. In the case of a Janus droplet with the correct refractive indices, the droplets will have an effective focal length of infinity and will appear transparent.

2.2 Optical Modeling

In order to model the droplet based compound lenses, both geometric and wave optics were used. When the optical axis is aligned with the droplets' symmetry axis, the optical system is axisymmetric and can be modeled in two dimensions. The droplets' symmetry axis aligns with the gravitational field due to the difference in density between the light hydrocarbon phase and the dense fluorocarbon phase. We exploit this alignment in our theoretical and experimental study of the droplets' optical characteristics. All these calculations were done under the assumption that the overall droplet shape is spherical ($\gamma_{FH} \ll \gamma_F, \gamma_H$) and that each of the interfaces is spherical (low Bond number).

2.2.1 Geometric Optics

The ray tracing algorithm presented in Chapter 1, as well as in detail in Appendix B, was used to predict how light interacts with the droplet lenses as shown in Figure 2.2. In this case, equally spaced rays were propagated through the droplets from the top, parallel to

the symmetry axis. Unsurprisingly, as the internal interface curvature decreases, the focal length of the droplet lenses increases. As the droplet inverts, so too does the lensing, going from a positive converging lens to a negative diverging lens.

Figure 2.2: Ray tracing through droplet micro-lenses. a) Side-view micrographs of heptane (dyed with Sudan Red 7B) and FC770 bi-phase droplets. b) Ray tracing calculation showing direction of light propagation through the droplets.

Another useful geometrics optics tool is the ABCD Ray Transfer Matrix, which can be quickly used to determine the effective focal length (EFL), the front focal length (FFL), the back focal length, (BFL) and the locations of the principle planes.

The ray transfer matrix considers a ray that starts at an initial input plane and travels to a final output plane both perpendicular to the optical axis. For a ray starts a distance x_1 from the optical axis with angle θ_1 from the optical axis, the position and angle of the ray

at the output plane can then be approximated by:

$$\begin{bmatrix} x_2 \\ \theta_2 \end{bmatrix} = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \begin{bmatrix} x_1 \\ \theta_1 \end{bmatrix} \quad (2.1)$$

Figure 2.3: Comparing ray transfer matrix and ray tracing. The back focal length (BFL) calculated from the ray transfer matrix and from raytracing as a function of droplet morphology. The volume ratio was $v_r = 1$, and the refractive indices were $n_1 = 1.39$ and $n_2 = 1.27$

This ray transfer matrix for the droplets was calculated numerically using Matlab. The transfer matrix consisted of the product of transfer matrices for each of the interfaces of the droplet and propagation distances within the droplet. The matrices are as follows: a ray entering the drop (water to hydrocarbon with radius of curvature $\frac{1}{R_d}$), propagating a distance $R_d - d + R_i$ to the interface between hydrocarbon and fluorocarbon, being refracted at this interface, propagating the rest of the way through the droplet, and finally being refracted at

the outer interface (fluorocarbon to water):

$$\begin{bmatrix} A & B \\ C & D \end{bmatrix} = \overbrace{\begin{bmatrix} 1 & 0 \\ \frac{n_2-n_m}{n_m R_d} & \frac{n_2}{n_m} \end{bmatrix}}^{\text{Out Of Drop}} \underbrace{\begin{bmatrix} 1 & R_d-R_i+d \\ 0 & 1 \end{bmatrix}}_{\text{Through Second Phase}} \overbrace{\begin{bmatrix} 1 & 0 \\ \frac{n_1-n_2}{n_2 R_i} & \frac{n_1}{n_2} \end{bmatrix}}^{\text{Internal Interface}} \underbrace{\begin{bmatrix} 1 & R_d-d+R_i \\ 0 & 1 \end{bmatrix}}_{\text{Through First Phase}} \overbrace{\begin{bmatrix} 1 & 0 \\ \frac{n_m-n_1}{n_1 R_d} & \frac{n_m}{n_1} \end{bmatrix}}^{\text{Into Drop}} \quad (2.2)$$

From this, the effective focal length (EFL), back focal length (BFL) and front focal length (FFL) can be calculated

$$EFL = -\frac{1}{C}, \quad BFL = -\frac{A}{C}, \quad FFL = -\frac{D}{C} \quad (2.3)$$

Figure 2.4: Volume ratio. a.) Ray tracing diagrams showing light propagation through bi-phase droplets of various volume ratios. b.) Effective focal length as a function of volume ratio for several different contact angles. Generally, larger volume ratio results in larger focal lengths for the same contact angle, as a larger volume ratio corresponds to a larger internal radius of curvature.

In order to compare with experiments, refraction through the cover-slip after the drop was also included in the ray transfer matrix. The locations of the focal points were consistent

between the ray transfer matrix and ray-tracing as shown in Figure 2.3. For far off-axis rays, the ray tracing shows that these rays will strike the optical axis closer to the droplet than the predicted BFL. This demonstrates that spherical aberrations are present in these compound lenses.

This transfer matrix can also be used to quickly predict how various parameters affect the focal length of the droplet lenses, such as the volume ratio (Figure 2.4) and the refractive indices (Figure 2.5). While the volume ratio of course does affect the focal length of the droplets as it affects the curvature of the internal interface, the contact angle and refractive indexes play a larger role. This means that if there is a small amount of variation in volume ratio during droplet production the droplet lenses will still have very similar focal lengths.

The refractive index contrast is extremely important in determining both the focal length in a specific geometry, as well as the range of focal lengths available to the droplet over all morphologies. In particular, having a large range of tunability in focal length relies on the internal interface being the primary source of refraction. If the refractive index contrast at the water-oil interfaces is large, than those interfaces dominate the refraction. In this scenario the internal interface can only adjust the focal length in a small window, which could still be extremely useful in the situation of fine tuning an already mostly aligned system.

2.2.2 Finite Difference Time Domain

For very small droplets, the geometric optics approximation breaks down and wave optical effects need to be considered. Finite Difference Time Domain Simulations (FDTD) were used to model the optical behavior of bi-phase emulsion droplets in this regime. The FDTD simulations were completed using the open source software package MIT Electromagnetic Equation Propagation (MEEP) [28], using the Python-Meep interface.

Double emulsion and Janus droplets of heptane ($n_H = 1.387$) and FC770 ($n_F = 1.27$) with a radius of 5 μm in water ($n_w = 1.33$) were illuminated with a 500 nm wavelength monochro-

Figure 2.5: Parameters affecting focal length. The effective focal length (EFL) as a function of various parameters including contact angle, volume ratio, and refractive indices. Unless otherwise stated, the droplet parameters were $v_r = 1$, $n_1 = 1.39$, $n_2 = 1.27$, and $\theta_c = 45^\circ$.

matic line light source. Equal volumes of heptane and FC770 were simulated ($v_r = 1$), and the shape of the overall droplet, as well as shape of the internal interface, were assumed to be spherical, such that Equation 1.1 yields the interface location. A perfectly matched layer (PML) was used as the boundary condition on all edges of the cell, and the resolution was 32 units per μm . The simulation was run until a stationary state was reached such that the intensity no longer varied between time steps.

The far field scattering distribution was calculated using the Fraunhofer diffraction:

$$U(\sin \theta) = \int_{\mathbf{x}} A(\mathbf{x}') e^{-i \frac{2\pi}{\lambda} \sin(\theta) \mathbf{x}'} d\mathbf{x}' \quad (2.4)$$

where A is the amplitude of the field across the simulation cell. These far-field scattering calculations and the visualization of the light intensity were done in Matlab.

Figure 2.6: Finite difference time domain simulations of droplet lenses. Top row: Spatial Intensity near bi-phase emulsion using FDTD simulations. The excitation source was 500 nm continuous wave illumination, the droplet radii were 5 μm and the internal radius from left to right was 3.96 μm , 4 μm , 6 μm , 9 μm , 20 μm , and ∞ (flat interface). **Bottom row:** Far-field radiant intensity calculated by Fraunhofer diffraction of the electromagnetic field after the droplets.

Figure 2.6 shows the results of these FDTD simulations for various curvatures of the internal interface. As expected, the smaller the internal radius of curvature, the more strongly the droplet will focus light. In the far-field, this results in a larger distribution of radiant intensity. Essentially, when illuminated in transmission Janus droplets with a flat internal interface will scatter far less than double emulsions. This can be seen experimentally as well (See Section 2.3.5).

The effect of rotating a Janus droplet can be seen in Figure 2.7. For small rotations it is possible to use the droplet's rotation to shift the direction of light propagating through the system. Small deflections do not disrupt the shape of the wavefront too much, however large rotations result in light being reflected from the internal interface, rather than primarily

Figure 2.7: Finite difference time domain simulations of Janus droplet rotations a-d) Spatial intensity near bi-phase emulsion using FDTD simulations for droplet rotations and corresponding far-field angular distribution. **e)** Angular location of intensity peak in the far-field as a function of droplet rotation.

refracted which causes a messier far field distribution. Such rotations can be achieved by magnetic [14] or thermal (Chapter 5) effects.

2.3 Experimental Characterization of Droplet Lenses

Beyond optical modeling predictions, the variable focal length is also demonstrated experimentally. In these experiments, we used a combination of both a hydrocarbon-stabilizing surfactant, sodium dodecyl sulfate (SDS), and a fluorocarbon-stabilizing surfactant, such as Zonyl FS-300 or Capstone FS-30 to control the droplet morphology. The concentration of these surfactants determines the interfacial tensions of each of the oils with the surrounding aqueous medium, which then determines the internal interface curvature and thus the lensing properties of the droplets. The morphology of the droplets for a given set of surfactant concentrations was determined using the side-view microscopy setup presented in Section 1.4.1.

2.3.1 Z-Scans of 3D Light Field Behind Droplet Lenses

In order to map the light field behind heptane-FC770 droplets, the droplets were illuminated with a collimated beam of quasi-monochromatic light of a 540nm wavelength. The light field in the volume behind the droplets was recorded by vertically scanning the image plane of an inverted microscope (Figure 2.8a). Variation in the concentrations of SDS and Capstone FS-30 in the surfactant mixture added to the aqueous phase allowed us to alter the droplets' internal interface curvature, resulting in a variation of their focal length (Figure 2.8b).

Figure 2.8: 3D light field formed by droplet lenses. a) Schematic of the setup used to record the light field behind the droplets. The bottom objective scans through the z-direction. b) Iso-surfaces of the reconstructed light fields behind the droplets for different internal droplet morphologies. Representative image data sets captured immediately behind the droplets show slices of the scan, from which the light field was reconstructed. Droplet sketches are offset upwards by 10 μm to not obstruct slice images.

2.3.2 Image Formation

The native function of a lens is to form an image. In order to evaluate the image formation capabilities of the droplets, including experimentally quantifying their optical power, an object was placed in front of the droplets so that they would project an image at varying

distances (Figure 2.9a). Specifically, a grid pattern was projected in the aqueous medium above the droplets. The image of the object formed by the droplets was recorded using an inverted microscope. By varying the concentrations of SDS and Zonyl surfactant in the aqueous medium surrounding the droplets, the internal interface shape could be adjusted. By projecting the image of an object through the lenses and by measuring object-to-lens and lens to image distances (Figure 2.9a-d), the micro-lenses' effective focal length was quantified (Figure 2.10).

Figure 2.9: Capturing the image projected by droplet lenses. a-b) Schematic of the optical setup used for focal length and image forming analysis. A grid image (c) is projected in front of the droplets (d) to serve as the object for the micro-lenses. The image (e) formed by the droplets is recorded using a 10x objective. Scale bars: 100 μm .

In order to calculate the focal length of the droplets from the locations of the input and output images, it is necessary to consider the whole aqueous medium-droplet-coverslip system, as shown in Figure 2.10a. The location of the image formed (in air, $n = 1$) by the droplets is related to the input location (in water, $n_w = 1.33$) by the equation:

$$\frac{n_w}{x_1 - p_1} + \frac{1}{x_2 - p_2} = \frac{1}{f} \quad (2.5)$$

where p_1 and p_2 are the locations of the principle planes relative to the center of the droplet. See A.3 for more about of this relationship. For each droplet morphology, a number of input image locations and their corresponding image output locations were measured, and this equation was used as fit as demonstrated in Figure 2.10b. This method allowed the effective focal length to be measured as a function of internal radius of curvature, as shown in Figure 2.11.

Figure 2.10: Determination of the focal length from image location. a) Ray diagram for a compound thick lens located at the edge of two different media. b) Example plot of the image location used to determine focal length. The dashed red line is the least squares fit to Equation 2.5 with fitting parameters $f = 13.8 \pm 0.4$, $p_1 = 2.2 \pm 0.5$ and $p_2 = 2.2 \pm 0.9$ in units of droplet radius. The solid black line shows the expected image locations using the ray transfer matrix for a droplet with internal radius of curvature $R_i = 2.03$ (determined from the side view of the droplet) and volume ratio $v_r = 1$

The internal interface curvature of the droplets was determined by fitting a circle to the interface shape observed in side-view micrographs, taking into account refraction due to the outer droplet phase (Section 1.4.2). Knowing this curvature, we could compare the expected effective focal length acquired using the paraxial approximation and the ray transfer matrix calculations with the experimentally determined effective focal length (Figure 2.11a). This shows that FC770–heptane droplets formed with volume ratio 1:1 can vary in focal length from 3.5 times the diameter of the droplet to infinity, and can switch between positive and

Figure 2.11: Focal length and numerical aperture of droplet lenses. **a)** Effective focal length as a function of internal radius of curvature R_i , normalized by the droplet diameter R_d . Error bars represent uncertainty in fit parameter f and uncertainty in measurement of internal curvature. The solid black line shows the expected focal length of the system given by the ray transfer matrix method. **b)** Numerical aperture NA as a function of internal radius of curvature R_i , given by $\text{NA} = n \sin(\tan^{-1} \frac{R_d}{f(R_i)})$. Here, the refractive index of the medium in which the image is formed is $n = 1$ (the image is formed in air). Error bars represent measurement uncertainty propagated from the uncertainty shown by the error bars in (b).

negative focal lengths. For example, a double emulsion droplet of $100\mu\text{m}$ diameter, with heptane as the core phase and the fluorocarbon FC 770 as the shell phase, has a focal length of $350\mu\text{m}$ and acts as a converging lens. While the experiments presented here were limited to lenses with constant volume ratio of 1:1, it is worth mentioning that a variation in volume ratio results in a change in radius of curvature of the internal interface and consequently in changes of the lenses' focal length provided that the triple phase contact angles are kept constant as was shown in section 2.2.1. The numerical aperture (NA) was then calculated by

$$\text{NA} = n \sin \left(\tan^{-1} \frac{R_d}{f} \right) \quad (2.6)$$

In this case, the refractive index is $n = 1$ (the image is formed in air). The highest achievable numerical aperture for these droplets is 0.12. This could potentially be increased by increasing the refractive indices of the droplet phases, however this comes at the cost of reducing the range of tunability of the droplet lenses.

2.3.3 Point Spread Function and Modulation Transfer Function

To estimate the droplet lenses' optical quality, we measured the lenses' Point Spread Function (PSF) and Modulation Transfer Function (MTF). From these, the resolution limit of the lenses can be determined. The PSF gives the two-point resolution criterion, the distance between two object points for which they can still be distinguished unambiguously in the image projected by a lens. From the MTF, the Abbe diffraction limit can be determined. The Abbe diffraction limit defines the maximum spatial frequency of a sinusoidally varying intensity pattern that can be resolved with sufficient contrast by the lens.

The PSF of droplets was experimentally estimated by imaging the focus formed by droplets that were illuminated with collimated white light, which originated from an optical fiber with a $50\mu\text{m}$ diameter core and is collimated by a spherical lens ($f = 150\text{ mm}$). The droplet's PSF was captured using a custom-built microscope composed of a 50x Olympus objective ($\text{NA} = 0.5$), a Thorlabs tube lens ($f = 200\text{ mm}$) and an Allied Vision ProSilica GT3300C camera. Only the camera's red channel (maximum quantum efficiency at 620 nm) was used, expecting that the droplets' resolution would be at least comparable or better for smaller wavelengths. The experiment was performed with droplets with a highly curved internal interface, assuming that their shorter focal length and higher numerical aperture $\text{NA} \approx 0.12$ would result in the best obtainable resolution (though may be the furthest from diffraction limited as it may have the largest spherical aberrations). The measured PSF can be seen in Figure 2.12.

