

Partial Coalescence of Oil and Water: Spreading Behavior and Material Synthesis

BY

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THESIS

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Dedication

To my mother, father and brother, for everything.

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Summary

Interactions of oil and water form the basis of numerous natural systems including oil spills, food dressings, cosmetic compounds and pharmaceutical drugs. The impact of a single drop of oil onto an air-water interface represents one of the most elemental interactions between oil and water, and thus presents a model problem to understanding the underlying physics involving such droplet-interface interactions. Previous reports have focused on the outcomes of a drop impact onto an identical bulk, characterizing the interaction of a two phase system. There is also ample literature on high velocity impacts of drops onto interfaces, with evaluations of the effect of the Weber number(We) on the final outcome. However, the comprehensive behavior of a drop upon gentle contact with an interface in a three phase system needs further examination.

The current study essays to shed light on the complex dynamics taking place during the gentle impact of an oil drop onto an air-water interface in the context of oil spills. Using high speed imaging, the dynamics of drop deformation during the merger of an oil drop with a bulk liquid in a three phase system is investigated experimentally. The merger is found to either proceed in a single event of complete coalescence or in a cascade of multiple events of partial coalescence where a small portion of the drop detaches itself from the merging oil film at every stage. The mechanism adopted by the drop in coalescing with the bulk liquid is found to depend greatly on the physical properties of the oil drop as characterized by the Ohnesorge

number ($Oh_p = \mu_p / \sqrt{\rho_p \sigma D_p}$) of the drop where μ_p , ρ_p , σ , and D_p represent the viscosity, density, surface tension, and the diameter of the drop respectively. The transient topological features transpiring during the intermediate stages of transition from a drop to a film scale as a function of the Oh_p and are theoretically validated using appropriate force balances.

Additionally, the spreading behavior of the oils following two distinct impact scenarios - (1) upon impact onto the air-water interface and (2) succeeding the emergence of a drop from below the surface is investigated. It is found that the spreading characteristics during coalescence and emergence are heavily dependent on the viscosity of the oil and bulk liquid respectively, ultimately determining the extent of film coverage over the liquid substrate. The spreading characteristics are scaled against the physical properties of the oil and bulk liquids, and to validate the spreading behavior of the oils, a theoretical model based on the damped harmonic motion is presented.

Finally, through material synthesis, attempts are made to control the dewetting events which lead to the emergence of oils in underwater oil spills. It is demonstrated that through manipulation of the production of the initial parent drop, compounds such as armored drops, and single and double emulsions can be created to suit the needs of applications like drug delivery, and emulsion stabilization.

List of Symbols

A	Hamaker Constant
c	Viscous damping coefficient
D	Diameter of a drop
F_0	Step force acting on the drop after rupture
g	Acceleration due to gravity
h	height of the drop at any instant
j	prefactor coefficient added to natural frequency
k	Restoring spring coefficient
ℓ	Arbitrary dimensional scale
l	length scale
m	mass of a drop
R	Radius of the drop
r	radius of a spreading film
S	Spreading coefficient
t	Time since initiation of spread
τ	Time scale
u	Velocity
V	Velocity parameter
ϑ	Velocity scale
$\mathbb{V}$	Volume of a drop

ω_n	Natural frequency of system
ω_d	Damped frequency of system
σ	Surface (Interfacial) tension
μ	Dynamic viscosity of drop/liquid
ν	Kinematic viscosity
ρ	Density of liquid
δ	Ratio of density difference between water and oil to density of water
Re	Reynold's number
We	Weber number
Ca	Capillary number
Oh	Ohnesorge number
Bo	Bond number
Fr	Froude number

Subscripts

b	bulk liquid
d	daughter drop
p	parent drop
in	Inertial force
ca	Capillary force
gr	Gravitational force
vi	Viscous force
tip	parameter of the apex of the drop
$wave$	parameter of the capillary wave traveling on the drop
ic	inertio-capillary
iv	inertio-viscous
ivc	inertio-visco-capillary
vc	visco-capillary
gc	gravity-capillary
ig	inertio-gravity

Chapter 1

Introduction

The interaction of oil and water is ubiquitous in nature, rendering its presence in everyday human life. The interactions span many industrial, biological, and environmental applications such as oil recovery through CO₂ [44, 65], lab-on-a-chip technology for drug delivery, medical diagnosis [128], and oil spill mitigation [80, 55] etc. The spreading of oils on a surface, one of the most prevalent processes in nature, has been a subject of academic interest for decades owing to its implications on natural and man-made phenomenon such as oil spills and ink-jet printing. The current study investigates a specific interaction of oil and water involving the spreading of oils on surfaces. This chapter discusses the prerequisite concepts essential to understanding the principal objectives and results of this study. It also attempts to lay the groundwork for this thesis by establishing the context and motivation behind the current investigation.

1.1 Wetting and Dewetting

The spreading of oils has its origins in the central concepts of wetting and dewetting of two liquid phases, and thus it is important to understand the fundamentals of spreading before proceeding to examine the motivation for the study. Wetting or

dewetting phenomena ultimately are a consequence of the resultant surface energy of the system. Consider a liquid drop placed on a solid surface with air as the ambient fluid. The shape of the drop on the surface is determined by the competition between the force of adhesion of the drop and solid, and the force of cohesion between the molecules of the liquid drop. Figure 1.1 shows the various possible drop shapes and the corresponding degree of wetting when a drop is placed on a solid surface. If

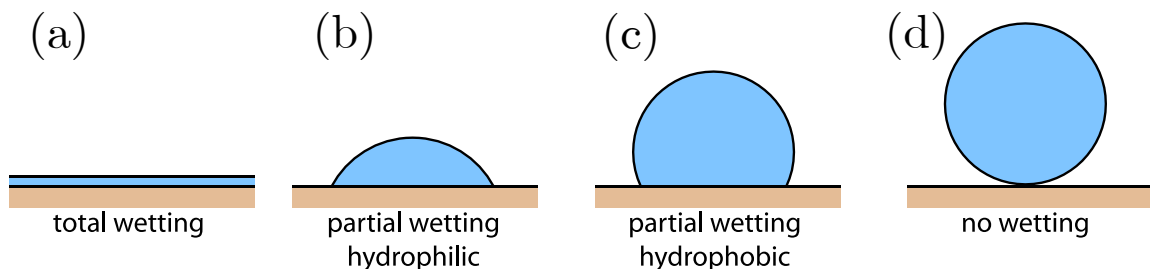


Figure 1.1: The different degrees of wetting of a liquid drop on a solid based on the interaction between the liquid, solid and the ambient air. (a) Shows a complete wetting signifying a strong adhesive force between the liquid and solid, while (b) and (c) represent partial wetting showing moderate degrees of adhesive and cohesive force. (d) Represents a case of very low wetting signaling a weak adhesive force between the drop and the surface.

the adhesive forces between the drop and the surface are relatively larger than the cohesive forces of the drop, the drop tends to wet the surface completely such as in Figure 1.1(a), whereas if the cohesive forces in the drop are comparatively higher than the adhesive forces, the drop tends to avoid any contact with the surface, bunching up and retaining a near spherical shape as shown in Figure 1.1(d). Contrast to the process of wetting, the bunching up of a liquid to minimize the surface energy is known as *dewetting*, and is found in multiple situations in real life such as instant drying of skin after a shower[119, 47]. In different scenarios, different wetting regimes are favorable. For example, self cleaning on lotus leaves require spontaneous dewetting while some applications of protective coating and painting require complete wetting of the liquid. Depending on the relative degree of adhesive and cohesive forces, the liquid partially wets the surface as in Figure 1.1(b),(c). In any case of wetting, although most

relevant to the case of partial wetting, the precise geometry of the resting drop can be determined using the Young's relation [176] as shown in Equation 1.1 and Figure 1.2. When a drop rests on the surface of a solid, the interfacial and surface tensions act along the surfaces and interfaces as shown in Figure 1.2, where σ represents the surface or interfacial tension, and the subscripts sv , lv and sl denote the interfaces solid-vapor, liquid-vapor, and solid-liquid respectively. When the drop is in equilibrium, these

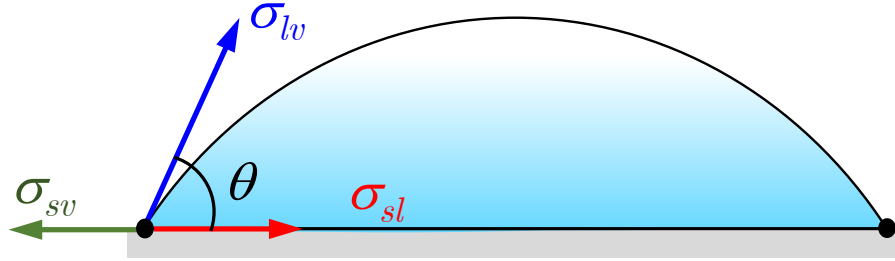


Figure 1.2: A simple representation of a drop resting on a solid substrate. A partially wetting drop rests on a surface with a contact angle of θ . The contact angle can be estimated using the interfacial tensions acting at the three phase contact line.

three forces are in balance and maintain the shape of the drop. The balance of these three forces simplifies to the Young relation as shown in Equation 1.1.

$$\sigma_{sv} = \sigma_{sl} + \sigma_{lv} \cos(\theta) \quad (1.1)$$

The contact angle θ can thus be calculated as shown in Equation 1.2 if one has knowledge of the three interfacial tensions.

$$\theta = \cos^{-1} \left(\frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} \right) \quad (1.2)$$

Similar to wetting, if a liquid is forced to cover the surface of a substrate such that the surface energy of the system is high, it tries to dewet the surface to minimize the surface energy. Figure 1.3 shows the different stages in the dewetting of a film. Now consider a drop which inherently wets a surface ie. a system with a dominant adhesive force, and suppose that it is introduced to the surface gently. The drop initially has

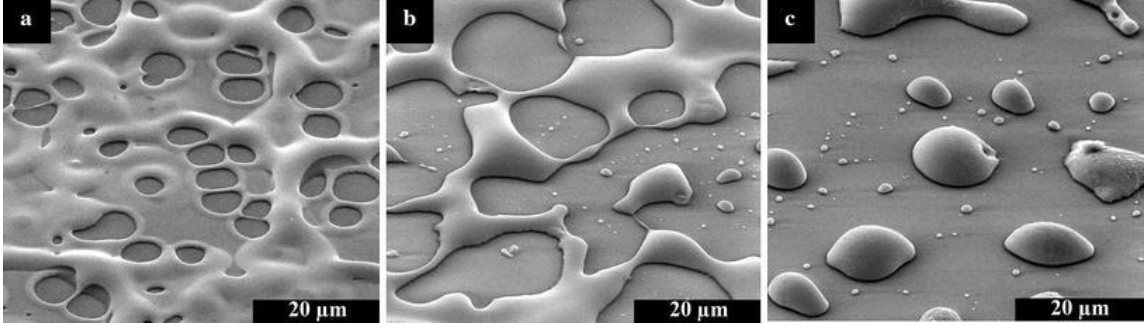


Figure 1.3: SEM images showing dewetting of a glassy thin film on a solid substrate. (a) shows the formation of holes due to rupture of the thin film. (b) shows an intermediate stage in the dewetting of the film where the holes merge and promote bunching up of the liquid. (c) shows bead formation after the liquid has dewet the surface. The SEM images are adapted from [53]

a spherical shape as in Figure 1.1(d), however, the equilibrium state of the liquid represents complete wetting (Figure 1.1(a)). As the drop comes in contact with the surface, it *spreads* to transition from the non-equilibrium state to the equilibrium state. This process of attaining the equilibrium state for a specific liquid-surface combination is known as spreading. The spreading of a drop can not only be driven by the adhesion forces between the drop and surface but can also be a result of the gravitational forces in the case of drops whose characteristic length is larger than the liquid's capillary length. If the diameter of the drop is greater than the capillary length ($l_c = \sqrt{\sigma/\rho g}$) where σ is the surface tension, ρ is the density, and g is the acceleration due to gravity, then the gravitational forces overshadow the capillary forces and deform the drop to form a puddle. However, this flattening of the drop due to gravity is out of the scope of this study since the characteristic length of the drops are well below the capillary length.

Similar to spreading/wetting, the dewetting of a liquid can take place through different processes. The two most common mechanisms of dewetting are the spinodal dewetting (Figure 1.3) and dewetting due to nucleation. If a liquid film is of considerable thickness (>100 nm), then the film is inherently stable. If an external agent causes rupture on the liquid film, then the film minimizes its surface energy by

retracting and forming beads. The presence of impurities like dust serve as nucleation sites and promote nucleation induced dewetting. Spinodal dewetting occurs when the thickness of the liquid film is < 100 nm. As the thickness is very low, any fluctuations in the thin film causes instability and the film spontaneously ruptures. These holes grow rapidly and merge, causing the liquid to bead up. This type of dewetting is commonly observed in paints. Dewetting can also be observed on liquid substrates if a liquid is forced to cover the surface of a second liquid [102].