The standard definition of the Rayleigh two-point resolution criterion consists of determining the distance from the center of the lenses' PSF to its first minimum. With this definition, the theoretically achievable resolution r_{th} of a diffraction-limited lens is given by $r_{\text{th}} = 1.22\lambda/2\text{NA}$. From the experimental PSF estimate we find that the droplets can resolve details down to a feature size of $r_{\text{exp}} = 3.7\mu\text{m}$. The theoretical two-point resolution limit of a comparable diffraction limited lens is $r_{\text{th}} = 3.1\mu\text{m}$.

Figure 2.12: Optical quality. a) Point spread function (PSF) estimate of droplets with a numerical aperture $NA \approx 0.12$ for red light (pink line). The theoretical PSF for a diffraction limited lens with equal NA is shown as a dashed black line. The area under the curves is normalized to unity. Insets show the theoretical 2D PSF (black dashed frame) and the experimentally determined PSF (pink frame). The experimentally determined two-point resolution limit amounts to $r_{\text{exp}} = 3.7 \mu\text{m}$. b) Modulation transfer function (MTF) for the same droplets. The cut-off frequency above which the image contrast is less than 10% amounts to $f_{\text{exp}}^{10\%} = 0.22$ cycles per μm . Insets show the theoretical 2D MTF (black dashed frame) and the MTF determined from the experimentally obtained PSF (pink frame).

An estimate of the Modulation Transfer Function (MTF) of the same droplets can be made based on the experimentally obtained PSF estimate. The MTF is obtained by Fourier-transforming the PSF after subtraction of background noise, removal of “salt and pepper” noise (due to hot pixels) using a median filter in a 3×3 pixel neighborhood area, and averaging over angular slices of the imaged Airy disk pattern. The resulting PSF and MTF curve must be seen as a conservative estimate as the recorded PSF still possesses residual blur from the microscope optics. The MTF’s cut off frequency at a remaining image contrast of at least 10% of the original object contrast is found to be $f_{\text{exp}}^{10\%} = 0.22$ cycles/ μm , which corresponds to a sinusoidal intensity variation of $4.5 \mu\text{m}$ period. The theoretical line pattern resolution limit for a comparable lens is $3.2 \mu\text{m}$ ($f_{\text{th}}^{10\%} = 0.31$ cycles/ μm). The discrepancy between the measured and the theoretical resolution limits is likely due to spherical aberrations.

2.3.4 Micro-lens Arrays and Uniformity

Using microfluidic devices, it is possible to create mono-disperse samples of the droplets, where not only do the droplets each of have the same volume ratio and contact angles, they also have the same size. When placed into a dish, the droplets will pack hexagonally forming arrays of droplet lenses. For an object located above this array of lenses, each lens will form an image of that object, from a slightly different view, as can be seen in Figure 2.13. The curvature of the internal interface determines the focal length of the droplet lenses, which sets the magnification for a given object distance (the image location also varies).

Figure 2.13: Lens array. Schematic showing image formation with multiple droplet lenses. **Top row:** Top view micrographs of droplets with increasing internal radius of curvature and **bottom row:** corresponding images formed. There is cross talk between the images formed by adjacent droplets (images overlap).

To test the uniformity of these arrays, we looked at the PSFs of a large sample of these droplets. Figure 2.14 shows that when light is focused through several lenses of the same size, all point spread functions have similar shapes. This leads to the conclusion that all lenses have very similar focal lengths, and numerical aperture. The droplets are in a double emulsion configuration, which has the highest numerical aperture. The Rayleigh two-point resolution resulting from analysis of the lenses' Airy patterns as imaged with a 4x objective with NA of 0.13 is $(5.7 \pm 0.8)\mu$. The difference in resolution with respect to the values stated

in section 2.3.3 is due to the convolution of the droplets' point spread functions with the point spread function of the 4x objective, which was used to image a larger region of droplets at the same time.

Figure 2.14: Droplet homogeneity and point spread function uniformity. **a)** An array of uniform droplet lenses. **b)** Point spread functions (PSF) of the droplets shown in (a). Scale bars: 500 μm **c)** Fit to the Airy disk. **d)** Distribution of the minimum in the Airy pattern, which is a measure of the Rayleigh two-point resolution limit.

2.3.5 Scattering and Transmission

A unique aspect of these droplets is that the focal length is continuously variable from positive to negative values, meaning that there is a droplet morphology where the focal length is infinite. Rays of light that enter the droplet parallel, exit parallel. The geometry for which this occurs can be found by finding when $C = 0$ in the $ABCD$ matrix in equation

2.2. In the case of heptane and FC770 droplets with a 1:1 volume ratio, this occurs in droplets with a nearly flat internal interface. Essentially, refraction at the water-hydrocarbon interface is reversed by the refraction at the fluorocarbon-water interface. These differences in microscale light manipulation between double emulsions and janus droplets translate into differences in macroscopic optical properties.

Finite difference time domain simulations show that the radiant intensity distribution is very different between double emulsions and flat interface Janus droplets (Figures 2.6 and 2.15a-c). In particular, a strongly focusing double emulsion will scatter light in a cone with an opening angle of almost 20° . On the other hand, the Janus droplet with a nearly flat interface transmits light with an angular spread of only a few degrees.

The variation of the far-field angular intensity distribution of light scattered by the lenses as a function of their internal curvature results in changes in the macroscopic appearance of droplet assemblies. Figure 2.15d shows a film of polydisperse emulsion droplets covering an area of several square centimeters illuminated from behind. In the dark areas of the smiley, the droplets are in the double emulsion morphology, and in the light areas, they are in the flat interface Janus morphology. These images were taken by Lauren Zarzar. She localized variations in droplet morphology by employing an optically switchable azobenzene surfactant to change the morphology of the emulsions droplets, as described in [14, 68]. Irradiation of selected areas of droplets with UV light using a “smiley face” photomask, induces a transformation of the exposed droplets from the transparent Janus geometry to a strongly scattering double emulsion geometry. Simple visual inspection reveals a clear optical contrast when viewed in transmission.

The FDTD simulations predicted that droplets with an internal curvature somewhere between the extremes of the double emulsion state and the flat-interface Janus configuration scatter light in a cone with an opening angle larger than that of the Janus droplets, but smaller than that of the double emulsions (Figure 2.15b).

Figure 2.15: Multi-phase droplet scattering. a–c) 2D finite difference time domain simulations of droplets of 5 μm radius for incident light of 500 nm wavelength. The internal radii of curvature are 4 μm (a), 9 μm (b) and infinite (c). The far field angular distribution of intensity was determined by applying the Fraunhofer diffraction equation to the near field calculated by the FDTD simulation. d) Localized exposure of light-sensitive surfactants to UV light leads to a local variation in droplet morphology and scattering behaviour, which is used to create an image. The dark zones in the image are where droplets have switched to the double emulsion state (a). They scatter light more strongly and therefore appear darker than the flat interface Janus droplets (c). Scale bar 500 μm . e) Schematic showing two different geometries for observing the photo-patterned droplet films, corresponding to the perceived images shown in f and g. The labels a, b and c correspond to the droplet geometries shown in panels a–c. f, g) Photo-patterned droplets viewed from above (f) and at an angle (g). Scale bars = 5 mm. Images in d, f, and g were taken by Lauren Zarzar.

To test whether it was possible to achieve intermediate levels of perceived brightness, we looked at the scattering of an intermediate state. To this end, Lauren irradiated a droplet assembly through a MIT photomask in which a piece of scattering Scotch tape was placed over the stem of the “i” to partially block UV transmission. Our expectation was that the partially-blocked area would display smaller variations in curvature of the droplet-internal interfaces as compared to the fully-exposed areas. Consistent with this design, we observed a significant decrease in pattern brightness in the modified photomask region of the sample,

when observed in direct transmission (Figure 2.15f).

The double emulsions scatter light into a larger angular range; consequently, when the same sample is viewed at an angle, the areas that were exposed to the UV radiation appeared brighter (Figure 2.15e). Hence, we observe an inversion of the image (Figure 2.15g) consistent with FDTD simulations. In short, we can vary image contrast in the droplet films by photochemically modulating the degree of curvature of the droplets' internal interface.

2.4 Summary

Multi-phase droplets of optically distinct, immiscible hydrocarbons and fluorocarbons in aqueous media can act as compound lenses with a tunable droplet-internal optical interface. Adjustment of the droplet's interfacial tensions with the aqueous phase allows for a continuous and reversible variation from double emulsions, through Janus configurations, to inverted double emulsions. Depending on the configuration, the droplets refract and transmit light differently. Double emulsions with the optically denser fluid as the droplet-core phase strongly focus light, and can project real inverted images. Janus droplets with a flat internal interface do not significantly disturb the light wavefront, when the surface normal of the internal interface is aligned with the light propagation direction. Double emulsions with the optically denser fluid as the droplet-shell phase show strong light scattering and act as diverging lenses, forming virtual upright images. A controlled modification of the droplet morphology consequently results in a predictable variation of the droplets' light focusing and scattering behavior.

These emulsion-based micro-lens droplets formed from heptane and FC770 have a dynamically tunable focal length that can vary from $\pm 3.5\times$ the drop diameter to $\pm\infty$. With a resolution limit around $4\text{ }\mu\text{m}$, the reconfigurable micro-lenses do not show diffraction limited performance (resolution limit of $3\text{ }\mu\text{m}$ for a comparable diffraction-limited micro-lens), which can be attributed to the presence of spherical aberrations. Microfluidics allows for

the creation of mono-disperse droplets and tunable multiphase droplet microlens arrays with uniform optical properties.

The configuration of the droplet emulsions also affects their macro-scale optical appearance, which can be used for the creation of patterns and images. Light scattering is significantly more pronounced for droplets in the double emulsion geometry, while droplets with a flat internal interface induce much smaller perturbations in the propagating light wavefront. This allows for the creation of microscopic and macroscopic patterns with tunable contrast, which could form the basis for light field displays capable of creating 3D images and projecting variable information content into different directions.

2.5 Looking forward

The droplets' variable focal length and their capability to form images are properties that are particularly relevant for a variety of application scenarios related to miniaturized imaging devices. Arrays of micro-lenses, for example, find application in digital integral microscopic imaging and photography [5, 4]. One of the main challenges in three-dimensional image acquisition is the limited depth of field [3]. The tunable focal length lenses could provide the means to address this limit. While the resolution limit of standard high numerical aperture microscope objectives is at least an order of magnitude higher, the microscopic droplet compound lenses have clear advantages in applications where device size, simplicity and the ability to reconfigure on-demand matters; this could be of particular interest in synthetic aperture integral imaging where in-situ reconfigurable optical components could help to enhance performance of the imaging device [69]. Liquid lenses with variable focal length could form the basis of adaptive micro-scale optical elements in miniaturized integral 3D imaging and sensing devices.

While we focused on heptane-FC770 droplets, there are a number of other materials that could be used in order to adjust the refractive index of the droplet phases. Experiments using

lenses formed from hexane and perfluorohexane showed similar optical characteristics as the heptane-FC770 droplets. Using halogenated liquids with high refractive index as constituents of the emulsion droplets would enable the formation of compound lenses with higher refractive power. This additional degree of freedom—the choice of emulsion formulation—could be used for correcting aberrations or for introducing a desired chromaticity.

One possibility of minimizing spherical aberrations in the droplets and increasing the resolution is to add another material to the droplets, so that triplet lenses can be formed. Toward this end, the droplet raytracer has been expanded to include tri-phase droplets as shown in Figure 2.16. These droplets can be made by incorporating another immiscible oil, such as a silicone oil [14]. Combining this additional degree of freedom of a second tunable interface, along with clever choices in refractive indices should allow for the droplet lenses to be optimized in order to minimize aberration and increase resolution.

Figure 2.16: Tri-phase droplet lensing. Example ray diagrams of droplets formed from three immiscible oils, with refractive indices $n_1 = 1.38$, $n_2 = 1.41$, and $n_3 = 1.27$.

The orientation of the droplets was set by gravity, with the lenses symmetry axis perpendicular to the substrate due to the density difference between the constituent lens components.

Future investigations may address the control of lens orientation and droplet morphology with forces other than gravity, including using stimuli such as magnetic fields, light, electric fields and thermal gradients (discussed in Chapter 5). The large number of material choices and tuning mechanisms offer a broad parameter space for tuning and controlling the fluid micro-lenses' dynamical optical properties, and simultaneously provide access to a multitude of enticing sensing paradigms and optical applications.

Chapter 3

Emissive Bi-Phase Droplets as Pathogen Sensors

3.1 Introduction

A key application of the multi-phase droplet system is in chemical and pathogen sensing. More than 9 million people in the United States are estimated to have contracted illnesses from foodborne pathogens each year [70]. Most methods of detecting foodborne pathogens are either prohibitively expensive, complicated to perform, or require long incubation steps [71]. New, simple, methods that can rapidly detect small amounts of pathogenic cells, ideally within a single six-hour work shift at a food production plant, are therefore required to efficiently prevent contaminated food from reaching consumers.

The multi-phase emulsion droplets are well situated to act as pathogen sensors. Chemical changes in the droplet environment trigger microscale changes in the droplet morphology. These changes in microscale morphology lead to changes in the macro-scale optical properties of the droplets. The previous chapter discussed how the refractive properties of these droplets change with the modification of droplet morphology. This chapter focuses on how

emissive properties of the droplets change with variations in droplet morphology, when a dye is dispersed within one of the droplet phases. Through tailored chemistry, these emissive differences can be used to detect specific molecules or even pathogens. In particular, fluorescent emulsions with boronic acid- functionalized surfactants allow for the detection of *Salmonella enterica* [16].

When an emissive dye is dispersed within the hydrocarbon phase, which has a higher refractive index than the fluorocarbon phase, a fraction of the emitted light can be confined due to total internal reflection (TIR). Figure 3.1 shows different possible trajectories of light being emitted from a bi-phase droplet. If the light is emitted near the center, most of the light will be refracted through the interfaces and exit the droplet. Depending upon the angle that the light hits the interface, a portion of it will be reflected and a portion refracted, according to the Fresnel reflection coefficients. However, if light is emitted from a location near the internal interface, it can strike the interface at an angle greater than the critical angle of incidence ($\alpha_c = \sin^{-1} \frac{n_F}{n_H}$) in which case it will be entirely reflected due to Total Internal Reflection (TIR). Depending on the droplet morphology and the light ray's reflection angles, it can either then be transmitted through the top hydrocarbon-water interface or be reflected there as well.

The light that undergoes TIR along the internal interface, but exits the droplet through the top interface will do so near the three-phase contact line. When such droplets are viewed in a upright fluorescence microscope, a distinct emission ring can be seen near the three-phase contact line (Figure 3.2). Similarly, when the droplets are viewed from the side, bright areas of emission can be seen near the three-phase contact line.

This chapter presents the ray-tracing model used to calculate how the emission of the droplets changes with morphology, i.e. with changes in surfactant concentration or surfactant effectiveness. This allows us to predict of intensity changes that can be expected from droplets which are primed to change their morphology in response to a stimuli in their environment.

Figure 3.1: Ray diagrams of fluorescent light emitted in the high index phase of the droplet. Much of the light will simply be refracted through the droplet interfaces, however some of the light emitted near the internal interface can undergo TIR. This light will either be refracted through the hydrocarbon water interface or be trapped within the droplet to re-circulate.

Figure 3.2: Micrographs of emission from bi-phase droplets. Side view (left) and top view (right) micrographs of emulsion droplets formed from toluene ($n_H = 1.49$) dyed with perylene and a 9:1 mixture of HFE-7500 and FC-43 ($n_F = 1.29$).

This work was done in collaboration with Dr. Lukas Zeininger working with Prof. Timothy Swager in the Department of Chemistry at MIT. All ray tracing results are my own work and all experimental L-curves were acquired by Dr. Zeininger. This work was conceptualized by Dr. Zeininger and Prof. Swager.

3.2 Angular Emission Distribution

3.2.1 Ray Tracing Emissive Emulsion Droplets

Ray tracing can be used to simulate how light will reflect and refract inside the bi-phase droplets in order to predict how their morphology will determine their emission properties. Ray tracing is only a first order approximation, as it doesn't take into account the effect of diffraction or interference. Diffraction particularly will play a role in smaller droplets, so we would expect the results to deviate for very tiny droplets (approximately less than $5\mu\text{m}$ wide).

In order to approximate a continuous fluorescing medium, a high density of randomly distributed rays were used, with randomly distributed starting directions. In 2D calculations, Matlab's `rand()` function was used to uniformly initialize starting coordinates (x, y) over the entire droplet area. If the initial coordinate (x, y) was located within the hydrocarbon phase, then a ray was propagated through the system by the ray tracing algorithm presented in Section 1.3.1 and Appendix B. Rays that intersected droplet interfaces more than 1000 times were eliminated (these rays are trapped within the droplet), as well as rays whose amplitude was less than 1% of the starting amplitude of the ray.

This ray tracing provides both spatial and angular distribution of the light exiting the droplets. In order to create an image of how the spatial light field around the droplets appears it is necessary to bin the rays spatially. For each pixel (unit of space) around the droplet, the intensities of all the rays passing through that pixel are summed together. This could, in principle, be done by looping through all the rays in the system and testing whether each strikes each pixel, however this would be computationally very expensive. A faster way of doing this is to divide the space into slices and then analytically determine where each ray would intersect each slice and bin accordingly. This is shown in Figure 3.3. The problem with this is that if the space is divided into vertical slices, and the ray of light is traveling in

Figure 3.3: Displaying ray tracing intensity near droplets. For horizontal rays, space is divided into vertical slices, while for vertical rays, the space is divided into horizontal slices. The red x's indicate the rays that are ignored when looking in each scenario. For more horizontally traveling rays, vertical slices are used, and vice versa. This ensures that no pixels are missed. The two intensity "images" are then added together.

a general vertical direction then some pixels are missed. This is easily overcome by separating rays into two categories (horizontally traveling rays and vertically traveling rays- each ray is only in one of these two categories ensuring no double counting occurs), calculating the intensity and then summing these two "images" back together. In 2D calculations, the angular distribution of the light can simply be binned by angle.

In 3D calculations, the density of starting rays was 20 million rays per unit volume. The units of the calculation were such that the droplet radius was 1. Matlab's `rand()` function was again used to initialize starting coordinates (x, y, z) within the volume of the hydrocarbon phase, as well as to initialize the starting direction (φ, θ) . In order to homogeneously distribute starting ray-directions in 3 dimensions, The polar coordinate was initialized by $\theta_i = \cos^{-1}(2p_i - 1)$ where p_i is uniformly distributed between 0 and 1 [72]. The azimuthal angle φ was initialized randomly between 0 and 2π . Due to the high computational time, only the angular

distribution was considered for the 3D calculations. Once the rays exited the droplet, their intensity was summed and binned according to their direction. Because the rays were binned by their solid angle, the intensity of each bin was corrected by $\sin \theta$.

3.2.2 Results

2D ray tracing reveals regions of high intensity near the three-phase contact line (Figure 3.4), consistent with the hypothesis that light undergoes total internal reflection along the droplet internal interface and then exits near the three-phase contact line. Similarly, there are peaks in the angular distribution corresponding to light undergoing TIR along the internal interface.

Figure 3.4: Ray tracing results in 2D. a-e) Spatial distribution of intensity of emitted light near the droplets calculated by ray tracing in 2D. There is enhanced emission near the three-phase contact line. In particular the droplet in (c) directs light vertically. **f)** Corresponding angular emission distributions for droplets in (a), (c), and (e).

For use as a transduction mechanism in a chemical or pathogen sensing scheme, the light is collected by an optical fiber positioned perpendicular to the droplet carpet, parallel to the symmetry axis of the droplets. This fiber collects light emitted from the droplets in a small angular range. The intensity of light collected by this fiber can be approximated by integrating the angular intensity distribution calculated from ray tracing from 0 to 5 degrees, the range over which the fiber can collect light. This intensity varies as a function of the droplet's three-phase contact angle (measured using the side-view microscope discussed in Section 1.4.1).

The dependence on contact angle (for droplets with a volume ratio of $v_r = 1$) is shown in the

Figure 3.5: Full angular emission distribution in 3D. a) Diagram showing that θ is measured from the vertical. b) Azimuthally averaged polar distribution of intensity. The arrows mark peaks that correspond with emission of TIR light. The highlighted region denotes the angular range collected by a vertically mounted fiber as shown in figure 3.6.

Figure 3.6: The L-curve. a) Diagram of fiber collection of light emitted vertically from droplets. b) Intensity measured normal to the droplet carpet as a function of droplet shape. The experimental data was measured by Lukas Zeininger.

'L-Curve' visualized in Figure 3.6. For double emulsions, most of the TIR light is directed towards the sides and misses the fiber. As the droplets open up, there is an initial decrease in collected intensity. In these geometries the distribution of emitted light is complicated due to the possibility of TIR occurring again along the water-hydrocarbon interface. As the droplets open up more, there is an increase in collected light as the TIR light is directed towards the fiber (the peak collection occurs for a contact angle near 25°). For contact

angle larger than this, the light begins to be directed more towards the sides of the droplets, missing the optical fiber.

3.2.3 Enhancing the Effect

Understanding that the largest change in emission intensity is due to total internal reflection along the internal interface allows us to enhance the effect. There are a number of ways that we can think of to reduce the amount of background fluorescence so that the emission that is responsive to changes in the droplet morphology is relatively stronger. One avenue to do this, is to change the refractive indices such that more light undergoes TIR and more light is directed towards the optical fiber. Another possible way of increasing the percentage of light undergoing TIR is limit the fluorphore to the region near the internal interface where TIR occurs. This could be accomplished by isolating the dye at the interface itself, or by introducing a third droplet phase that occupies the space above the interface, but does not contain any dye. This section explores these different possibilities through ray tracing. For each L-curve, the curve is normalized such that the intensity from the flat interface Janus droplet is 1.

Changes in Refractive Index

A simple way of enhancing the change in emission that occurs per change in droplet morphology is to adjust the refractive indices. Figure 3.7 shows the effect of adjusting the refractive index of the hydrocarbon phase. For a higher refractive index hydrocarbon phase, there is a greater difference in the collected emission as a function of droplet morphology. This can easily be attributed to an increase in the fraction of light that undergoes TIR. For the same reason, there is an increase in the emissive response for a *decrease* in refractive index of the fluorocarbon phase (Figure 3.8). Enhancing the refractive index contrast between the two oils results in an increase in the emissive response of the droplets as a function of droplet morphology.

Figure 3.7: Varying n_h . L-curve calculated from 2D raytracing for droplets with different refractive indices for the hydrocarbon phase. The refractive indices of the fluorocarbon and aqueous medium were held constant at $n_f = 1.29$ and $n_m = 1.33$ respectively.

Figure 3.8: Varying n_f . L-curve calculated from 2D raytracing for droplets with different refractive indices for the fluorocarbon phase. The refractive indices of the hydrocarbon and aqueous medium were held constant at $n_h = 1.49$ and $n_m = 1.33$ respectively.

The effect of changing the refractive index of the aqueous medium is shown in Figure 3.9. This shows that for a higher refractive index medium, there is *less* of a difference in emission as a function of droplet morphology. This is slightly counter-intuitive as one would expect that an increase in refractive index of the aqueous medium should result in greater out-coupling of the light from the high index hydrocarbon. However this does not appear to be the case. Likely what is happening in this scenario is that the transition from high refractive index hydrocarbon to lower refractive index water has a lensing effect that directs more light in the general vertical direction. This effect is smaller than changing the refractive index of either of the oils and so is probably not worth pursuing. It is easy to increase the refractive index of the water (This could be done by adding a higher refractive index material to the water solution, such as glucose) but it is a challenge to lower it.

Figure 3.9: Varying n_m . L-curve calculated from 2D raytracing for droplets with different refractive indices for the aqueous medium. The refractive indices of the fluorocarbon and hydrocarbon were held constant at $n_f = 1.29$ and $n_h = 1.49$ respectively.

Isolating Dye at Internal Interface

One way of increasing the percentage of light that undergoes TIR is to localize the dye to the region where TIR occurs, near the internal interface. For example, this could be done by binding the fluorophore to a surfactant or particle that sits at the interface. In Figure 3.10 the standard L-curve is compared with the case where the dye is isolated at the internal interface. This was approximated using ray tracing where the rays had random starting directions, but were only initiated with starting positions within 0.02 units of the internal interface, on both sides, ($R_d=1$ unit). These curves were normalized such that the flat Janus state (Contact angle = 90°) emission is equal to 1. This is very much only an approximation as diffraction effects are likely present in this scenario and cannot be captured with ray tracing. Still, this result shows that isolating the dye at the internal interface has the potential to dramatically increase the signal to noise ratio of these droplet sensors.

Figure 3.10: Dye isolated at internal interface. L-curve calculated from 2D raytracing for droplets with dye isolated at the interface as compared with dye throughout the hydrocarbon phase. The refractive indices were $n_h = 1.49$, $n_f = 1.29$ and $n_m = 1.33$. Both curves were normalized such that the emission from the flat janus droplet was equal to one.

Tri-Phase Droplets

Another potential way of cutting back on the amount of background emission that does not undergo TIR or is significantly affected by the changes in droplet morphology is to add a third droplet phase such that the light is only emitted from the middle phase. The spatial distribution of light from tri-phase droplets formed with refractive indices from top to bottom, $n_1 = 1.35$, $n_2 = 1.49$ and $n_3 = 1.29$ is shown in Figure 3.11.

Figure 3.11: Emission from tri-phase droplets Spatial distribution of intensity of emitted light near tri-phase droplets calculated by ray tracing in 2D. The refractive indices are $n_1 = 1.35$, $n_2 = 1.49$ and $n_3 = 1.29$, with the medium $n_m = 1.33$. The light is emitted from the middle phase (n_2).

Figure 3.12 shows a comparison between a tri-phase droplet with a similar morphology bi-phase droplet. There is a significant increase in the fraction of light that is effected by the droplets morphology. In this calculation, the shape of the third phase was kept constant, but it could of course also change with changes in the environment, which could change the optical response as well.

3.3 Summary and Applications

When a fluorescent dye is dispersed within the higher refractive index phase of the multi-phase droplets, a portion of the light emitted by the dye will undergo total internal reflection. The direction and quantity of light emitted in this way depends on the refractive indices and morphology of the droplet. When collecting the light from above the droplets, there is a morphology for which a peak amount of light will be collected, (contact angle $\theta_F \approx 25^\circ$), then as the droplets open up towards a flat Janus configuration the collected intensity decreases.

Figure 3.12: L-curve for tri-Phase droplets. Comparison between Tri-phase droplet where an extra phase with refractive index $n = 1.35$ has been added above the high index phase. The comparison bi-phase droplet had increased volume ratio ($v_r = 1.5$) in order to match tri-phase morphology.

The difference in intensity between the peak state and the flat Janus state can be increased by increasing the portion of light that undergoes TIR such as by increasing the refractive index contrast of the two oil phases or isolating the dye near the internal interface.

Lukas Zeininger along with others in Tim Swager’s group utilized these emissive droplets as sensors for food-borne pathogens. By developing boronic acid functionalized surfactants that could bind to mannose or anti-*Salmonella* Typhimurium IgG antibodies they created droplets that would change their configuration in the presence of *Salmonella enterica* serovar Typhimurium.

When there is no antibody or sugar present, these droplets were initialized to the configuration where the most light is directed towards the collection fiber ($\theta_F \approx 25^\circ$). Once the antibody or sugar is added, it binds to the boronic acid. This increases the effectiveness of the boronic acid as a surfactant (decreasing the interfacial tension between the hydrocarbon and the aqueous medium). The droplets then open up towards the flat Janus configura-

Figure 3.13: Pathogen sensing. **a)** Carbohydrates or antibodies bind to boronic acid surfactant, pushing droplets towards the Janus state. Bacteria take up the carbohydrate or antibody removing it from the droplets so that they return to partially closed state. **b)** Diagram of the L-curve. Droplets are initialized (1) with highest emission intensity; after addition of antibody or carbohydrate droplets open up and the amount of collected emission decreases (2), and then if salmonella remove the carbohydrates or antibodies droplets return to initial high emission state. **c)** Side-view micrographs of droplets in these states. **d)** Emission from droplets in the presence of heat killed salmonella. Recreated from [16]; this data and graphics were created by Lukas Zeininger.

tion, reducing the optical signal that the fiber detects. If the bacteria are present, they will pull the antibody (or sugar) from the boronic acid, pushing the emulsions back towards the partially closed configuration and increasing the optical signal. This sensing scheme could be extended to targeting other bacteria or biomacromolecules, multiplexed sensing assays, and the real-time monitoring of bacteria growth, and thereby could enable early detection of food-borne pathogens helping to reduce food poisoning around the world.

Chapter 4

Structural Color from Interference of Light Undergoing Total Internal Reflection at Concave Interfaces

4.1 Introduction

This chapter discusses how structural color can be generated from bi-phase droplets, an effect that actually extends to any concave interface under which multiple trajectories of Total Internal Reflection (TIR) can occur. The effect was first observed in Professor Lauren Zarzar's lab at Penn State. They noticed that under certain lighting conditions, monodisperse samples of certain bi-phase droplet morphologies would be colored, and that this color was iridescent (varied with the viewing angle) as shown in Figure 4.1.

The following discussion focuses on understanding why this coloration occurs and how it can be controlled. This research was done as a collaboration between the Laboratory for Bio-inspired Photonic Engineering here at MIT and the Zarzar group at Penn State. In particular, Amy Goodling, a Ph.D student working for Professor Zarzar conducted most of

Figure 4.1: Macro-scale color from monodisperse droplets. A sample of bi-phase emulsions with fixed illumination viewed from different azimuthal angles as shown in the diagram. Photographs by Amy Goodling

the experiments while Professor Kolle and I contributed the calculations and optical insights.

4.1.1 Experimental Observations

The initial macroscopic experimental observations told us a number of things. First, only mono-disperse droplet samples had pronounced color. Poly-disperse samples of droplets, with the same volume ratio and contact angle as the colored droplets, would have a glittery white appearance. The droplets that exhibit this effect are partially enclosed Janus droplets with the higher refractive index phase on the interior. The colors were only visible when a fairly collimated light was used to illuminate them. The observed colors vary with angle, and have a strong azimuthal dependence.

When viewed in an upright reflection microscope, as shown in Figure 4.2, the colors emanate from near the three-phase contact line. This suggests that the colored light is undergoing total internal reflection along the internal interface of the droplet, as shown in the diagram in

Figure 4.2b. This explains how the light is reflected strongly from the droplets, but doesn't explain why the color separation occurs.

Figure 4.2: Microscopic view of colored droplets. a) Color emanates from the edges of the droplets indicating that the reflected light is undergoing total internal reflection. b) Diagram of light being reflected along internal droplet interface by TIR.

In order to visualize the entire iridescence map at once, the Zarzar group used a hemispherical screen (half a ping-pong ball) to capture all of the scattered light from the droplets in a single measurement, an experimental setup conceptualized by Prof. Kolle and designed by the four of us. A diagram of this setup can be seen in Figure 4.3. A small hole in the ping-pong ball allows a collimated fiber light to illuminate the sample from a small angular range. The light that is reflected from the droplets then hits the translucent dome, scattering to the camera. This allowed the entire output angular color distribution to be captured in just a couple measurements. This same technique was also used to measure the optical characteristics of direct write colloidal structures [73]. The commercial version of a device to do these types of measurements is known as an Imaging Sphere.

Figure 4.3: Ping-pong ball to measure reflection distribution. Diagram showing how light reflected from the sample scatters off the translucent ping-pong ball. A small hole cut into the side allows collimated light to enter and hit the sample. The polar angle θ is measured from the sample normal, and the azimuthal angle φ is measured from the input illumination. Quantitative angular information can be captured from both top view and side-view images of the ping-pong ball scatterogram.

4.1.2 Overview of the Color Generation Mechanism

There are a variety of different physical processes that lead to color. Dyes and pigments produce color by absorbing some parts of the electromagnetic spectrum more strongly than others [74, 75]. Rainbows from water droplets in the atmosphere and from prisms arise due to color separation from refraction at an interface with material dispersion [76]. Plasmonics creates color from interactions between photons and electron resonances in conductive materials, such as gold nano-particles [77]. Structural color [78, 79] occurs when nano-scale periodicity causes interference of light, such as in peacock feathers, butterfly wings, and opals [80, 81, 82].

As there are no dyes, pigments, or plasmonic materials present in the emulsion droplets, nor a nanoscale periodicity, the first hypothesis was that the color arises from material dispersion, much like atmospheric rainbows. The wavelength dependence of the refractive index would cause different colors of light to be refracted differently through the top interface of the droplet. Ray tracing calculations taking into account material dispersion however did not produce the color separation observed in the droplets, even when a non-spherical interface

shape is considered, as shown in Figure 4.4. Moreover, the color effect can be seen in other microscale concave structures such as printed domes and pendant water drops as shown in Figure 4.5.

Figure 4.4: Color is not from material dispersion. a) Refractive index variation as a function of wavelength for the droplet components. b) 3D ray tracing diagram of light undergoing TIR in the droplets. c) Calculated color distribution due to material dispersion- only a small amount of blue coloration occurs. d) Experimental color distribution for a similar droplet geometry and illumination.