1.2 Spreading on Solid Surfaces

Following an understanding of the spreading of drops or slicks, the spreading of drops on different surfaces can now be explored. As described in [section 1.1](#), the spreading of drops on surfaces arises from various factors ranging from gravitational effects as well as surface energy effects (adhesion between phases). The spreading of drops on solid surfaces form the basis of innumerable everyday applications such as ink-jet printing, pesticide deposition on plants, and also drainage of water from highways[145, 19]. In fact it is a very rare occurrence to find a surface that does not contain a layer of fluid on its surface. The spreading of drops on solid surfaces depends largely on the surface chemistry of the surface and the properties of the liquid drop. the surface chemistry can be modified to a great extent either chemically or physically. Chemically, the surface can be modified through standard techniques like silanization [27], or plasma treatment [169], while the physical modification is brought about by manipulating the surface roughness. Occasionally, there can be a combination of the physical and chemical modifications where the silanization process is performed on the textured surfaces. [Figure 1.4](#) shows the various possible methods of surface modification through chemical and physical methods. A relatively recent approach to manipulate the wettability of the surface is the concept of Liquid Impregnated

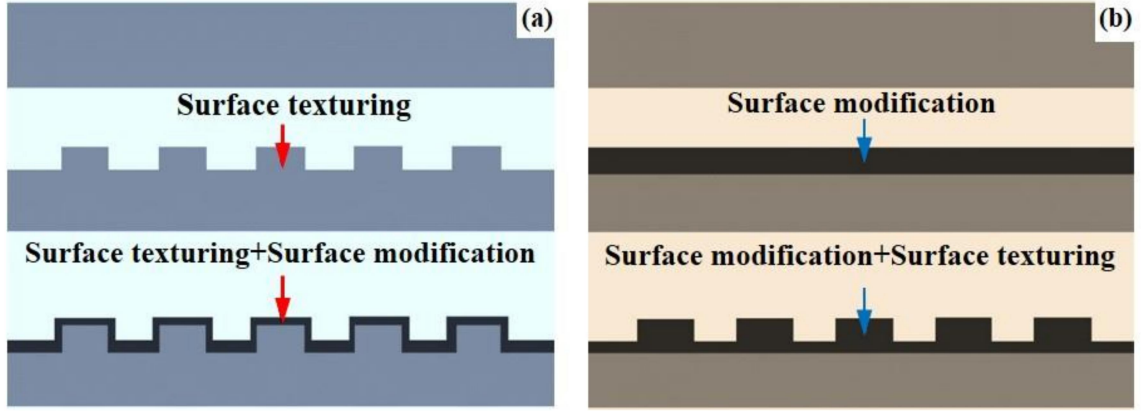


Figure 1.4: The different types of surface modifications done physically and chemically to manipulate wettability of liquids on the surfaces. (a) Shows surface texturing followed by a chemical surface modification while (b) shows the chemical modification followed by a physical texturing.

Surfaces (LIS), where the textured surface is further infused with a liquid to enhance the water repelling properties [129]. The LIS surface is a novel example of physically manipulating the surface to control the interaction between the liquid and surface. Now with the understanding of the different surface modifications, we can proceed to explore the possible states of existence of a drop on a modified surface. Considering a uniform textured surface, the two most popular models which describe the wetting regimes of a resting drop are the Wenzel (W) [165] and the Cassie-Baxter (CB) models [106]. Figure 1.5 shows the possible states in which a drop can rest on a uniform textured surface. In the cassie-Baxter state (Figure 1.5(a)), the liquid does not penetrate the surface asperities and is pinned to the top of the roughness features with an air cushion between the drop and the true surface. On the contrary, in the Wenzel state (Figure 1.5(b)), the liquid penetrates the asperities and is in contact with the roughness features, increasing the adhesive forces between the drop and the surface. When the drop is in either the Wenzel or Cassie-Baxter state, there exists an apparent contact angle symbolizing a contact angle as if the surface had no texture. In the case of the Wenzel state, the apparent contact angle is given by the θ_w as shown

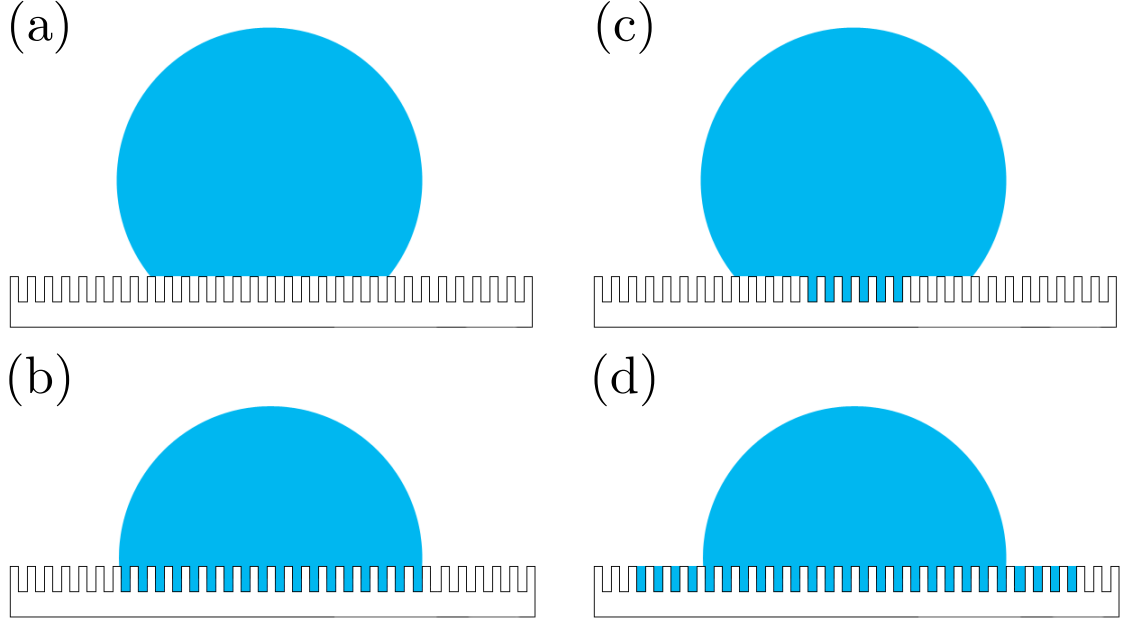


Figure 1.5: The different wetting regimes and wetting transitions of a drop on a textured surface. (a) shows the Cassie Baxter state. (b) represents the Wenzel state while (c) represents the mushroom state observed during the transition from Casie-Baxter to Wenzel state. (d) represents the surface film state where the liquid penetrates the texture on the surface.