Figure 4.5: TIR color in other concave microscale structures. a) microscale domes created with multiphoton near-IR direct laser writing. SEM image and corresponding macroscale color. b) Pendant water droplet coalescing on a polystyrene petri-dish lid (inset scale bar: 1 cm) and upright microscope reflection image of similar water droplets showing the same colorful rings seen in bi-phase emulsions. Scale bar 200 μm . These structures and images were created by Amy Goodling and Lauren Zarzar.

This left us back with structural color caused by interference. While there is no nano-scale periodicity in the geometry, it is possible for light to take different paths through the structure and interfere as shown in Figure 4.6. When light travels along each of these different trajectories through the concave structure, it will acquire a phase shift that depends on the distance traveled, as well as the shift upon each reflection. For a given input and output

Figure 4.6: Cascading TIR interference Diagram showing different possible trajectories of light along the concave interface of a sessile drop or printed dome structure for a fixed input and output angle. The number of bounces is denoted by m . The interference of these different paths leads to the color.

direction, the intensity spectrum will be the squared magnitude of the coherent sum of the complex amplitudes of light waves propagating along the different possible trajectories.

$$I = \left| \sum_{m_{\min}}^{m_{\max}} A_m \exp \left(i \frac{2\pi n_1}{\lambda_0} l_m \right) r^m \right|^2 \quad (4.1)$$

In this equation, the summation index m is the number of bounces for each trajectory. The bounds are set geometric constraints on how light can enter and exit the droplet and for which trajectories TIR can occur. A_m is an amplitude scaling factor, derived from conservation of energy, l_m is the physical path length of each trajectory, and r_m is the complex Fresnel coefficient, which depends on the local angle of incidence, the refractive index contrast of the interface, and the polarization and effects a phase shift upon each reflection. The phase shift acquired due to the propagation of light will depend on the wavelength of the light so that constructive interference will differ for different wavelengths, resulting in the colors observed from specific directions.

Section 4.2 derives each of the quantities in Equation 4.1 and compares the calculated color patterns with a experimental results obtained from a 3D printed cylindral microstructure.

Section 4.3 extends this sum to three dimensions and Section 4.4 presents the results of the full model and compares them with the color distributions of partially index-matched bi-phase droplets. Section 4.5 presents applications of this color generation mechanism, in particular in sensing scenarios.

4.2 Theoretical Color Separation in Two Dimensions

4.2.1 Interfering Light Trajectories

In order to model the color seen from the droplets or concave cavities, we first restrict the calculation to a single input illumination direction θ_{in} and output observation direction θ_{out} along a circular (2D) interface. The first step is to determine all the possible trajectories with these input and output angles. Consider a ray of light traveling at a global input angle θ_{in} and striking a curved interface at local incidence angle α as shown in Figure 4.7. Since the angle of incidence equals the angle of reflection, the reflected ray will effectively be rotated by an angle $\pi - 2\alpha$. This happens for each reflection so that after m reflections the ray has been rotated by the amount of $m(\pi - 2\alpha)$. This means that the direction of the outgoing ray is given by:

$$\pi + \theta_{\text{out}} = \theta_{\text{in}} + m(\pi - 2\alpha). \quad (4.2)$$

This equation represents a constraint between θ_{in} , θ_{out} , m , and α . Not every pair of m and α are possible for a given set of input and output angles $(\theta_{\text{in}}, \theta_{\text{out}})$. In fact, we can determine a minimum number of bounces (m_{min}) for which total internal reflection can occur, and a maximum number of bounces m_{max} that the geometry allows.

If we wish to consider only the rays that undergo TIR, then m_{min} is set by the critical angle of incidence, $\alpha_c = \sin^{-1} \left(\frac{n_2}{n_1} \right)$, and found from Equation 4.2:

Figure 4.7: Angle diagram. a) Diagram of relationship between local incidence angle α , and global incidence and exit angle θ_{in} and θ_{out} . **b)** Diagram showing the two directions of propagation along the interface, with the same input and output angles.

$$m_{\min} = \left\lceil \frac{-\theta_{\text{in}} + \theta_{\text{out}} + \pi}{\left(\pi - 2 \sin^{-1} \left(\frac{n_2}{n_1}\right)\right)} \right\rceil \quad (4.3)$$

The maximum number of bounces can be calculated by considering the limiting case where rays either strike at the contact line, or just pass by it, as shown in Figure 4.8, which gives

$$\alpha_{\max \text{ in}} = \frac{\pi}{2} - \left| \frac{\pi}{2} - (\eta + \theta_{\text{in}}) \right|. \quad (4.4)$$

This is the maximum possible local angle of incidence for this illumination angle. Similarly, there is a maximum local angle of incidence that can be seen by an observer at θ_{out} given by

$$\alpha_{\max \text{ out}} = \frac{\pi}{2} - \left| \frac{\pi}{2} - (\eta - \theta_{\text{out}}) \right| \quad (4.5)$$

Of these two limiting angles the smaller one puts a limit on the maximum local angle of

Figure 4.8: Limiting local angle of incidence.

incidence, giving

$$\alpha_{\max} = \min \left(\frac{\pi}{2} - \left| \frac{\pi}{2} - (\eta + \theta_{\text{in}}) \right|, \frac{\pi}{2} - \left| \frac{\pi}{2} - (\eta - \theta_{\text{out}}) \right| \right). \quad (4.6)$$

Using Equation 4.2 this sets a limit on the maximum number of bounces that can occur:

$$m_{\max} = \left\lfloor \frac{\theta_{\text{out}} - \theta_{\text{in}} + \pi}{(\pi - 2\alpha_{\max})} \right\rfloor \quad (4.7)$$

For each of the allowed trajectories with number of reflections between $m_{\min}$ and $m_{\max}$ we need to determine the optical path length. Any two planes perpendicular to the incoming and outgoing rays could be used, but the most convenient planes are those that include the center of curvature of the interface, as shown in Figure 4.9. From these planes, the physical path length of each trajectory is simply given by

$$l_m = 2mR \cos(\alpha). \quad (4.8)$$

The other piece of information needed to determine the total phase change for each trajectory

Figure 4.9: Diagram of optical path length through concave structure with radius R . When calculating optical path lengths for interference, the distance must be calculated from planes perpendicular to the rays' direction (any of the dashed lines for example); convenient planes to use are those that also include the center of curvature (shown in green). It is straightforward to see geometrically that the distance between the input plane and the first bounce is $R \cos(\alpha)$. The distance between bounces is $2R \cos(\alpha)$, and the distance from the last bounce to the final plane is $R \cos(\alpha)$. This means the total physical path length through the drop from input plane to output plane is: $l = R \cos(\alpha) + (M-1)2R \cos(\alpha) + R \cos(\alpha) = 2MR \cos(\alpha)$.

is the phase change upon each reflection, given by the complex Fresnel reflection coefficients:

$$r_s = \frac{n_1 \cos(\alpha) - in_2 \sqrt{\left(\frac{n_1}{n_2} \sin(\alpha)\right)^2 - 1}}{n_1 \cos(\alpha) + in_2 \sqrt{\left(\frac{n_1}{n_2} \sin(\alpha)\right)^2 - 1}}$$

$$r_p = \frac{n_2 \cos(\alpha) - in_1 \sqrt{\left(\frac{n_1}{n_2} \sin(\alpha)\right)^2 - 1}}{n_2 \cos(\alpha) + in_1 \sqrt{\left(\frac{n_1}{n_2} \sin(\alpha)\right)^2 - 1}}$$

The subscript s and p represent TE and TM polarization respectively. The complex amplitude change of a ray incident at θ_{in} that undergoes m bounces before leaving in the direction of θ_{out} is

$$C_{m,s,p}(\theta_{\text{in}}, \theta_{\text{out}}) = r_{s,p}^m \exp\left(i \frac{2\pi n_1}{\lambda_0} l_m\right) \quad (4.9)$$

The total intensity is the coherent sum of all of these different trajectories, given by

$$I_{\text{total}} = \left| \sum_{m_{\min}}^{m_{\max}} \sqrt{\frac{\cos(\alpha_m)}{m}} \exp\left(i \frac{2\pi n_1}{\lambda_0} 2Rm \cos(\alpha_m)\right) r_{s,p}^m \right|^2 \quad (4.10)$$

Here, $\sqrt{\frac{\cos(\alpha_m)}{m}}$ is an amplitude scaling factor derived from energy conservation in the section 4.2.2.

The effect of polarization is small (see Figure 4.10) and so we can just consider unpolarized light (treat each trajectory as 50% TE and 50% TM and average). From here on, the s and p subscripts are dropped.

Figure 4.10: Effect of polarization. Comparison of polarization states for index-matched droplet parameters $R = 25\mu\text{m}$, $\eta = 71^\circ$, $\theta_{\text{in}} = 21.41^\circ$, $\varphi_{\text{out}} = 180^\circ$, $n_1 = 1.37$, and $n_2 = 1.27$. The difference is calculated from the intensity $|I_s - I_p|$ then converted to color.

This captures all of the trajectories propagating along the interface from left to right, however it is also possible for light to propagate along the interface in the opposite direction for the same angle pair as shown in Figure 4.7b. This light can be represented in the model by accounting for the same pair of incidence and exit angles in reverse ($-\theta_{\text{in}}$, $-\theta_{\text{out}}$). This light exits at a distance farther than the coherence length of white light (light source dependent,

but generally on the order of several micrometers) from the light propagating in the other direction. Therefore, we do not expect interference between these two sets of trajectories and consequently treat these two sets of paths as adding up incoherently:

$$I = \left| \sum_{m_{+min}}^{m_{+max}} \sqrt{\frac{\cos(\alpha_{m+})}{m}} \exp\left(i \frac{2\pi n_1}{\lambda_0} 2Rm \cos(\alpha_{m+})\right) r_{+}^m \right|^2 + \left| \sum_{m_{-min}}^{m_{-max}} \sqrt{\frac{\cos(\alpha_{m-})}{m}} \exp\left(i \frac{2\pi n_1}{\lambda_0} 2Rm \cos(\alpha_{m-})\right) r_{-}^m \right|^2 \quad (4.11)$$

with $\alpha_{m\pm} = \frac{\pi}{2} - \frac{\pi \pm (\theta_{out} - \theta_{in})}{2m}$.

This sum represents the full spectrum expected for a given pair of input and output angles $(\theta_{in}, \theta_{out})$ in two dimensions.

4.2.2 Amplitude Scaling Factor: Conservation of Energy

The spectrum seen for a given input and output angle pair is the sum over all the possible trajectories between those angles, however each trajectory does not contribute equally. This can be seen intuitively in Figure 4.11a. A bundle of rays that undergoes a smaller number of reflections is far less spread out than a bundle undergoing a large number of reflections. Since the ingoing intensity for each bundle is equal, the outgoing intensity for any given single output angle must be smaller for the bundle that is more spread out. This can be quantified by considering conservation of energy. First, assume that the intensity across the incoming beam is constant (i.e. a plane wave):

$$I(a) = constant \equiv I_0. \quad (4.12)$$

Here, a is a parameter describing the location along the input beam as shown in Figure

Figure 4.11: Diagram of ray bundle spread. **a**, 10 evenly spaced rays that undergo 2 bounces (red) and 6 bounces (blue). The rays that underwent 6 bounces are far more spread out. **b**, Diagram of relevant quantities in deriving this spread; a is a parameter describing a point along the wavefront, x_{in} is the point along the substrate where the light enters the dome and d is the distance from the center of curvature to the interface between the substrate and the dome.

4.11b. The parameter a is related to the distance along the top of the dome x_{in} where the light enters by:

$$x_{\text{in}} = a \cos(\theta_{\text{in}}) \quad (4.13)$$

The intensity as a function of the parameter x_{in} is also constant. If we consider a small area dx the power entering the structure in this area is

$$dP = \cos(\theta_{\text{in}}) I_0 dx \quad (4.14)$$

The light will spread as it bounces along the internal interface, so that this power will be spread over an area $d\theta_{\text{out}}$. The outgoing radiant intensity I_m for trajectory (labeled by m) is:

$$dP = I_m d\theta_{\text{out}} \quad (4.15)$$

Since the power is conserved, this means that the relative radiant intensity is:

$$I_m = \cos(\theta_{\text{in}}) I_0 \frac{dx}{d\theta_{\text{out}}} \quad (4.16)$$

In order to determine $\frac{dx}{d\theta_{\text{out}}}$, note that the outgoing angle (see Equation 4.2) is given by

$$\theta_{\text{out}} = \theta_{\text{in}} - \pi + m(\pi - 2\alpha) \Rightarrow d\theta_{\text{out}} = -2m d\alpha. \quad (4.17)$$

And the local angle of incidence in terms of the position x_{in} is:

$$\sin(\alpha) = \frac{x_{\text{in}}}{R} \cos(\theta_{\text{in}}) + \cos(\eta) \sin(\theta_{\text{in}}) \Rightarrow d\alpha \cos(\alpha) = \frac{dx_{\text{in}}}{R} \cos(\theta_{\text{in}}). \quad (4.18)$$

Putting these together gives

$$\frac{dx_{\text{in}}}{d\theta_{\text{out}}} = \frac{dx_{\text{in}}}{d\alpha} \frac{d\alpha}{d\theta_{\text{out}}} = -\frac{\cos(\alpha)}{2m \cos(\theta_{\text{in}}) R}. \quad (4.19)$$

Plugging this into Equation 4.16 gives a relative radiant intensity for each trajectory:

$$I_m = I_0 \frac{\cos(\alpha_m)}{2mR}. \quad (4.20)$$

The factor $\frac{I_0}{2R}$ is the same for every term in the summation, and so can be absorbed into a single constant factor that we can set to 1. This yields the relative *amplitude* scaling factor of

$$A_m = \sqrt{\frac{\cos(\alpha_m)}{m}}. \quad (4.21)$$

4.2.3 Converting Spectra to Color

Equation 4.11 gives us a spectra for each illumination and viewing angle pair. In order to convert these spectra to the colors that would be seen by the human eye, the tristimulus values are calculated to give the corresponding coordinates in the CIE xyz color space. These tristimulus values are obtained by multiplying the spectra by each of the CIE standard color matching functions ($\bar{x}(\lambda)$, $\bar{y}(\lambda)$, $\bar{z}(\lambda)$) and integrating over the visible wavelength range

[83].

$$X = \int_{\lambda} I(\lambda) \bar{x}(\lambda) d\lambda, \quad Y = \int_{\lambda} I(\lambda) \bar{y}(\lambda) d\lambda, \quad Z = \int_{\lambda} I(\lambda) \bar{z}(\lambda) d\lambda.$$

For displaying the data on screen and for printing, we convert xyz color values to sRGB values. First, the linear RGB coordinates are found from [84]

$$\begin{pmatrix} R_{\text{lin}} \\ G_{\text{lin}} \\ B_{\text{lin}} \end{pmatrix} = \begin{pmatrix} 3.2404542 & -1.5371385 & -0.4985314 \\ -0.9692660 & 1.8760108 & 0.0415560 \\ 0.0556434 & -0.2040259 & 1.0572252 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}, \quad (4.22)$$

then the values are gamma-corrected using the formula

$$C = \left\{ \begin{array}{c|c} 12.92C_{\text{lin}} & C_{\text{lin}} < 0.0031308 \\ 1.055 * C_{\text{lin}}^{\frac{1}{2.4}} - 0.055 & \text{otherwise} \end{array} \right\}, \quad (4.23)$$

where C is each of the RGB triplet.

4.2.4 Experimental Comparison

Quantitative Ping-Pong Ball Angle Measurements

In order to compare the model and the experimental results, it is useful to quantitatively determine the scattering angles from the ping-pong ball color maps. From a top view image it is straightforward to quantitatively map image pixels to light reflection angles (θ, φ) . The pixel coordinates (x, y) are measured from the center of the hemispherical screen (found by manually fitting a circle to the edges of the ping-pong ball in ImageJ). The relation between image coordinates and light reflection angles is given by $(x, y) = (R_p \cos(\varphi) \sin(\theta), R_p \sin(\varphi) \sin(\theta))$, where R_p is the radius of the ping-pong ball, in pixels.