in [Equation 1.3](#)

$$\cos(\theta_w) = r \cos(\theta_c) \quad (1.3)$$

where θ_c is the contact angle of the drop on an untextured surface of the same material, and r is the surface roughness ratio defined as the ratio of the true area of the surface to the projected area of the surface. In the case of the Cassie-Baxter state, the apparent contact angle is given by θ_{cb} as shown in [Equation 1.4](#)

$$\cos(\theta_{cb}) = f \cos(\theta_c) - 1 + f \quad (1.4)$$

where f is the area fraction of the surface which is in contact with the liquid. Empirically, it is found that the Cassie-Baxter state represents a hydrophobic surface while the Wenzel state represents a hydrophilic surface [67, 115]. An example in real life showing the contrast of the Cassie-Baxter and the Wenzel states is the resting of drops

on a lotus leaf and a rose petal respectively. On a lotus leaf, the surface roughness promotes the Cassie-Baxter state and the drop slides off very easily, while on a rose petal, the surface texture promotes a Wenzel state. Accordingly, the drops of water on a rose petal seldom roll off and are pinned to it even at extreme angles or when tilted upside down. This remarkably adhering ability is known as the “petal effect” [61]. However, a drop deposited on a surface does not remain in a certain wetting state indefinitely. During the transition of a drop from the Cassie-Baxter state to the Wenzel state, the drop first penetrates the asperities at the center of the drop giving rise to a “mushroom state” as shown in Figure 1.5(c)[83]. The liquid nucleates at the center of the drop as the air pockets become thermodynamically unstable. The liquid then spreads to the edges of the drop to minimize surface energy, until the drop reaches the Wenzel state. This process of spreading of the liquid through the porous surface is known as hemiwicking[15]. In a few cases, if the thermodynamic stability is not reached, or if the the surface energy of the system is not at its lowest possible point, the liquid further penetrates the surface asperities beyond the periphery of the drop leading to a state known as the “sunny side up” state[83] as shown in Figure 1.5(d). The Cassie-Baxter equation however suffers an inconsistency with respect to the apparent contact angle of the drop. To overcome this inconsistency in the equation, various mechanisms at the triple line of contact have been proposed, more popular of which is the existence of a precursor film [24, 20]. The precursor layer is discussed later in the chapter in section 1.4

1.3 Spreading on Liquid Surfaces

Th spreading on liquid surfaces follows more complex dynamics than the spreading on solid surfaces due to the non-rigid nature of the substrate. The wetting properties of the drop on the substrate play a very important role in determining the dynamics of

spreading as will be discussed in this section.

As is the case with drops spreading on solid surfaces, the adhesion forces between the liquids and the cohesion force of the spreading liquid plays the most important role in determining the wetting state of the drop on the substrate as well as the mechanism of spreading. The adhesion and cohesion forces depend on the surface energies of the two liquids and can be represented as a function of the surface and interfacial tensions of the liquids. To clearly understand the role of surface and interfacial tensions in the wetting and spreading of liquids on liquid substrates, let us consider a model case of an oil spreading on the surface of water. The implicit assumption naturally is that the oil and water are absolutely immiscible. Due to a non rigid structure of the liquid surface, an oil resting on the surface of water does not show the non-wetting behavior such as the case in [Figure 1.1\(d\)](#). Instead it either completely wets the surface as in [Figure 1.1\(a\)](#) forming a slick of oil on the surface of water, or partially wets the surface by forming a lens of oil on the surface. The oils, based on their behavior of wetting are termed spreading and non-spreading oils on that particular liquid substrate. If the oil spreads continuously, forming a thin layer of oil, it is known as a spreading oil, while an oil which partially wets the surface forming a lens is known as a non-spreading oil. This behavior of spreading and non-spreading oils can be characterized mathematically using the concept of spreading coefficient (S) which is an estimate of the tendency of a liquid to spread on a surface. The spreading coefficient gives the relative measure of the adhesive and cohesive forces in a 3 fluid system. When a drop is deposited on the surface of the water, it spreads on the surface in an attempt to reach its equilibrium condition based on its tendency to either completely or partially wet the surface. Consider the case of an immiscible oil spreading on the surface of water as shown in [Figure 1.6](#). The schematic in [Figure 1.6](#) shows the various surface and interfacial tensions acting on the spreading lens in the case of a spreading and non-spreading oil. where σ_{wa} and σ_{oa} refer to the surface tensions of water and oil respectively, while σ_{ow}

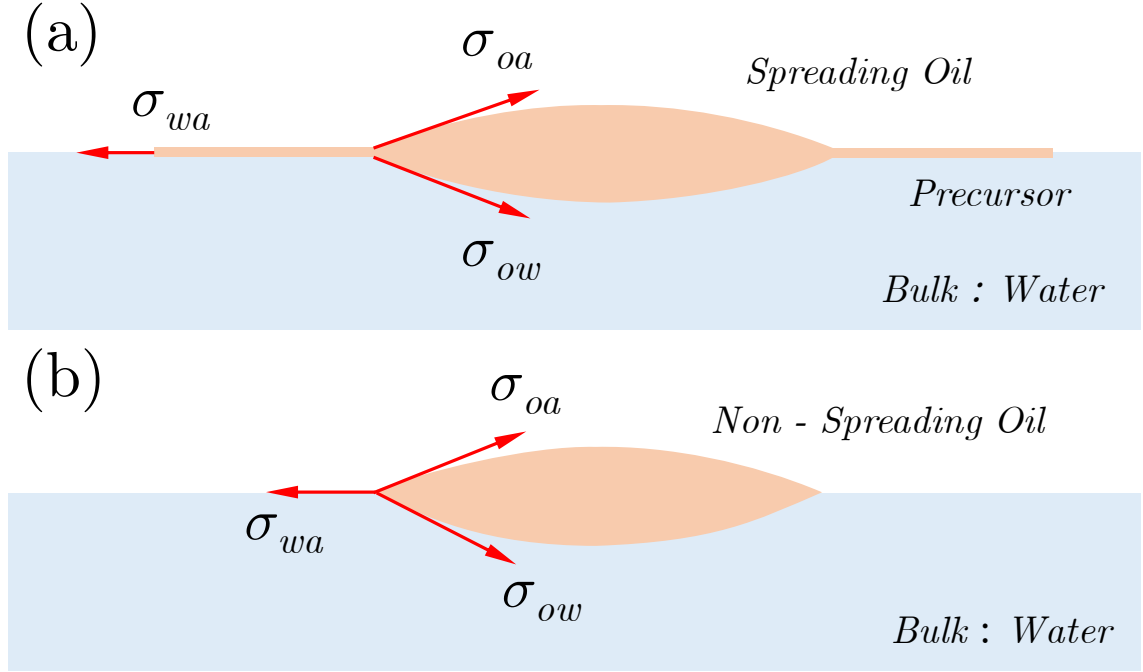


Figure 1.6: The surface tensions σ_{wa} and σ_{oa} , and the interfacial tension σ_{ow} in the case of (a) spreading oils, and (b) non-spreading oils. (a) Shows the presence of the microscopic precursor film in spreading oils.

refers to the interfacial tension of the oil and water. As these interfacial and surface tensions act to reduce the surface energy of the system, they either work towards the adhesion or cohesion of the oil in question. The spreading coefficient, which is the difference in the work of adhesion and the work of cohesion, can be mathematically represented using the surface and interfacial tensions as shown in [Equation 1.5](#).

$$S = \sigma_{wa} - \sigma_{oa} - \sigma_{ow} \quad (1.5)$$

Depending on the surface tensions and interfacial tension of the two phases, a system of two liquids can have either a positive or a negative spreading coefficient. In the event that the spreading coefficient is positive, the oil spreads on the substrate. If the spreading coefficient is negative, the oil is known as a non-spreading oil. If the oil is a non-spreading oil, a lens is formed on the surface of a bulk liquid and a finite contact angle exists. If the oil is a spreading oil, then the presence of a microscopic layer,

known as the precursor layer is observed. The microscopic precursor film continuously spreads on the surface of the water regardless of the macroscopic features of the drop. Even if macroscopically, the drop shrinks and reduces in area, the precursor film continues to spread. However, *Wyart et al.*[26] suggested that the structure of a drop on a surface cannot be predicted by the knowledge of the spreading coefficient (S) alone. An additional parameter, namely the Hamaker constant A must be specified to accurately describe the shape of the resting drop on a surface. Table 1.1 shows the different combinations of the spreading coefficient S and the Hamaker constant A resulting in corresponding wetting regimes.