Unfortunately, the top view of the hemispherical screen does not always capture all of the

information for wide reflection angles, particularly when the illumination near $\theta_{\text{in}} = 0$ and the illumination fiber is in the way of the image. Due to the ping-pong ball screen being translucent, light scattering from the underlying petri dish surface can sometimes be seen through the screen, so the most direct spot between the sample and the camera is also slightly obscured. For these reasons, we found imaging at side angles often gave the most reliable colors. We define the viewing direction of the camera as $(\theta_{\text{cam}}, \varphi_{\text{cam}})$. Mapping back from this view can be done with a coordinate transformation. First, we define a new pair of angles (Δ, γ) measured from the camera to sample axis as shown in Figure 4.12. As before, the image pixel locations corresponding to these angles are

$$(x, y) = (R_p \cos(\gamma) \sin(\Delta), R_p \sin(\gamma) \sin(\Delta)). \quad (4.24)$$

Figure 4.12: Camera angle. Global coordinate system shown as well as the projected system, when imaged at an angle. Δ is the angle measured from the camera axis, and γ is the azimuthal angle in this rotated coordinate system. By converting from (Δ, γ) coordinates to the global (θ, φ) coordinates, we can quantitatively determine the angle to which each color is scattered from photographs taken at an angle.

In order to determine (Δ, γ) in terms of (θ, φ) , consider a point on the surface of the

ping-pong ball in 3D:

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} \cos(\varphi) \sin(\theta) \\ \sin(\varphi) \sin(\theta) \\ \cos(\theta) \end{pmatrix}. \quad (4.25)$$

We then rotate these coordinates first by φ_{cam} around the Z-axis then by θ_{cam} around the Y-axis to get new coordinates corresponding to the coordinate system of the camera:

$$\begin{pmatrix} X' \\ Y' \\ Z' \end{pmatrix} = \begin{pmatrix} \cos(\theta_{\text{cam}}) & 0 & \sin(\theta_{\text{cam}}) \\ 0 & 1 & 0 \\ -\sin(\theta_{\text{cam}}) & 0 & \cos(\theta_{\text{cam}}) \end{pmatrix} \begin{pmatrix} \cos(\varphi_{\text{cam}}) & -\sin(\varphi_{\text{cam}}) & 0 \\ \sin(\varphi_{\text{cam}}) & \cos(\varphi_{\text{cam}}) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} \quad (4.26)$$

The angles (Δ, γ) are related to these coordinates by:

$$\gamma = \tan^{-1} \left(\frac{Y'}{X'} \right), \quad \Delta = \cos^{-1}(Z') \quad (4.27)$$

which we then use to find the pixel (x, y) corresponding to each value of (θ, φ) .

2D Model and Experimental Comparison

For comparison with the 2D model, we simplified the experimental system to cylindrical segments. Provided the incident light direction is perpendicular to the cylinder symmetry axis, the reflected rays are expected to all lie within the plane perpendicular to that axis (Figure 4.13a), so that the 2D model should apply. Prof. Zarzar and Amy Goodling printed arrays of cylindrical segments (Figure 4.13b) using multiphoton near-IR direct laser writing and applied the ping-pong ball scattering measurement again to this system (Figure 4.13c). Since there is some divergence in the input beam, the model was averaged over a five degree input cone and the spectrum for the illumination was multiplied with the spectra calculated from Equation 4.11.

Figure 4.13: Comparison of 2D model with 3D printed cylindrical segments. **a)** Scanning Electron Micro-graph of cylindrical dome structure. The higher-magnification image shows the cylindrical edge (scale bar, 20 μm) and the lower-magnification inset shows a portion of the structure array (scale bar, 200 μm). **b)** Diagram of horizontal cylindrical segments with η , the contact angle, defined. **c)** Ping-pong ball image with lines of constant θ overlaid. **d)** Comparison of TIR interference model and experiment. The experimental color bar was unwrapped from c, as described in the previous section. Lithography printed cylindrical dome array was fabricated by Bryan Kaehr and SEM and ping-pong ball images were taken by Amy Goodling.

4.3 Extension to Three Dimensions

The model presented in Section 4.2 can be generalized to 3D by taking into account that each light trajectory along a concave spherical surface lies in a plane that contains the incident ray, the exiting ray, and the center of curvature of the interface. This allows the problem to be treated in a similar way to the 2D case, once the orientation of this plane and the relevant angles within it are known. Without any loss of generality, we may represent the incoming ray as

$$\vec{R}_{\text{in}} = -(\sin(\theta_{\text{in}}), 0, \cos(\theta_{\text{in}})),$$

where we have assumed an azimuthal angle $\varphi_{\text{in}} = 0$, and the outgoing ray as

$$\vec{R}_{\text{out}} = (\sin(\theta_{\text{out}}) \cos(\varphi_{\text{out}}), \sin(\theta_{\text{out}}) \sin(\varphi_{\text{out}}), \cos \theta_{\text{out}}).$$

The plane containing both rays will also contain the center of curvature of the spherical interface, as shown in Figure 4.14. Analogously to the angular difference between θ_{in} and θ_{out} in the 2D case, we define an angle ψ which is the difference in angle between these two rays. In terms of the global coordinates ψ is given by

$$\cos(\psi) = -\vec{R}_{\text{in}} \cdot \vec{R}_{\text{out}} = \sin(\theta_{\text{out}}) \sin(\theta_{\text{in}}) \cos(\varphi_{\text{out}}) + \cos(\theta_{\text{in}}) \cos(\theta_{\text{out}}). \quad (4.28)$$

Figure 4.14: Diagram showing 3D coordinate system. a) The equivalent 2D coordinate system is shown. b) Several different planes of incidence are shown with the corresponding effective opening angle η_{eff} .

In analogy with Equation 4.2, the relationship between the local angle of incidence, the number of bounces, and ψ is

$$\pi - \psi = m(\pi - 2\alpha). \quad (4.29)$$

We also need to determine the allowed trajectories in the summation, ie m_{min} and m_{max} . All of the reflections take place in the plane containing the input and output ray, which is

defined by the unit normal

$$\vec{n} = \frac{\vec{R}_{\text{in}} \times \vec{R}_{\text{out}}}{\sin(\psi)} = \frac{1}{\sin(\psi)} \begin{pmatrix} -\cos(\theta_{\text{in}}) \sin(\theta_{\text{out}}) \sin(\varphi_{\text{out}}) \\ \cos(\theta_{\text{in}}) \sin(\theta_{\text{out}}) \cos(\varphi_{\text{out}}) - \sin(\theta_{\text{in}}) \cos(\theta_{\text{out}}) \\ \sin(\theta_{\text{in}}) \sin(\theta_{\text{out}}) \sin(\varphi_{\text{out}}) \end{pmatrix}, \quad (4.30)$$

where the $\sin(\psi)$ factor is the normalization to obtain a unit vector $\vec{n}$. We now need to find the effective incidence angle β_{in} , the effective exit angle β_{out} , and the effective contact angle η_{eff} within this plane. In this plane, we define the basis $(\vec{u}, \vec{v})$ such that $\vec{u}$ is parallel to the global surface (i.e. horizontal) and perpendicular to $\vec{n}$, and $\vec{v}$ is perpendicular to both $\vec{u}$ and $\vec{n}$ (see Figure 4.14). Expressed mathematically this gives

$$\vec{u} = B(\vec{n} \times \hat{z}) = B \begin{pmatrix} n_y \\ -n_x \\ 0 \end{pmatrix}, \quad (4.31)$$

where B is a normalization factor

$$B = \frac{1}{\sqrt{n_x^2 + n_y^2}} = \frac{1}{\sqrt{1 - n_z^2}} = \frac{|\sin(\psi)|}{\sqrt{\sin^2(\psi) - \sin^2(\theta_{\text{in}}) \sin^2(\theta_{\text{out}}) \sin^2(\varphi_{\text{out}})}}. \quad (4.32)$$

and

$$\vec{v} = \vec{n} \times \vec{u} = B \vec{n} \times (\vec{n} \times \hat{z}) = B((\vec{n} \cdot \hat{z}) \vec{n} - \hat{z}). \quad (4.33)$$

In this coordinate system, we can determine the effective angle of the incoming ray to be:

$$\cos(\beta_{\text{in}}) = \vec{v} \cdot \vec{R}_{\text{in}} = B((\vec{n} \cdot \hat{z}) \vec{n} \cdot \vec{R}_{\text{in}} - \hat{z} \cdot \vec{R}_{\text{in}}) = B \cos \theta_{\text{in}}. \quad (4.34)$$

and the outgoing effective angle θ_{out} :

$$\cos(\beta_{\text{out}}) = \vec{v} \cdot \vec{R}_{\text{out}} = B((\vec{n} \cdot \hat{z}) \vec{n} \cdot \vec{R}_{\text{out}} - \hat{z} \cdot \vec{R}_{\text{out}}) = -B \cos(\theta_{\text{out}}). \quad (4.35)$$

We also need a measure of the arc length of the spherical interface in the ray propagation plane; in analogy with the 2D case, we will use an effective contact angle (η_{eff}), given by

$$\cos(\eta_{\text{eff}}) = B \cos(\eta). \quad (4.36)$$

It should be noted that η is the contact angle measured from a flat surface, such as in the case of the sessile drops or the printed domes and cylinders. In the case of the index- matched drops this is NOT the contact angle between the various liquid phases, but can better be thought of as the opening angle.

Similarly to equation 4.6 and the maximum possible local angle of incidence is then

$$\alpha_{\text{max}} = \min \left(\frac{\pi}{2} - \left| \frac{\pi}{2} - (\eta_{\text{eff}} + \beta_{\text{in}}) \right|, \frac{\pi}{2} - \left| \frac{\pi}{2} - (\eta_{\text{eff}} - \beta_{\text{out}}) \right| \right) \quad (4.37)$$

and the maximum number of reflections is given by

$$m_{\text{max}} = \left\lfloor \frac{\pi - \psi}{(\pi - 2\alpha_{\text{max}})} \right\rfloor. \quad (4.38)$$

With all of these equivalent values determined, the intensity that results from interference of all the possible ray trajectories for light entering along $\vec{R}_{\text{in}}$ and leaving along $\vec{R}_{\text{out}}$ is then given by the sum of the trajectories' complex amplitudes derived for the 2D case (Equation 4.11), provided that the effective incidence and exit angles β_{in} , and β_{out} , and the effective opening angle η_{eff} are used.

4.4 Results and Comparison to Experiments

From the 3D model, theoretical angular color distribution maps were created from the calculated intensities $I(\lambda, \theta_{\text{out}}, \varphi_{\text{out}})$. The spectra were converted to an sRGB image with axes $(\theta_{\text{out}}, \varphi_{\text{out}})$, as shown in Figure 4.15. In order to visualize the data in a manner similar

to the ping-pong ball projections, an image transformation was applied; the (x, y) coordinates of this image (measured from the center) relate to the direction of observation via the equations $x = k \sin(\theta_{\text{out}}) \cos(\varphi_{\text{out}})$ and $y = k \sin(\theta_{\text{out}}) \sin(\varphi_{\text{out}})$ where k is an arbitrary scaling factor to set the image size. Nearest neighbor pixels were pulled from the $(\theta_{\text{out}}, \varphi_{\text{out}})$ image for each (x, y) pixel in the final images.

Figure 4.15: Simulation data representation. The color is calculated for $(\theta_{\text{out}}, \varphi_{\text{out}})$. This is then converted to coordinates matching the ping-pong ball projection.

In order to validate the model, we compared its results with experimental results obtained with bi-phase droplets. The aqueous medium was index-matched to the heptane droplet phase, allowing us to disregard refraction at the droplets' curved upper interface. We compared our theoretical and experimental results for a number of droplet sizes (Figure 4.16a), illumination conditions (Figure 4.16b), and droplet shapes (Figure 4.16c) and found close agreement. These results match well and suggest that we should be able to design specific, desired structural color patterns and fabricate the required surface to generate the predicted iridescence.

Figure 4.16: Comparison of 3D model with index-matched bi-phase droplets. a) Effect of size (radius of curvature) where the contact angle and illumination were fixed at $\eta = 71^\circ$ and $\theta_L = 30^\circ$ respectively. b) Effect of illumination angle (using the same droplet sample as in a(i)). c) Effect of droplet morphology ($\theta_L = 30^\circ$). Scale bars in a and c: $50 \mu\text{m}$. Droplets, droplet images, and ping-pong ball color distributions were created by Amy Goodling.

We also compared the reflection spectra from micro-replicated polymer dome structures in water with the modeled spectra as shown in Figure 4.17. The shape and location of these curves are in close agreement, with a small peak in the shorter wavelength range and larger peak at longer wavelengths both of which blue shift as the azimuthal angle increases.

The three-dimensional model can be used to better understand how various geometrical and material-specific parameters affect the color distribution. The total phase change for a given path, and thus the interference condition, depends on the product $n_1 R$ in the optical path length and the refractive index contrast in the Fresnel coefficient $r_m(\alpha_m, \frac{n_1}{n_2})$. The allowed trajectories for a given $(\theta_{\text{in}}, \theta_{\text{out}})$ are set by the opening angle η as well as illumination and observation directions. Figure 4.18 show how each of these parameters affects the colors observed as a function of observation direction θ_{out} for the azimuthal angle $\varphi_{\text{out}} = 180^\circ$. Figure 4.18a shows that as the radius of curvature R increases, the color patterns shift to

Figure 4.17: Spectral comparison of 3D model with replicated dome structures. a) Ping-pong ball image and b) experimental spectra of dome structures. c) Model color distribution and d) spectra. The radius of curvature of the domes and model was $18.2 \mu\text{m}$ with refractive index $n_1 = 1.495$ in water ($n_2 = 1.33$), and opening angle $\eta = 70^\circ$. The *s on the color distributions represent the direction the spectra were taken from. e) The same curves as in b and d, showing that there is a good match between theory and experiment. Dome structures and ping-pong ball image created by Amy Goodling.

larger angles and the spread of colors decreases, consistent with experimental observations. The angular location of the color bands varies almost linearly with the illumination direction

θ_{in} . This can be understood by interpreting a change in illumination angle θ_{in} as a rotation of all ray paths around the center of curvature of the interface. Once rotated too far, a ray trajectory may no longer be available, which is evident in the sharp changes in color in Figure 4.18b. The opening angle, η , does not affect the phase of the light; consequently, the locations of the color bands are constant as η is varied. However, whether a specific trajectory is possible strongly depends on η (Figure 4.18c). Regions of grey indicate that only one possible trajectory exists and thus there is no interference that could lead to color. The effect of the refractive index contrast can be seen by adjusting n_2 (Figure 4.18d). The sharp change in colors as n_2 decreases corresponds to where TIR begins to occur for another trajectory. In reality, these separation lines are likely smoother than shown here, as we have not included light that is reflected with high amplitude but below the critical angle.

Figure 4.18: Parameters that affect colors observed from cascading interference TIR. The color distribution as a function of θ_{out} when changing: **a)** the radius of curvature, **b)** the illumination direction within the medium (θ_{in}) with refractive index n_1 , **c)** the opening angle η , and **d)** the refractive index of the fluorocarbon phase, n_2 . The default parameters used were $R = 25\mu\text{m}$, $\eta = 71^\circ$, $\theta_{\text{in}} = 21.4^\circ$, $n_1 = 1.37$ and $n_2 = 1.27$, and one parameter at a time was varied. These results for θ_{in} and θ_{out} in the index-matched medium are related to the measured angles by Snell's law.

4.5 Towards Droplet Color Sensors

From these results, it is natural to consider using the color of the droplets as a sensor similarly to the emissive droplets. This section discusses initial calculations for this goal, including predicting the color variation as a droplet changes morphology and taking into account the top droplet interface in color calculations.

4.5.1 Color as a Function of Droplet Morphology

So far we have modeled the expected color of the droplets with only geometric parameters of opening angle, η , and radius of curvature R_i . If we wish to consider how a single sample of bi-phase droplets color changes as the interfacial tensions change in order to induce a color response as a sensor, then we would want to know how the color changes as the droplets change shape. Before considering how the color changes, we first need to determine how the changes in interfacial tension change the internal radius of curvature and opening angle. While both η and R_i change, for a given droplet radius, R_d and volume ratio, v_r , there is only one possible value of η for each value of R_i , so that the first step in understanding how changing interfacial tension strength changes the expected color is to determine $\eta(R_i)$ for a fixed droplet radius and volume ratio.

In order to do this, we will first use the simplifying assumption that the overall droplet shape is spherical¹. This is generally true when the interfacial tension between the two phases is significantly lower than the interfacial tensions with the surrounding medium, that is to say $\gamma_{HF} \ll \gamma_H, \gamma_F$. Under this assumption, the relationship between the internal radius of curvature, R_i , the overall droplet radius, R_d , the distance between the center of curvature of the interface and the droplet center, d , and the volume ratio ($v_r = \frac{v_H}{v_F}$) is given by Equation 1.1:

$$(d + R_d - R_i)^2(d^2 + 2d(R_i - R_d) - 3(R_d + R_i)^2) + 16d\frac{R_d^3}{1 + v_r} = 0.$$

¹Given the sensitivity of color to small changes in morphology, probably this assumption is not fully valid for all morphologies, and may result in errors.

These parameters can be seen geometrically in Figure 4.19. Similarly, the relationship between the opening angle η and the other geometry parameters is:

$$\cos(\eta) = \frac{d^2 - R_d^2 + R_i^2}{2dR_i} \quad (4.39)$$

Figure 4.19: Geometric parameters for color in droplets. Diagram showing droplet parameters (R_i, R_d, d) with color calculation parameters (R_i, η) .

For a given droplet, the droplet radius and the volume ratio are fixed, whereas the internal radius of curvature and the opening angle can vary. The goal then is to find a relationship between the opening angle and the internal radius of curvature. This can be done by eliminating d from the above equations numerically. Figure 4.20 shows several possible paths through the η, R_i space. Along each line, the volume ratio and the droplet size is fixed and morphology is varied (for example by changing interfacial tensions). Varying the volume ratio changes the curvature of the path, and changing the overall droplet size of course just shifts the path to the right or left.

From the morphology, we would like to know how the color varies for a given illumination and viewing direction. Using the ping-pong ball type mapping, we could see the color distribution for all angles, if we instead fix the viewing direction, we can then map in 2D all the possible colors that could be seen for that viewing and illumination pair. Figure 4.21 shows this color

Figure 4.20: Droplet geometry parameter trajectory. The geometric parameters that determine the color pattern seen are the radius of curvature and the opening angle. When a single droplet changes morphology, both these parameters change. This shows the relationship between these two parameters for several drop radii and volume ratios. As the droplet opens, it will move along one of these lines.

space for the index-matched droplets ($n_1 = 1.37, n_2 = 1.27$) illuminated at 30° and viewed from $\theta = 30^\circ, \varphi = 90^\circ$.

This illumination and viewing pair only has colors for a small range of opening angles, and in that range of opening angles, the droplet changes opening angle far faster than curvature, so the colors are mostly static. For the case of $30 \mu\text{m}$ drop, the color shift is only from blue-purple to blue-green. Another viewing angle that I chose by looking at how the entire angular color distribution changes as a function of morphology is $\theta = 30^\circ, \varphi = 120^\circ$ produces the color space shown in Figure 4.21b. We would likely be better off if we can shift the color space down to where the droplet curve is more horizontal- to smaller opening angles. To create a color-based sensor from the droplets, there are several parameters that could be optimized including illumination angle, viewing angles, droplet size, and volume ratio.

Figure 4.21: Color possibilities from a single viewing direction as a function of droplet morphology. a) Illuminated at 30° and viewed from $\theta = 30^{\circ}, \varphi = 90^{\circ}$. b) Illuminated at 30° and viewed from $\theta = 30^{\circ}, \varphi = 120^{\circ}$. The red line shows a trajectory a droplet could take through this color space as its morphology is varied. The corresponding color change that could be expected is shown to the right of each color space.

4.5.2 Taking into Account the Top Droplet Interface

If the droplets were to be used in a sensing system, it would be ideal to use the simplest system to fabricate as possible. Index matching the medium is an added complication that would not be done in practice, so it would be ideal to be able to include the top hydrocarbon-water interface in the color calculations.

Including the top interface in an analytical calculation is challenging (and may even be impossible). The direction that light is refracted through that interface depends upon the location along the interface that it strikes. This means that the families of trajectories we have been looking at so far get all intermixed as they are refracted through that top interface. The ray tracer however can handle this type of calculation. To this end, a coherent version of the ray tracer presented in Section 1.3.1 was developed. The phase of each ray is tracked of by employing a complex amplitude, which is updated when the rays propagate. The phase change due to reflection is kept track of by using a complex polarization vector (as the phase change upon each reflection is polarization-dependent). The rays can then be binned and added coherently in order to calculate the interference leading to color. Figure 4.22 shows the

results using the ray tracer to calculate the color of index-matched and non-index-matched droplets.

Figure 4.22: Including the hydrocarbon-water interface. Comparison of output color distribution in 2D between the analytical model developed in this chapter and color calculated from ray tracing in index-matched aqueous medium ($n_m = 1.37$) and in water ($n_m = 1.33$). **a)** Comparison for bi-phase droplet with $R_i = R_d = 30\mu\text{m}$ and $\eta = 70^\circ$, illuminated at $\theta_{in} = 15^\circ$. **b)** Comparison for bi-phase droplet with $R_i = R_d = 30\mu\text{m}$ and $\eta = 85^\circ$, illuminated at $\theta_{in} = 15^\circ$.

While there are small differences in the color calculated by the ray tracing and the analytical model, they are generally in good agreement. The downside of the ray tracing calculation is that it is computationally far more time-consuming than the analytical approach (90 seconds for the ray tracing vs 0.5 seconds for the analytical calculation in 2D). When the top interface is no longer index-matched, the colors do shift, but the difference is only a few degrees. A larger effect would be expected if the incoming light hits the top interface at a glancing angle, such as in the case of Figure 4.22b. Here, we can see that the top interface plays a large role in determining the color distribution. In other words, the quick analytical model gives a good approximation when the light is nearly perpendicular to the top droplet interface, but gives a poor approximation when the incoming light is at a glancing angle. The analytical

model can be used as a first approximation when the contact angle θ_F is near $\frac{\pi}{2}$ such that TIR light strikes the top interface at nearly normal incidence, but fails as $\theta_F \rightarrow 0$ or π .

4.6 Conclusion

Light reflected by total internal reflection in concave micro-structures results in iridescent colors over a wide angular range. These colors are due to interference of light taking different trajectories along the internal interface of the droplets. This chapter presented a model that explains those colors using geometric approximations for light trajectories, showing that the color can be explained by simple interference of the different possible light paths. The color seen for a given viewing direction depends on a variety of parameters, including the size of the concave interface, the refractive indices above and below the interface, and the opening angle. The model developed here explains these same structural colors in a variety of concave micro-structures which the Zarzar group have been developing, and likely extends to other systems as well.

4.7 Code Availability

The Matlab code used to generate the color distributions in this chapter can be downloaded from github here:

<https://github.com/snnagel/Structural-Color-by-Cascading-TIR>

Chapter 5

Thermal Actuation of Bi-Phase Droplets

5.1 Introduction

The previous chapters discussed how multi-phase droplets interact with light, in particular how the droplets *control light*. This Chapter focuses instead on how light, or the heat produced by the absorption of light, can *control droplets*. Experimentally, these multi-phase droplets can be manipulated (rotation and some translation) with relatively low temperature gradients induced by a focused near-infrared laser in an aqueous medium. The motion of the droplets can be attributed to thermal Marangoni flows within the droplets, due to the local heating from the focused laser.

We first observed this effect when trying to optically trap the droplets, in order to see if it was possible to position the lenses using only light. Optical traps, also called optical tweezers, use gradients in light intensity to manipulate dielectric particles. When a near-IR laser was focused near the droplets, they rotated such that the internal droplet phase was oriented closer to the laser focus, as shown in Figure 5.1. If this only occurred for droplets

with a high index core, or for droplets very close to the laser focus it might be attributed to an optical force. However, droplets with low refractive index FC770 as the internal material also rotated such that the internal material was closer. Similarly droplets far from the laser spot would also rotate towards the focus.

Figure 5.1: Double emulsion droplets follow laser point.

While the optical forces can not account for this effect, thermal effects can. Marangoni flows occur when a gradient in interfacial tension results in a net stress on the interface, inducing a flow along the interface towards the direction of higher interfacial tension. These gradients can be caused by chemical gradients (such as in the famous example, tears of wine [85]) or by thermal gradients [86]. Chemical gradients have been shown to cause double emulsions to act as self propelling micro-swimmers [87]. The behaviour of a single-phase droplet or bubble in a temperature gradient is well understood [88, 89]. In the case of a single phase droplet with no stabilizing surfactants the gradient in temperature induces Marangoni flows along the outside of the droplet away from the heat source. The flows push against the surrounding medium, such that the drop or bubble will move towards the heat source.

The problem of thermo-capillary motion of a compound drop comprised of one drop inside another is discussed theoretically by Morton *et al.* [90]. They found that the presence of an internal drop increases the overall speed of the drop. Thermo-capillary flows in partially

engulfed multi-phase drops have also been studied by Rosenfeld *et al.* [91]. This work showed that the speed of these multi-phase drops could be much faster than single phase drops, but for some geometries and viscosities the multi-phase drops move much more slowly than a single phase drop and in some scenarios even move away from the heat source.

Experimentally the situation is more complicated due to the presence of surfactants, which are necessary for stabilizing the droplets, preventing coalescence [92], and controlling the droplets' morphology [14]. When exposed to an increase in temperature surfactants may cause an *increase* in interfacial tension due to an increase in chemical cohesion [93], acting in opposition to traditional thermal marangoni forces. The redistribution of surfactants on the surface will also act to mitigate any interfacial tension gradients [94, 95].

This chapter shows experimentally that bi-phase emulsion droplets with low interfacial tension between the constituent materials will re-orient so that the center of curvature of the internal interface is closer to the heat source, when a thermal gradient is applied. We also show that the Marangoni forces acting on the double emulsions is far stronger than that of single phase droplets, when stabilized with surfactant, and thus require a far lower thermal gradient or laser power to be manipulated than do single-phase droplets in the same solution.

5.2 Thermal Marangoni Flows

When a thermal gradient is applied along a fluid interface, a gradient in interfacial tension occurs. The gradient in interfacial tension causes a net force along the interface, resulting in flows. In the case of the bi-phase emulsion droplets, there are three interfaces along which these thermo-capillary forces can occur: the water-hydrocarbon interface, the water-fluorocarbon interface, and the hydrocarbon-fluorocarbon interface, as shown in Figure 5.2. While each of these interfaces could contribute to the motion of the droplet, it appears that the hydrocarbon-fluorocarbon interface contributes the most strongly, as will be made evident throughout this chapter. To better understand these flows, we used particle tracking

Figure 5.2: Temperature gradient induces interfacial tension gradients. These gradients occur on all three interfaces however, the gradient in interfacial tension along the internal interface appears to be strongest.

to visualize the flows around and inside the droplets.

5.2.1 Flow tracking in Aqueous Medium using Particle Image Velocimetry for Droplets Imaged from Above.

In order to measure the flow field around the droplets, we used Particle Image Velocimetry (PIV) in order to track the motion of small fluorescent particles in the medium around the droplets. These experiments were done with Matthäus Mittasch in the Kreysing Group at the MPI-CBG in Dresden, while I was a visiting student there in the Summer of 2015.

Emulsions were placed between two coverslips with parafilm used as a spacer in order to not crush the droplets. Fluorescent beads were dispersed through the aqueous medium as trackers. A 1455nm laser was focused to induce thermal gradients and an Andor Zyla sCMOS 5.5 Camera was used to collect images at 76 frames per second. Matlab's PIVlab was used for imaging processing and resulting flow fields were averaged over 30 frames as we assume that the system to be at steady state.

Figure 5.3 shows a droplet of heptane, a droplet of FC770, and a double emulsion droplet

of heptane in FC770 in a thermal gradient with the strength of flows around each of the droplets. while the single phase droplets induce very little flow, the bi-phase droplet causes large flows. This indicates that the water-oil interfaces result in very little Marangoni flow and that the primary cause of these flows around bi-phase droplets is the interface between the heptane and FC770.

Figure 5.3: Comparison of thermocapillary flows around single-phase and bi-phase droplets. Negligible flows observed around droplets formed from a)heptane and b)FC770 while c)double emulsion droplets induce strong flows.

5.2.2 Visualizing Flows from Side-View Imaging

We were able to visualize internal flows within droplets of toluene and hfe7500 (a 3M Novec Engineered fluid) that were synthesized by Dr. Lukas Zeiniger from the Swager group. The toluene phase contains a self-immolative polymer that formed small globules. These globules act as tracers allowing us to visualize the flow inside the bi-phase droplets, as shown in Figure 5.4. This is not an ideal system so particle tracking as the globules have a low contrast, and may coalesce, making it very difficult to get quantitative information. Qualitatively however, it is easy to see that the flows always occur along the internal interface, away from the laser. The rest of the flows within the droplet can be attributed to mass conservation.

Figure 5.4: Droplet internal flows. A frame of a video showing small particles inside of toluene-hfe7500 bi-phase droplets. The particles were not distinct enough for tracking, so the arrows indicating flow direction are drawn by hand. The red dot marks the approximate location of the laser.

5.3 Estimating the Forces

Thermocapillary motion has been used to manipulate single-phase droplets in the past [96, 97, 93]. Often, the temperature gradients applied in order to manipulate such droplets are very large ($\Delta T = 30^\circ$ near the laser focus). An advantage of the bi-phase emulsion system is that much smaller temperature gradients are required to manipulate the droplets. This section aims to estimate the gradients required and the forces involved in causing the droplets to rotate.

5.3.1 Quantifying the Laser-induced Thermal Gradient.

For macroscale systems, thermal imaging can be accomplished utilizing blackbody radiation, however blackbody radiation at room temperature occurs in the regime of about $10\mu\text{m}$ wavelength light, much too long for estimating the temperature gradients that cause the droplets to rotate. Instead a common method of visualizing temperature fields on the microscale utilizes the temperature dependent absorption and emission properties of fluorescent dyes. The most common dye for this purpose is Rhodamine B [98], which can exhibit a 2-3% decrease in fluorescence per degree C increase in temperature. In the case of Rhodamine B, higher

temperatures act to suppress the emission of the dye, resulting in a negative temperature dependence, as shown in Figure 5.5. This dataset was collected with the Kreysing group at the Max Planck Institute of Molecular Cell Biology and Genetics while I was a visiting student there. We used an Andor Zyla sCMOS 5.5 Camera. The lowest temperature change that we were able to measure with this technique (because of noise) was about 5°C. At that laser power the drops will rotate, as well as for far lower laser powers. So the necessary temperature gradient required to rotate the droplets is smaller than this.

Figure 5.5: Temperature mapping using Rhodamine dye. a) Calibration curve of temperature dependence of Rhodamine B fluorescence. b) Temperature map around 1455 nm wavelength laser spot with laser current of 1600mA.

These samples were created by forming simple microfluidic channels between two coverslips, using parafilm as a spacer. A solution of Rhodamine B and 1% agarose (used to minimize thermophoresis and convection) was flowed through the channel and allowed to cool and solidify. For each sample, a calibration curve was created using a Peltier element for cooling and heating the entire sample with a digital thermometer attached. Examples of calibration curves can be seen in Figure 5.5a. The fluorescence of the Rhodamine dye is linear with temperature in the range of interest. The Peltier element was then turned off and the laser

turned on, and the fluorescence recorded for various laser currents. Integration time was kept constant at 1ms, and 2x2 pixel bins were used. The same setup as was used for the top view PIV flow data was used for this experiment.

While this was a strong start to quantifying the laser-induced thermal gradient, there are a few shortcomings. The first is the use of Rhodamine B. While it could give us an estimate of the temperature gradient, it cannot be used in systems with SDS present. In order to enhance the absorption of the laser, a near-IR absorbing dye (NIR1054B QCR solutions corp) can be added to increase absorption of the 975nm laser diode we use in lab. This dye also interacts with Rhodamine B, forming precipitates. The setup used for the initial measurements utilizes a very expensive camera, that could not be used in the side-view experiments.

Figure 5.6: Diagram of side-view microscope setup used for temperature mapping. The sample containing droplets and the fluorescent dye was mounted on bracket with a heating coil on a three axis translation stage. For calibration, the temperature was measured using a thermocouple on the outside of the coverslip.

To extend the temperature measuring technique to the aqueous droplet medium (with the absorbing dye, and surfactants) we needed to switch dyes. There are a number of organic dyes

that have a temperature response [99] but another commonly used dye is Fluorescein. While most organic dyes have a negative temperature dependence like Rhodamine B, Fluoresceins response is more complicated as it is excitation wavelength dependent [100]. Following [99], we switched to 2'7'dichlorofluorescein (Fluorescein 27). This dye for short wavelength excitation (below 500nm) has a negative fluorescence response with increasing temperature, due to suppressed emission, similar to other organic dyes. Conversely, for a longer wavelength excitation (532nm) it has a positive temperature response, due to increased absorption. In this case, the excitation is near the emission peak, and the optimal light to collect is not the longer wavelength light, but rather the anti-stokes shorter wavelength emission. While this is not the strongest emission, it does have a high temperature dependence.

Figure 5.7: Temperature dependence of the fluorescence of Fluorescein 27 for three different samples with two different concentrations and types of surfactant.