Table 1.1: Types of Wetting Regimes

Spreading Coefficient(S)	Hamaker Constant(A)	Wetting Regime	Precursor
$S > 0$	$A > 0$	Complete wetting	No
$S > 0$	$A < 0$	Pseudo Partial Wetting	Yes
$S < 0$	$A > 0$	Partial Wetting	No
$S < 0$	$A < 0$	(pseudo) partial wetting	Maybe

1.4 Precursor Layer - The Huh Scriven Paradox

The precursor layer in partially wetting liquids on solids and in non-spreading liquids on liquid substrates. As discussed in section 1.2 and section 1.3, the precursor layer is one of the most widely accepted mechanism to theoretically eliminate a singularity at the three phase contact line, and has been experimentally verified [76]. Consider a drop spreading on a solid surface such that the three phase contact line is moving with a velocity U . Figure 1.7 shows a schematic of the scenario where the liquid advances on the solid substrate. For convenience of calculations, the liquid is assumed to be at rest and the solid substrate is assumed to move with a velocity U in the opposite direction. From a no-slip boundary condition, the fluid elements at the lowest layer of the drop move towards the right at a velocity U , and from mass conservation, the velocity at

the top most part of the cross section moves to the left. The vertical velocity gradient at any arbitrary cross section at a distance x is given by $du_x/dz = U/h(x)$, where $h(x)$ is very small, and hence $h(x) \approx \theta x$. Calculating the viscous dissipation per unit volume as proposed by Landau and Lifshitz [95], we obtain Equation 1.6

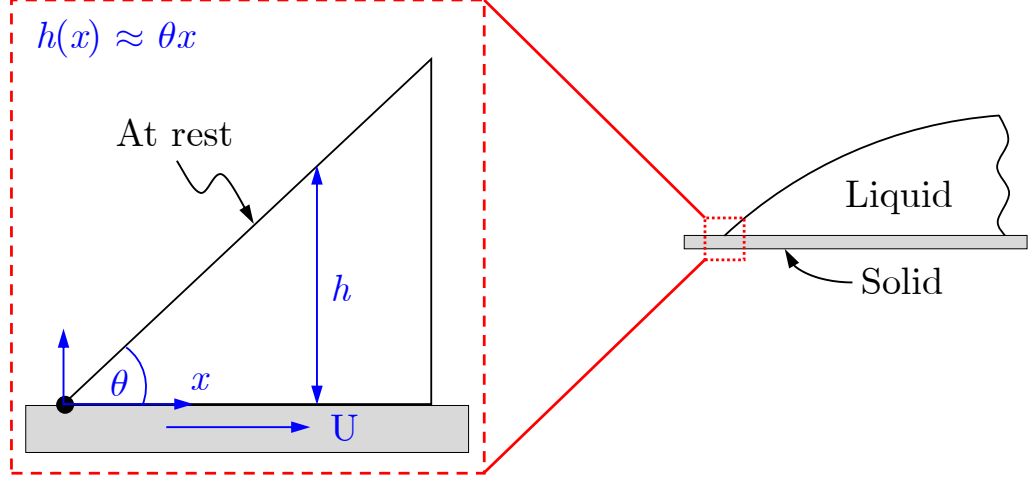


Figure 1.7: The schematic showing the assumed geometry of the advancing drop at the three phase contact line. For convenience of calculations, the liquid is assumed to be at rest and the solid substrate is assumed to move with a velocity U in the opposite direction.

$$\epsilon \approx \mu \left(\frac{du_x}{dz} \right)^2 \quad (1.6)$$

where ϵ is the viscous dissipation, and μ is the dynamic viscosity of the liquid. Calculating the viscous dissipation per unit length and unit time at the contact line by integrating the expression for ϵ , we obtain Equation 1.7

$$\epsilon_C L \simeq \mu \int_L^{L_{out}} \left(\frac{U}{h} \right)^2 h dx = \frac{\mu U^2}{\theta} \ln \left(\frac{L_{out}}{L} \right) \quad (1.7)$$

where L is the assumed thickness of the liquid at the contact line and L_{out} is an arbitrary length scale far from the contact line of the liquid such as the radius of the drop. If the drop strictly maintains a contact angle θ at the contact line, then the value of L must be zero. This, along with a no slip boundary condition, means an

infinite viscous dissipation at the contact line. This, however, is not possible, and hence to account for a finite thickness at the contact line, the concept of a precursor layer which continuously spreads ahead of the macroscopic features of the drop is proposed. The Equation 1.6 and Equation 1.7 have been adapted from [20]. The precursor layer has been experimentally observed using techniques such as ellipsometry, atomic force microscopy, etc [20, 76].

The precursor layer in the case of a liquid substrate, arises from a finite contact angle at the three phase contact line in the case of a non-spreading oil. Similar to a drop spreading on a solid substrate, the finite contact angle at the three phase contact line along with the no-slip boundary condition enforces a logarithmic divergence of the viscous dissipation at the contact line. Hence the precursor layer, which has been experimentally and numerically verified, is introduced to avoid a singularity at the contact line [20].

1.5 Motivation and Objectives for the Thesis

Following the review of common drop interactions with interfaces, and the mechanisms of spreading of liquids, we revert back to fundamental questions concerning the origins and the practical relevance of these interactions. *What causes these interactions? What are the outcomes of these interactions? and Where do these interactions present themselves in nature and everyday life?* The answers to such questions form the basis of the motivation for this thesis. As mentioned in previous sections, there are a multitude of scenarios in daily life where the interaction of oil and water at interfaces become important. This section discusses the most significant phenomenon involving such interactions, which motivates the current study.