The calibration (Figure 5.7) for this is less clean than for the Rhodamine B agarose solution measured in Dresden, however a clear trend can be seen. This data was taken using a Thorlabs 4070C-USB TE cooled CCD scientific camera. The temperature was adjusted with a heating coil (McMaster-Carr) attached to a L-bracket used as a vertical sample mount for the horizontal microscope. The temperature was measured at the outside of the coverslip

using a thermocouple, as shown in Figure 5.6 The thermal response of the dye solution varied slightly between samples and may have depended on the surfactants and other dye in the system [101]. For that reason, a calibration curve was taken for each droplet sample and the temperature fit for that curve was used.

This relation between fluorescence and temperature allowed us to measure the temperature field around the 975 nm laser focus for various laser powers, as shown in Figure 5.8. The raw data is very noisy so a radial average around the center of the focus was taken. This was then fitted to the function

$$T = A(r - r_0)^{-b} + C \quad (5.1)$$

These fits could then be extended and used as an approximation to the thermal gradient that the droplet was experiencing, so that we can measure rotation as a function of the strength of the thermal gradient.

Figure 5.8: Temperature mapping around laser focus. a-c) Temperature distribution calculated from Fluorescein 27 emission around laser focus (with laser currents 0.6A (a), 1A (b), and 1.4A (c)).

5.3.2 Gravitational Torque

The rotation of the bi-phase droplets under a thermal gradient is opposed by the gravitational torque acting on the droplets, so that the two torques are balanced. By determining the gravitational torque on the droplets, we can estimate the torque due to the thermal gradients. This gravitational torque can easily be calculated by considering the rotation angle, relative densities of the liquids, and center of mass of the droplet:

$$\tau_g = R_{cm} M g \sin \theta \quad (5.2)$$

$$= \frac{g \sin \theta \pi (\rho_H - \rho_F)}{12} ((d - R_i)^2 (d^2 - 3R_i^2 + 2dR_i) + 3R_d^4 - 4R_i^3 d) \quad (5.3)$$

Where ρ_H and ρ_F are the mass densities of the hydrocarbon and fluorcarbon oil respectively, θ is the rotation angle of the droplet, $g = 9.81 \text{ m/s}^2$, and R_d, R_i, d , are the same droplet geometric parameters (radius, internal radius of curvature, and off center distance respectively)

used throughout this work. A derivation of this equation is provided in Section A.4.

5.4 Results and Discussion

Figure 5.9 shows how different droplet morphologies respond to the laser induced thermal gradient. This shows that the more highly curved the internal interface, the more the droplets rotate in the presence of a thermal gradient. In each panel, the laser is focused at the point marked in red with the laser current kept constant at 1.5A

Figure 5.9: Rotation of bi-phase emulsions depends on droplet morphology. Droplets with large internal curvature rotate in the thermal gradient more strongly than Janus droplets with a flat internal interface. The red spot denotes the laser location. The arrows in the right-most panel indicate the direction of flow, as tracked by polystyrene beads in the medium. Scale bars: 50 μm

While it is unsurprising that the torque on a perfect Janus droplet with a flat interface is less than that on a droplet with a curved internal interface (as in the case of this geometry, the internal interface contributes zero torque), it is a bit surprising that no rotation is seen on the perfect Janus droplets. There is no reason that the gradient in interfacial tension along the top hydrocarbon interface and bottom fluorocarbon interface should perfectly balance. One explanation for this is that stress due to the interfacial tension gradient on the internal interface is far stronger than the stresses exerted by either of the external interfaces. Indeed, bi-phase droplets induce far stronger flows in the surrounding media than single

phase droplets of either of the same materials in the presence of surfactants, as was shown in Figure 5.3.

The amount of rotation of a double emulsion of FC770 in heptane (0.5%wt SDS aqueous medium) as a function of thermal gradient is shown in Figure 5.10. The temperature distribution was determined by the method described in section 5.3.1. The fit was used to estimate the temperature drop ΔT across the droplets. The equivalent gravitational torque necessary to balance the rotation was determined by Equation 5.3. This shows that there is an approximately linear relationship between temperature gradient and the torque due to thermocapillary forces. Moreover, it shows that the necessary thermal gradient is actually quite small $< 0.5^\circ\text{C}$ across the width of the droplet.

Figure 5.10: Rotation of double emulsion in various temperature gradients. **a-c)** Overlay of droplet micro-graphs with temperature distribution around laser spot with laser currents 0.6A (a), 1A (b), and 1.4A (c). The temperature distribution was calculated using the fit described in section 5.3.1 and the overlay was done by thresholding the micrographs of the droplets. **d)** Droplet rotation as function of temperature drop across the droplet, as measured at the points shown in b. **e)** Corresponding gravitational torque calculated from those rotations.

Figure 5.11 shows the translation of a double emulsion of heptane in FC770 falling past a laser spot. Near the laser focus, the droplet orients towards the heat source and then swings around, shifting towards the laser spot. This shows that beyond rotations, the heat source does exert a net force on the droplets, and in the case of a double emulsion of heptane in FC770, this force is towards the heat source.

Figure 5.11: Translation of droplets in thermal gradients. a) Micrographs showing that a droplet falling past a laser spot is deflected. b) Vertical location of the droplet as it falls, both when the laser is on and when the laser is off and c) horizontal location, showing that the droplet is deflected by roughly $5\mu\text{m}$.

5.5 Summary

Bi-phase emulsion droplets will re-orient in the presence of a focused laser spot. These rotations can be attributed to thermocapillary effects along the internal interface of the droplets due to local heating from the laser. While multi-phase emulsions are stabilized along the outer interface by surfactants, the internal interface is surfactant-free. This means that this interface can respond to Marangoni forces without the mitigating effects of surfactant

molecules. This is evident by observing the flow field around bi-phase droplets as compared to single-phase droplets. This also helps to explain why there is a stronger rotation for droplets in double emulsion morphology as compared to flat interface Janus droplets. The effect of thermocapillary motion in multi-phase droplets will likely prove important in microfluidic sorting and micro-reactors. The effects may also be leveraged to manipulate mirolenses such as those presented in Chapter 2.

Chapter 6

Summary and Outlook

This thesis presented the optical characteristics of multi-phase droplets. These droplets have a dynamic, controllable, and stimuli-responsive morphology, making them strong candidates for micro-optical devices such as sensors and tunable micro-lens arrays. The droplets' morphology is set by the balance of interfacial tensions at the droplets' interfaces, which can be adjusted by tailoring the chemistry of the droplets' environment.

As refractive elements, these multi-phase droplets act as tunable compound lenses. While these droplet micro-lenses are not diffraction limited, they can be dynamically adjusted across a large range of optical refractive power, varying from small positive focal lengths (converging lenses) to infinite focal lengths, to small negative focal lengths (diverging lenses). In the far field, these different refractive characteristics lead to either a transparent appearance when the droplets are in the flat interface Janus configuration or to significant light scattering when in the double emulsion state.

The emissive properties of these droplets are also morphology-dependent, enabling the droplets to function as optical transducers in chemical and pathogen sensing systems. The dependence of the emission profile on the morphology is due to a portion of the light undergoing total internal reflection along the internal interface within the droplets. When this

totally internally reflected light exits at an angle that aligns with a collection fiber, a larger emission signal is detected than when the droplets are in other morphologies. This effect could be enhanced by increasing the portion of light that undergoes total internal reflection, such as by adjusting the refractive indices or isolating the dye near the internal interface.

It has been observed that under the right conditions, these droplets display structural color, caused by the interference of light undergoing total internal reflection along different trajectories at the internal droplet interface. A model was presented using geometric optics, that took into account optical path length differences and Fresnel phase shifts in order to elucidate the cause of color. This model/effect extends to a variety of systems; any system in which a microscale concave interface results in multiple trajectories of total internal reflection could display these colors.

Beyond the optical characteristics, the effect of thermal gradients on bi-phase emulsions was also studied. In a relatively small thermal gradient, the droplets will orient such that the internal droplet will be nearer to a heat source. The droplets will follow a focused near-infrared laser. This is due to thermal Marangoni flows resulting from the thermally-induced interfacial tension gradient along the droplet-internal interface.

While this work sets the foundation for understanding some of the optical effects within this material system, there is still a huge parameter space to explore. There is a wide range of materials that such droplets could be formed from, which could allow for correcting aberrations in the lenses, or enhancing total internal reflection for emission or structural color. The incorporation of active optical media, plasmonic elements, or magnetic nanoparticles could open up possibilities for tuning and controlling the emulsion's dynamic optical properties, and simultaneously provide access to a multitude of enticing sensing paradigms and optical applications.

Appendix A

Derivations

A.1 Droplet Morphology

Figure A.1: Droplet geometry.

The morphology of the bi-phase droplets is set by the interfacial tensions between the various liquids (γ_F , γ_H and γ_{FH}) and the volume ratio $v_r = \frac{V_H}{V_F}$, where V_H is the volume of hydrocarbon and V_F the volume of fluorocarbon. If the overall droplet is considered to be spherical, then

the volume of hydrocarbon is:

$$V_H = \frac{v_r}{1 + v_r} V_{\text{drop}} = \frac{4}{3} \frac{v_r}{1 + v_r} \pi R_d^3 \quad (\text{A.1})$$

with R_d being the droplet radius. The location of the interface can be determined from the internal curvature R_i by noting that the volume of hydrocarbon is equal to the volume of region A plus the volume of region B, as shown in Figure A.1, each of which can easily be obtained by calculating the volumes of the spherical caps:

$$V_H = V_A + V_B = \frac{\pi}{3} h_A^2 (3R_d - h_A) + \frac{\pi}{3} h_B^2 (3R_i - h_B) \quad (\text{A.2})$$

The height of the spherical caps is determined by the distance from the center of the droplet to the plane of the three-phase contact line h , such that:

$$h_A = R_d - h \quad \text{and} \quad h_B = R_i - d + h \quad (\text{A.3})$$

where d is the distance from the center of the droplet to the center of the sphere that defines the internal interface.

The location of the three-phase contact line is the intersection of the sphere forming the internal interface with the sphere that defines the overall droplet. In other words,

$$r^2 + h^2 = R_d^2 \quad \text{and} \quad r^2 + (d - h)^2 = R_i^2 \quad (\text{A.4})$$

Combining equations A.1, A.2, A.3, and A.4 and eliminating r, h, h_A and h_B yields:

$$(d + R_d - R_i)^2 (d^2 + 2d(R_i - R_d) - 3(R_d + R_i)^2) + 16d \frac{R_d^3}{1 + v_r} = 0. \quad (\text{A.5})$$

In the limit that $\gamma_{FH} \ll \gamma_F, \gamma_H$, it has been shown that the contact angles at the three phase

contact line are [20]:

$$\frac{\gamma_H - \gamma_F}{\gamma_{FH}} = \cos(\theta_F) = -\cos(\theta_H) \quad (\text{A.6})$$

which by applying the law of cosines yields:

$$\frac{\gamma_H - \gamma_F}{\gamma_{FH}} = \frac{R_d^2 + R_i^2 - d^2}{2R_d R_i} \quad (\text{A.7})$$

A.2 Paraxial Correction for Imaging Internal Interface Shape

Figure A.2: Diagram of magnification of internal interface. When the internal interface is measured through the outer oil-water interface it is magnified/demagnified depending on the refractive index contrast.

When the interface between the two liquids is imaged through the outer phase of the droplet, the image of the interface is magnified. In order to correct for the magnification, the paraxial approximation was used. Consider an object of height h located inside of a sphere of radius R and refractive index n_1 , which is positioned inside a medium of refractive index n_2 , as shown in Figure A.2. A ray leaving the object at an angle α will hit the interface of the drop at a height $a = h + R\alpha$ (under the assumption $\alpha \ll 1$). At this height, under the small

angle approximation, the surface normal is at an angle $\frac{a}{R} = \frac{h}{R} + \alpha$, such that the ray hits the surface at an angle

$$\theta_1 = \frac{h}{R} + \alpha - \alpha = \frac{h}{R} \quad (\text{A.8})$$

for all rays with $\alpha \ll 1$. Each ray is refracted according to Snell's law:

$$\theta_2 = \frac{n_1}{n_2} \theta_1 = \frac{n_1}{n_2} \frac{h}{R} \quad (\text{A.9})$$

Similarly, the height where all the rays converge (the image is formed) is given by:

$$h_i = R\theta_2 = \frac{n_1}{n_2} h. \quad (\text{A.10})$$

The paraxial approximation breaks down for large angles, which is the case for a large object located inside a sphere. However, the magnitude of the error is smaller than the uncertainty in the location of the interface (line thickness) in the images.

A.3 Focal Length From Image Location

In order to determine the droplet lenses' focal length, a pattern was projected in front of the droplets and used as the “object”. The image formed by the drops (the “image”) was recorded. By varying the location of the object, the image location can be varied, allowing us to determine the focal length of the drops. A form of the standard thick lens equation was used to find the focal length, accounting for the fact that the droplet-coverslip system formed a boundary between two different refractive index media, as shown in Figure 2.10. This section derives the lens equation used to determine the effective focal length of the droplet lenses from image and object locations.

Consider an object of height h_o located at a distance x_o from the center of the droplet. For a thick lens system, all refraction can be considered to happen at the principal planes, such

that a ray passing through the optical axis at the first principal plane (red ray in Figure 2.10) will be refracted according to Snell's law, which in the paraxial approximation is given by:

$$n_1\theta_1 = n_2\theta_2 \quad (\text{A.11})$$

with n_1 , n_2 , and θ_1 , θ_2 being the refractive indices and angles of the incident and refracted rays with the interface normal for medium 1 and 2, respectively. This can also be written in terms of the object and image heights h_o, h_i , the distance of the object to the first principal plane s_o and the distance of the image from the second principal plane s_i .

$$n_1 \frac{h_o}{s_o} = n_2 \frac{-h_i}{s_i}. \quad (\text{A.12})$$

A ray that hits the first principal plane parallel to the optical axis will be refracted at the second principal plane and pass through the back focal point, which gives

$$\frac{h_o}{f} = \frac{h_i}{s_i - f} \quad (\text{A.13})$$

with f being the focal length measured in the second medium. Combining Equations A.12 and A.13 yields a modified version of the lens equation:

$$\frac{n_1}{n_2} \frac{1}{s_o} + \frac{1}{s_i} = \frac{1}{f} \quad (\text{A.14})$$

In terms of the measured distances from the center of the droplet, this yields:

$$\frac{n_1}{n_2} \frac{1}{x_1 - p_1} + \frac{1}{x_2 - p_2} = \frac{1}{f} \quad (\text{A.15})$$

where p_1 and p_2 are the distances from the droplet center to the first and second principal planes, which were used as fitting parameters when determining the focal length of the droplets, as shown in Figure 2.10.

A.4 Droplet Center of Mass and Torque

In order to estimate the gravitational torque, we first need to identify the center of mass of the droplet from side-view images of the droplets. The center of mass of an object is given by:

$$\vec{R}_{\text{cm}} = \frac{1}{M} \iiint_V \vec{r} \rho(\vec{r}) dV \quad (\text{A.16})$$

where $\rho(\vec{r})$ is the density. The total mass (M) of the droplet is the sum of the mass of the hydrocarbon phase and the fluorocarbon phase:

$$M = \frac{4}{3} \frac{\rho_F + v_r \rho_H}{1 + v_r} \pi R_d^3 \quad (\text{A.17})$$

Within each phase of the droplet, the density is homogeneous so that equation A.16 can be written:

$$\vec{R}_{\text{cm}} = \frac{1}{M} \left(\rho_H \iiint_{V_H} \vec{r} dV + \rho_F \iiint_{V_F} \vec{r} dV \right) \quad (\text{A.18})$$

Figure A.3: Droplet geometry for calculating center of mass and gravitational torque.

The first term is the integration over the hydrocarbon phase and the second over the fluo-

rocarbon phase. Due to the symmetry of the droplets, only the z component of the center of mass will be off center (working in the coordinate system where the z -axis is aligned with the droplet symmetry axis). The integration over the hydrocarbon phase is straightforward by integrating over the partial sphere from the plane of the three phase contact line (located a distance $z = I = \frac{R_d^2 - R_I^2 + d^2}{2d}$ above the center of the droplet) to the H-W interface and from the H-F interface to the same plane, as shown in Figure A.3

$$\left[\iiint_{V_H} \vec{r} dV \right]_z = \left[\iiint_{V_A} \vec{r} dV \right]_z + \left[\iiint_{V_B} \vec{r} dV \right]_z \quad (\text{A.19})$$

The integral over the top partial sphere A is:

$$\left[\iiint_{V_A} \vec{r} dV \right]_z = 2\pi \iint_{r=0, z=I}^{r=\sqrt{R_d^2 - z^2}, z=R_d} r z dr dz \quad (\text{A.20})$$

$$= \pi \int_{z=I}^{z=R_d} (R_d^2 - z^2) z dz \quad (\text{A.21})$$

$$= \pi \left[\frac{z^2}{2} R_d^2 - \frac{z^4}{4} \right]_I^{R_d} \quad (\text{A.22})$$

$$= \pi \left(\frac{R_d^4}{4} - \frac{I^2 R_d^2}{2} + \frac{I^4}{4} \right) = \frac{\pi}{4} (I^2 - R_d^2)^2 \quad (\text{A.23})$$

and integral over the internal volume B is:

$$\left[\iiint_{V_B} \vec{r} dV \right]_z = 2\pi \iint_{r=0, z=d-R_I}^{r=\sqrt{R_I^2 - (z-d)^2}, z=I} r z dr dz \quad (\text{A.24})$$

$$= \pi \int_{z=d-R_I}^{z=I} (R_I^2 - z^2 - d^2 + 2dz) z dz \quad (\text{A.25})$$

$$= \pi \left[\left(\frac{R_I^2 - d^2}{2} \right) \frac{z^2}{2} - \frac{z^4}{4} + \frac{2dz^3}{3} \right]_{z=d-R_I}^I \quad (\text{A.26})$$

$$= \frac{\pi}{12} ((d - R_I)^2 (d^2 - 3R_I^2 + 2dR_I) + I^2 (6R_d^2 - 4Id - 3I^2)) \quad (\text{A.27})$$

combining these gives:

$$\left[\iiint_{V_H} \vec{r} dV \right]_z = \frac{\pi}{12} ((d - R_I)^2 (d^2 - 3R_I^2 + 2dR_I) + 3R_d^4 - 4I^3 d) \quad (\text{A.28})$$

The second term in equation A.18 is easily determined by subtracting integral determined above from a full sphere (which has a center of mass at $z=0$). ie

$$\iiint_{V_F} \vec{r} dV = 0 - \iiint_{V_H} \vec{r} dV \quad (\text{A.29})$$

for a spherical droplet.

The center of mass of the droplet is then:

$$\vec{R}_{cm} = \frac{\pi(\rho_H - \rho_F)}{12M} ((d - R_I)^2 (d^2 - 3R_I^2 + 2dR_I) + 3R_d^4 - 4I^3 d) \hat{z} \quad (\text{A.30})$$

The torque acting on the droplet when it is displaced from alignment is by an angle θ is then:

$$\tau_g = R_{cm} M g \sin \theta \quad (\text{A.31})$$

$$= \frac{g \sin \theta \pi (\rho_H - \rho_F)}{12} ((d - R_I)^2 (d^2 - 3R_I^2 + 2dR_I) + 3R_d^4 - 4I^3 d) \quad (\text{A.32})$$

This derivation was under the assumption that the more internal phase is the hydrocarbon phase, however the same result applies if the phases are switched simply by switching ρ_H and ρ_F . The gravitational torque calculated in this way can be used to calculate the torque acting on the droplets due to the thermal gradient.

Appendix B

Raytracing Algorithm and Documentation

B.1 Ray Tracing Implementation

This section presents the raytracing tool used for determining lensing and emissive properties of the bi-phase droplets. The raytracer was implemented in MATLAB and consisted of three primary components; a ‘drop’ object, a ‘ray’ object, and the raytracing algorithm.

The ‘drop’ object contains the physical parameters describing the bi-phase droplets, including the droplets size, internal radius of curvature, volume ratio, and refractive indexes. It also contains functions for determining the contact angles (given the internal radius of curvature and volume ratio) and displaying both 2D and 3D droplets in figures.

Each ‘ray’ object has properties¹ including the current position, direction, amplitude, and polarization, as well as an array of past locations. The ‘ray’ also has functions implement reflection, refraction, and propagation, and to draw the rays in 2D and 3D figures. Because the raytracing is done in both two and three dimensions, reflection and refraction are calculated

¹in MATLAB, object fields are referred to as properties

in terms of vector representations of light rays.

The raytracing algorithm takes a ‘drop’ and a ‘ray’, then propagates the ray through the drop by locating each intersection point and then calculating the refraction. The ray-tracer handled reflected rays by recursively calling the same algorithm for propagating the ray through the drop for each reflection. The Fresnel equations are used to determine the amplitude of the transmitted and reflected rays. Details of this algorithm are presented in section B.3.

Once the rays were propagated through the system the intensity could either be determined coherently or incoherently. If coherent illumination is assumed, the intensity is determined by summing the complex amplitude of the rays and then squaring the absolute value. For incoherent illumination, the intensity of each ray is determined by squaring the absolute value of the amplitude and then the intensities of all the rays is summed.

B.2 Vector Version of Snell’s Law

The ray tracer uses a vector version of snell’s law to calculate refraction directions in 3D. Consider a ray traveling in the direction $\vec{d}_1$ refracting through a surface with normal $\vec{n}$ from a material with refractive index n_1 to a material with refractive index n_2 . Refraction will take place within the plane formed by $\vec{n}$ and $\vec{d}_1$. Therefore consider a vector $\vec{t}$ perpendicular to $\vec{n}$ in this plane such that

$$\vec{d}_1 = \sin \theta_1 \vec{t} + \cos \theta_1 \vec{n} \quad (\text{B.1})$$

and

$$\vec{d}_2 = \sin \theta_2 \vec{t} - \cos \theta_2 \vec{n} \quad (\text{B.2})$$

as can be seen in Figure B.1. From equation B.1, $\vec{t}$ must then be:

$$\vec{t} = \frac{\vec{d}_1 + \cos \theta_1 \vec{n}}{\sin \theta_1} \quad (\text{B.3})$$

Figure B.1: Vector diagram for snell's law

The outgoing angle θ_2 can be determined using Snell's law:

$$n_1 \sin \theta_1 = n_2 \sin \theta_2 \quad (\text{B.4})$$

Using the identity $\sin^2 \theta + \cos^2 \theta = 1$, Snell's law can be written in terms of the cosines

$$\cos \theta_2 = \sqrt{1 - \left(\frac{n_1}{n_2}\right)^2 (1 - \cos \theta_1)} \quad (\text{B.5})$$

Substituting Equations B.3, B.4, and B.5 into Equation B.2 yields a vector form for Snell's Law:

$$\vec{d}_2 = \frac{n_1}{n_2} \vec{d}_1 + \left(\frac{n_1}{n_2} \cos \theta_1 - \sqrt{1 - \left(\frac{n_1}{n_2}\right)^2 [1 - \cos^2 \theta_1]} \right) \vec{n}; \quad (\text{B.6})$$

The angle θ_1 between the incoming ray and the surface normal is easily obtained from the dot product:

$$\cos \theta_1 = \vec{d}_1 \cdot \vec{n} \quad (\text{B.7})$$

since $\vec{d}_1$ and $\vec{n}$ each have unit length.

Similarly, rays are reflected at the same angle that they are incident of the surface

$$\vec{d}_{\text{ref}} = \sin \theta_1 \vec{t} - \cos \theta_1 \vec{n} \quad (\text{B.8})$$

B.3 Ray Tracing Algorithm

The algorithm used for the ray tracing takes as input a ‘drop’ object, a ‘ray’ object, the refractive index of the surrounding medium, and optionally a minimum amplitude (default 0.01) and maximum number of reflections (default 1000). It returns then a matrix of ‘ray’ objects including all the reflections and transmissions through the drop that have at least the minimum amplitude and have not exceeded the maximum number of reflections. The actual algorithm is as follows.

First the number of reflections that has occurred is tested, if it exceeds the maximum number of reflection events, then the current matrix is returned. Similarly if the ray is found to be at the outer surface of the drop, with a direction pointing away from the droplet, the function returns the current matrix of rays.

Next, the ray is tested whether or not it is outside the droplet, and if so, whether it will strike the droplet and where. If it does, it is propagated to that location and refracted through the interface (this could be into either phase). The algorithm is called again recursively for the reflected ray, with the entire output of this recursion added to the matrix of outgoing rays. The transmitted ray continues through the current instance of the algorithm. If the ray misses the droplet entirely, then just the ray is returned.

Next is tested whether or not the ray will strike the internal droplet interface; if it does, then it is propagated to that location and refracted through the interface, again the reflected ray is treated recursively, and the transmitted ray continues through this algorithm.

The ray is then tested to be inside the inner droplet phase, and if so, will it strike the internal droplet interface? If it does, it is propagated and refracted to that point.

Due to the recursive nature of the algorithm, at this point the next intersection must be the external interface of the droplet. This intersection point is determined and again the ray is propagated and refracted at that point and the reflected ray treated recursively.

The transmitted ray is added to the matrix of outgoing rays and returned.

B.4 Ray Tracing Code Documentation

B.4.1 ray.m

Constructor:

```
myRay=ray(loc, dir, n, amp, pol)
```

`loc` : 1×2 or 1×3 vector denoting location of the ray.

`dir` : 1×2 or 1×3 vector denoting direction of propagation of the ray

`n` : Refractive index of medium ray is located within.

`amp` : optional. Amplitude of the ray. Default 1

`pol` : optional. 1×3 vector denoting polarization. Default $[0, 0, 1]$. If the polarization passed to constructor is not allowed, then random polarization is assigned.

Properties:

`location` : Current location of the ray, 1×2 or 1×3 vector

`direction` : Current direction of the ray, 1×2 or 1×3 unit vector

`trajectory` : matrix of past locations of the ray.

numIntersections : number of intersections that ray has had. increased by refract/reflect methods

currentIndex : index of refraction of the medium the ray is currently located within

amplitude : Intensity is $|amplitude|^2$. note that this is the magnitude of the amplitude. Phase is included in polarization

amplitudeHistory : Array of past amplitudes of the ray.

polarization : Polarization vector. Points in direction of electric field, and includes amplitude and phase information

TIR=false : Boolean tag indicating whether at any time total internal reflection occurred.

OPL : Optical path length- updated when propagate is called.

Methods:

`r2=propagate(r, l)`

Propagates a ray a desired distance or to a specific location. The rays OPL and trajectory are updated.

`r` : input ray

`l` : either scalar or vector. If a scalar is give, the ray is propagated a distance `l` in the direction of the ray, if a vector is provided then the ray is propagated to that location, regardless of current direction of the ray.

`r2` : returned ray in new location with updated OPL and trajectory.

`[rayTransmitted, rayReflected] = refract (r, norm, n2)`

Refracts a ray through a interface.

`r` : input ray

`norm`: vector normal to interface

`n2` : refractive index on other side of interface

rayTransmitted : The transmitted ray

rayReflected : The reflected ray

rRef= reflect(r, norm, reflectance)

r : input ray

norm: vector normal to interface

reflectance: ratio of amplitude reflected to amplitude incident

rRef : The reflected ray

drawRay(r, rcolor)

plots the ray in the currently active plot.

r : input ray

rcolor : optional. Default 'k'. color that the ray should be plotted. Can be any matlab ColorSpec

[location, normal] = raySphereIntersection(r, Rad, loc)

Finds the intersection of a ray and a sphere.

r : input ray

Rad : radius of the sphere

loc : vector location of the center of the sphere

location: vector location of intersection of the ray with the interface

normal : vector normal to the interface at point of intersection

[location, normal] = rayPlaneIntersection(r, p)

Finds the intersection of a ray and a plane.

`r` : input ray

`p` : vector of the plane. The equation of the plane is $p(2)*x1+p(3)*x2+p(4)*x3=p(1)$, where $[x1, x2, x3]$ is the coordinate system.

`location`: vector location of intersection of the ray with the interface

`normal` : vector normal to the interface at point of intersection

```
[location, normal] = rayEllipseIntersection(r, a, b, loc )
```

Finds the intersection of a ray and an ellipse.

`r` : input ray

`a` : semi-major axis of ellipse

`b` : semi-minor axis of ellipse

`loc` : vector location of the center of the ellipse

`location`: vector location of intersection of the ray with the interface

`normal` : vector normal to the interface at point of intersection

B.4.2 drop.m

Constructor:

```
myDrop=drop(loc, Rd, Ri, outerI, innerI, vr, rotAng)
```

`loc` : 1×2 or 1×3 vector denoting location of the center of the droplet

`Rd` : Droplet radius

`Ri` : Internal radius of curvature

`outerI` : Refractive index of outer phase of droplet

`innerI` : Refractive index of inner phase of droplet

`vr` : Volume ratio of droplet

`rotAng` : Rotation angle of the droplet. In 3D this is the rotation of the droplet around the y-axis.

Properties:

`location` : Center of the droplet, 1×2 or 1×3 vector

`radius` : Radius of the droplet. R_d

`innerRadius` : Radius of curvature of internal interface. R_i

`innerIndex` : Refractive index of inner phase

`outerIndex` : Refractive index of outer phase

`volumeRatio` : The volume ratio. Internal phase to external phase.

`offCenterDist` : Distance from center of droplet to center of curvature of the internal interface. d .

`rotAngle` : Rotation angle of the droplet in degrees. In 3D, this rotation is around the y-axis

Methods:

`drawDrop(d, N, edgeC, colorO, colorI)`

plots the droplet in the currently active plot.

`d` : the drop object

`N` : optional. Number of points along edge to plot. default 100

`edgeC` : optional. edge color. Default $[0, 0, 0]$. Can be any matlab colorSpec.

`colorO` : optional. color of outer phase. Default the higher refractive index will be pink and the lower purple.

`colorI` : optional. color of inner phase. Default the higher refractive index will be pink and the lower purple.

`p=tangentPlane(dir, d)`

returns the plane tangent to the droplet in a given direction.

`dir` : 1×2 or 1×3 direction vector

`d` : the drop object

`p` : The tangent plane. The equation of the plane is $p(2)*x1+p(3)*x2+p(4)*x3=p(1)$, where $[x1, x2, x3]$ is the coordinate system.

`relativeCoord=ThreePhaseContactLine(d)`

returns the location of the three phase contact line, relative to the center of the droplet.

`d` : the drop object

`relativeCoord` : Relative (x, z) location of the three phase contact line, where z is along the axis of droplet, and x is distance from that axis. The origin in this case is at the center of the droplet.

B.4.3 `traceRay.m`

`traceRay.m` implements the algorithm described in section B.3. It takes a ray object and a drop object and returns a matrix of ray objects.

`[ outRays ] = traceRay( r, d, nm, minAmp, maxInteraction )`

`r` : a ray object

`d` : the drop object

`nm` : the refractive index of the surrounding medium

`minAmp` : optional. Minimum amplitude of the ray to continue the calculation. Rays with less than this amplitude are thrown away. Default 0.01.

`maxInteraction` : maximum number of times a ray is reflected or transmitted. Default 1000. Rays that strike interfaces more than this number of times are ignored. For example if a ray is trapped by TIR and never exits.

B.5 Code Availability

The ray tracing code and simple examples can be downloaded from github here:
<https://github.com/snnagel/MultiPhaseDropletRaytracer>

Appendix C

Other Information

C.1 Stability

Figure C.1: Droplet stability. a) Variation of droplet morphology composed of heptane and FC770 over time if diffusion of heptane is not suppressed. b) Droplet morphologies are stable if diffusion of heptane is suppressed by enclosing the system and priming the aqueous medium with heptane. In the last frame shown in (b) two smaller droplets that also appear stable have drifted into the frame. Scale bars: 100μm.

The solubility of hexane, heptane, and FC770 is extremely low in water; however, over sufficiently long time scales, diffusion of hexane or heptane through the aqueous medium into the

ambient environment can lead to changes in droplet morphology. This is easily prevented by keeping the droplets and the medium in a closed environment and by suppressing diffusion into the aqueous medium, which can be achieved through priming with the respective solvent. FC770, a long-chain fluorinated oil, was not found to diffuse into the aqueous medium on the timescale of days. Figure C.1a visualizes droplet morphology variation in suboptimal experiment condition, while Supplementary Figure C.1b shows that the droplets are stable, if the experimental conditions are appropriately controlled. For the heptane-FC770 droplets shown in the figure, we seal the sample chamber to prevent any exchanges with the ambient environment and saturate the aqueous medium with heptane, to avoid heptane diffusion from the droplets into the medium. Longer-term stability tests have not been conducted, though droplets have been observed to be in good condition several weeks after fabrication. A rich parameter space regarding the chemical composition of the droplets remains to be explored, in order to optimize emulsion droplet compound micro-lenses for specific application scenarios. The droplets' chemical make-up affects their range of focal length, resolution capabilities, and will also influence such parameters as boiling points, pressure stability, compatibility with surrounding media and interfacial interactions.

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