1.5.1 Oil Spills

Undoubtedly, oil spills, a phenomenon affecting thousands of human and aquatic lives, forms one of the most important scenarios warranting the current study. Oil spills release around 21,000 tonnes of crude oil into the oceans on an average every year. Although the amount of oil released into the oceans has reduced from about 314,000 tonnes in the 1970s to close to 21,000 tonnes in the 2000s annually, the unpredictability of the deep-water rigs pose a higher risk to the environment [85, 86]. The deep-water blowouts are also harder to contain and in most cases, the oil spilled is inestimable (Deepwater Horizon spill)[109]. Figure 1.8 shows a picture captured by conservation photographer Daniel Beltrá after the Deepwater Horizon oil spill. It was estimated

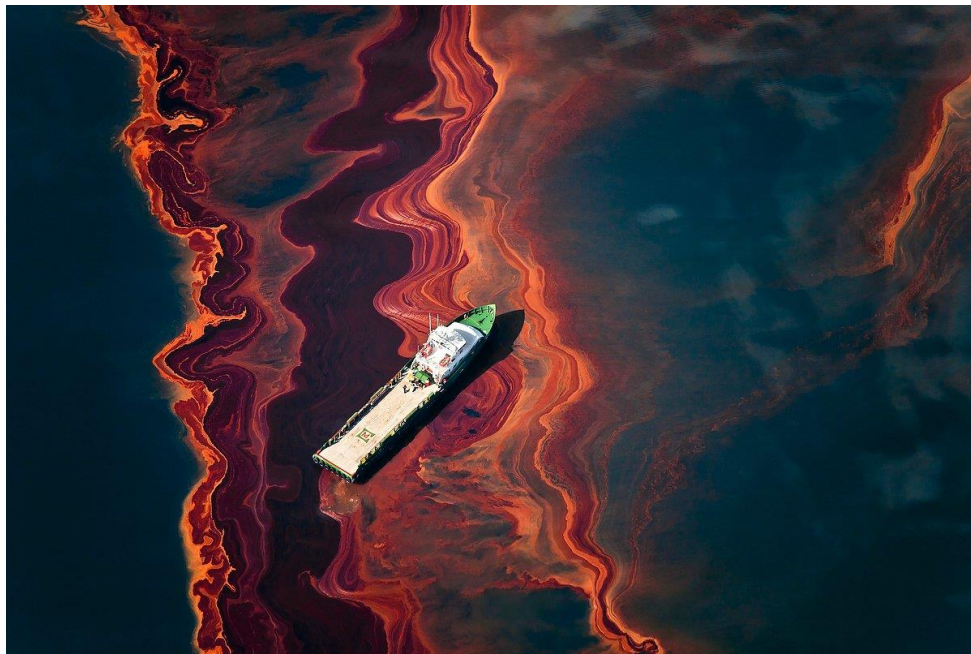


Figure 1.8: An oil slick spreading on the surface of water 22 days after the explosion at the Deepwater Horizon rig. A visual captured by conservation photographer Daniel Beltrá. (*Photo Courtesy: “Spill” book by Daniel Beltrá*)

that during the three months of spillage, the blowout released around 62,000 barrels of oil into the ocean each day [25]. Coral reefs, which house an abundance of flora and fauna including aquatic life crucial to the balance of the underwater ecosystem are damaged beyond redemption and are permanently lost to extinction.

The long term consequences of oil spills include extensive efforts to clean up the residue from the oceans, rehabilitation and conservation of aquatic and animal life, and the economic loss incurred by governments and private organizations. The department of tourism of Louisiana state, USA estimated that the \$247 million loss in leisure spending in tourism to the state after the 2010 gulf oil spill [56]. The aquatic life too is affected severely, an example of which is illustrated in Figure 1.9, which shows a brown pelican bird covered in a thick layer of oil. Thus, the events of oil spills which



Figure 1.9: A brown pelican covered in a thick layer of oil from the 2010 gulf of Mexico oil spill. (*Photo courtesy: National Geographic archives*)

have a tremendous impact on the environment, leaving long lasting traces on the economy, wildlife, and oceans necessitate the study of interactions of oil and water at interfaces. Fundamental processes such as drop impact onto air-water and oil-water interfaces, and the spreading of oils on water form an intrinsic part of the phenomenon of oil spills. Understanding the underlying physical processes occurring during the oil spills will significantly aid in mitigating any such events and also contain the extent of spillage in the event of a catastrophe.

1.5.2 Emulsions

Although events such as oil spills constitute undesirable outcomes, not all oil-water interactions are unwanted. Oil-water interactions when controlled can be used for a plethora of useful applications, the most widespread of which are emulsions. When any substance, solid or liquid, is microscopically suspended in another substance, the mixture is known as a *colloid*. An emulsion is a specific mixture in the broad family of colloids where the *dispersed* phase and the *continuous* phase both consist of immiscible liquids. Table 1.2 shows the different types of colloids that form when various immiscible substances are suspended in each other. Everyday examples are the milk, mayonnaise, butter, salad dressings, pharmaceutical drugs, and cosmetic creams and lotions.

Table 1.2: Types of colloids

Dispersed Phase	Continuous Phase	Type of Colloid	Example of Colloid
Solid	Solid	Solid Sol	Gem Stones
Solid	Liquid	Sol	Paints, Muddy water
Solid	Gas	Aerosol	Smoke dust
Liquid	Solid	gel	Cheese
Liquid	Liquid	Emulsion	Milk
Liquid	Gas	Aerosol	Fog
Gas	Solid	Solid Foam	Pumice Stone
Gas	Liquid	Foam	Froth

The most commonly observed emulsions consist of a mixture of oil and water. Figure 1.10 shows a salad dressing, a classic example of an emulsion. A salad dressing is a mixture of oil and vinegar, two immiscible liquids. Figure 1.10(a) shows the separation of oil and vinegar. After emulsification, the immiscible liquids form a mixture as shown in Figure 1.10. Depending on the dispersed phase and the dispersion medium, the emulsions consisting of oil and water can be categorized into two main types. If the oil is the dispersed phase, the emulsions are termed *oil-in-water* emulsions denoted as *o/w* emulsions. On the other hand if the water is the dispersed phase,

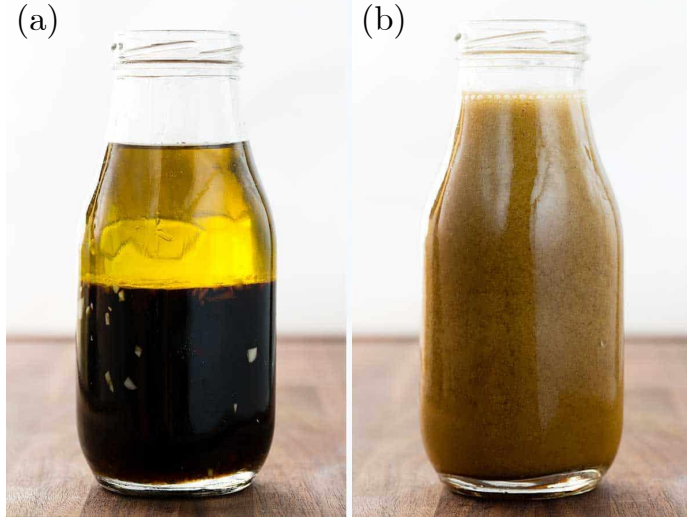


Figure 1.10: An emulsion is a mixture of two immiscible liquids. (a) shows oil floating on vinegar, while (b) shows a salad dressing, an emulsion of oil and vinegar.

the emulsions are termed *water-in-oil* emulsions and are denoted as *w/o* emulsions. One of the most commonly observed oil-water emulsions are cream and butter where cream is an *o/w* emulsion while butter is a *w/o* emulsion. Although these simple emulsions are found in everyday life, they can be further dispersed in other immiscible phase to form a *double emulsion*. Following convention, the double emulsions are named *oil-in-water-in-oil*, and *water-in-oil-in-water* emulsions, and are denoted *o/w/o* and *w/o/w* respectively. Figure 1.11 illustrates a schematic showing the difference in singular and double emulsions. These double emulsions are widely used in many upcoming fields such as microfluidics, nanofluids, and food preparation [116, 64]. Double emulsions are also used in drug delivery [137] to transport drugs to a targeted site in the body. Other uses for emulsions include the coating of photographic films with a layer of emulsions to bring out vivid colors in photographs [135].

Considering the numerous scenarios in which emulsions are used, the manipulation of the elementary interactions of oil and water such as wetting, dewetting, spreading, and impact onto interfaces will enable the advancement of fields like drug delivery, enhanced stability of foods and cosmetic lotions containing emulsions.

The complex physical processes constituting the numerous scenarios mentioned

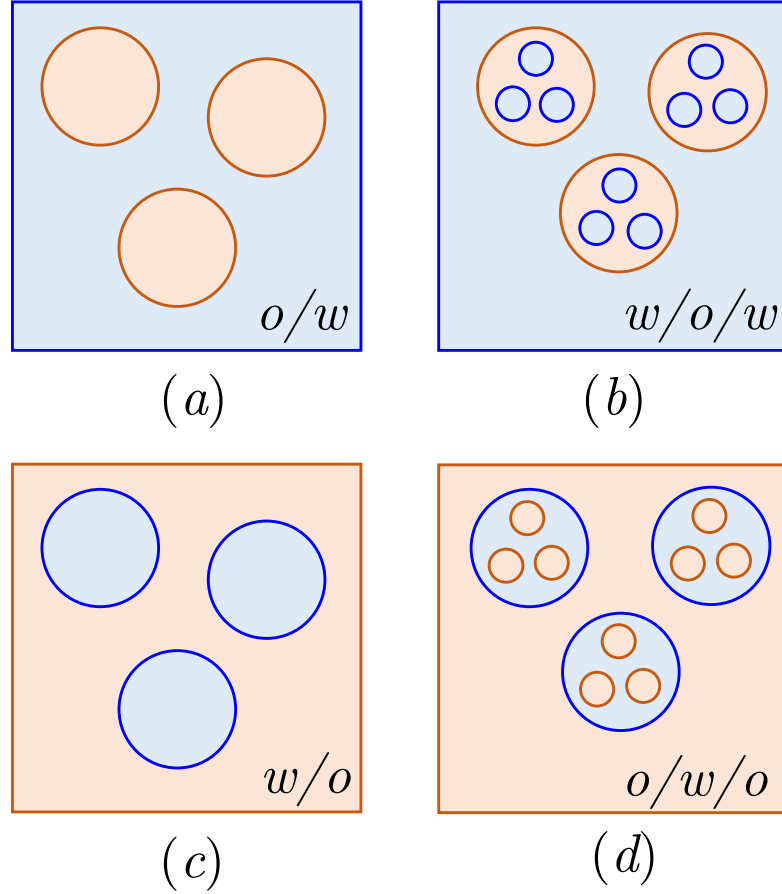


Figure 1.11: The formation of double emulsions from simple emulsions. (a) shows the two different simple emulsions, and (b) shows the two different double emulsions involving oil and water.

above can be understood by simplifying them down to model situations with fewer complexities. For example, a model scenario which represents the spreading of oil during an oil spill is the spreading of one drop on the surface of water. Similarly, the emergence of oil during an underwater oil spill can be modeled by the gentle impact of a drop at the interface of oil and water from beneath the surface of water. Likewise, the objectives of the current study are listed below based on the motivation for the study:

1. The study aims to understand the approach of a single drop of oil to the surface of water focusing on the transition from a drop resting on the surface to a spreading film.

2. The behavior of the spreading of these drops upon contact with the surface of the liquid is of interest and hence the spreading behavior of drops deposited onto the surface of a liquid is studied.
3. In the context of oil spills, the drops of oil can impact the surface of the water from beneath it. The interest of the present work is to understand the spreading of oil drops upon emergence from below the surface of a liquid. Thus the spreading behavior during such a process will be studied.
4. The drop dynamics taking place underneath the surface of the liquid during the emergence of a drop have been recently explored [102] and show an interesting behavior known as partial coalescence which will be discussed in detail in [chapter 2](#). The objective of this work includes manipulating the dynamics taking place underneath the surface to produce useful compounds like emulsions.

1.6 Important Features and Parameters

Since it has been established that the current work involves the interaction of drops and interfaces, it is prudent to understand the physical properties and parameters affecting drop transport in a medium and impact at an interface. When a drop moves or is at rest in a medium, it is acted upon with a lot of forces from the surrounding medium. Depending on the forces acting on the drop and the intrinsic physical properties of the drop, many of the drop's features such as the shape of the drop, velocity of the drop in the medium, and the behavior of the drop upon impact are determined. Salient physical properties which are relevant to the study are the density, viscosity, surface/interfacial tension, and the gravitational forces.

1.6.1 Non Dimensional Parameters

External forces acting on a drop influence its behavior. However, in real scenarios, the forces acting on a drop do not do so in isolation. When multiple forces act on an entity, the combined effect of the forces can be expressed using a single term. To this end, non-dimensional quantities which can be expressed as a function of the physical properties of the drop are frequently used to accurately describe the nature of systems involving drops. The most common non-dimensional numbers employed in a system involving drop impact are: Ohnesorge Number (Oh), Weber Number (We), Bond Number (Bo), Reynold's Number (Re) and Capillary Number (Ca).

The Ohnesorge number gives the ratio of the viscous forces to the inertial and capillary forces. the Oh gives information about the tendency of a drop to retain its shape as opposed to breaking into smaller fragments. [Equation 1.8](#) gives the mathematical definition of the Oh .

$$Oh = \frac{\mu}{\sqrt{\rho\sigma L}} \quad (1.8)$$

An example of the practical application of the significance of Oh is in the context of ink-jet printing. If the Oh of the dispensed ink is too low, the ink is trailed by unwanted “satellite” drops, and if the Oh of the ink is too high then the ink does not get dispensed completely[\[50\]](#).

The Bond number is the ratio between the gravitational and capillary or surface tension forces. [Equation 1.9](#) gives the mathematical definition for the Bond number. $\Delta\rho$ represents the difference in density of the drop and the surrounding medium.

$$Bo = \frac{\Delta\rho g L^2}{\sigma} \quad (1.9)$$

As mentioned in [section 1.6](#), the bond number which compares the gravitational forces and the surface tension forces determines the shape of the drop. For a stationary drop, a $Bo > 1$ signifies the dominance of gravitational forces and the drop is found to form

a puddle. A $Bo < 1$ signifies the dominance of surface tension forces and the drop is found to retain a spherical shape.

The Weber number describes the ratio of the inertial forces to the capillary forces. [Equation 1.10](#) gives the mathematical definition for the Weber number.

$$We = \frac{\rho V^2 L}{\sigma} \quad (1.10)$$

In a falling raindrop, the surface tension forces try to hold the drop together while the inertial forces try to break the drop into smaller fragments. For high We , the velocity of the drop increases tremendously and the surface tension fails to retain the shape of the drop breaking it into smaller fragments. Once the drop breaks into smaller drops, the characteristic length L also reduces and the We is restored to reasonable numbers. This is the reason raindrops cannot be bigger than a certain size.

Capillary number is a result of the comparison between viscous forces and the capillary forces. [Equation 1.11](#) gives the mathematical definition for the Capillary number.

$$Ca = \frac{\mu V}{\sigma} \quad (1.11)$$

In porous media, the flow of a liquid is determined by the Ca . For low Ca , the flow is dominated by the capillary forces while for high Ca , the viscous forces are dominant. Another instance where the Ca becomes significant is the transport of air bubbles inside a liquid. The viscous forces in the liquid tend to deform the drop while the surface tension tries to restore the shape to a sphere. It is important to note that this is different from the forces balance constituting the We .

The Reynold's number gives the relative importance of the viscous and the inertial forces. [Equation 1.12](#) gives the mathematical definition for the Reynold's number.

$$Re = \frac{\rho U L}{\mu} \quad (1.12)$$

The Re is instrumental in determining the order in a flowing jet. Lower Re represents a laminar flow dominated by viscosity while high Re signifies an inertia dominated turbulent flow.

In all the above equations defining the various non-dimensional parameters, the symbols denote universal notations for physical parameters unless noted otherwise. μ is the dynamic viscosity, ρ is the density, σ is the surface tension of the drop, L is the characteristic length (diameter of the drop in this case), g is the acceleration due to gravity and V represents the velocity of the drop.

1.7 Organization of the Thesis

In order to provide the reader with a comprehensive understanding of the current work, the thesis is organized as follows - First, in [chapter 1](#), the basic facets of droplet interactions are discussed with a focus on the spreading of drops on different substrates. The motivation for the thesis is also discussed, along with a brief introduction to the important parameters involved in the drop interactions of wetting and spreading.

[chapter 2](#) will go over the past work related to the current study, namely drop impact and spreading of oil on liquid substrates. It will elaborate on key findings of previous works such as partial coalescence, spreading laws, and wetting and dewetting phenomena, which provide the context and set the groundwork for the current work.

In [chapter 3](#), the experimental methods used to study the phenomena is discussed in detail. All the materials used in the study, along with their significance and role in the experiments are described in detail. The experimental setup for each experiment, the features studied, and the image analysis tools utilized in obtaining useful information is discussed in this chapter.

In [chapter 4](#), the results obtained for **Experiments 1** and **2** are discussed. The results pertaining to the topological transformations occurring during the transition

from a drop to a film, in addition to the spreading behavior of the oils upon deposition are discussed in detail in this chapter.

[chapter 5](#) details the results of **Experiment 3** which studies the spreading of drops when introduced beneath the surface of a liquid. The emergence of the liquids onto the surface is described on the basis of previous work, and the current findings pertaining to spreading behavior is discussed.

Next, the material synthesis techniques utilized in manipulating the dynamics and outcome of the emergence of a drop from below the surface of a liquid is discussed in [chapter 6](#). The methodologies employed in manipulating the drops and any additional particles added to the system are also described in this chapter.

Finally, [chapter 7](#) provides a summary of the entire work. The concluding statements regarding the results, and recommendations for future work are discussed in this chapter.

Chapter 2

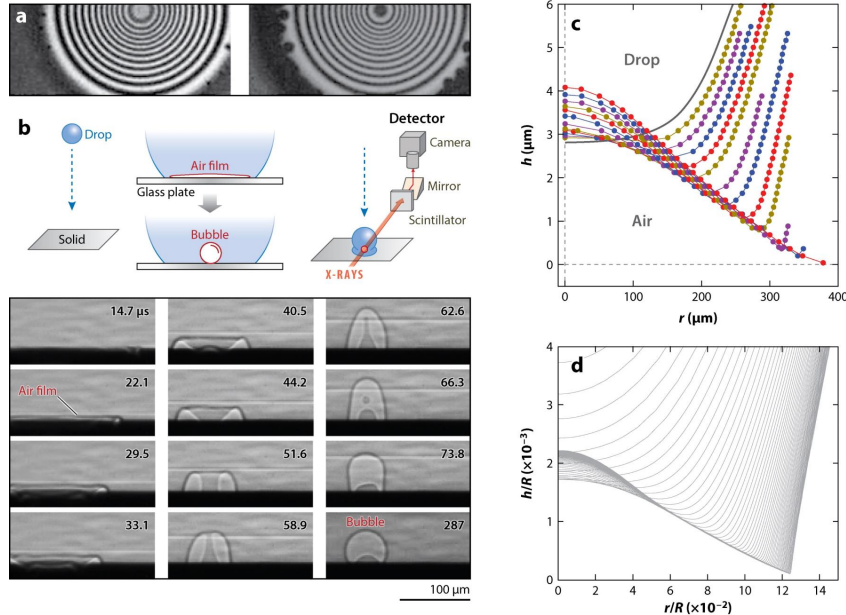
Literature Survey

In [chapter 1](#), it is established that the current study revolves around the dynamics arising from an interaction of a drop with an interface, more importantly the impact and spreading of a drop onto an air-liquid interface. Spreading of oils on a liquid surface, especially water, is a ubiquitous process that is commonly observed in everyday life. Similar to drop impact, multiple articles have been published on spreading of oil due to its implications on coastal eco-system and aquatic lives [85]. The study of emulsions and their degradation has gained importance in recent times owing to the needs of industries such as food and pharmacy, where the stability of the emulsions is crucial to the shelf life of the products [21, 22, 71, 63]. The coalescence of drops and the study of emulsions is also important in applications like sintering, paint manufacture, and targeted drug delivery. In the Oil and gas industry, the interaction between oil and water gains significance during sequestration of oil, where CO_2 and water, among other constituents are injected with high pressure into underground oil reserves to flush out the trapped oil[65, 44]. This process of CO_2 and water sequestration is especially useful in extracting oil from depleted reservoirs. Thus, it is imperative that the overall dynamics involving oil drop-water interaction be understood. It is thus preferable to be aware of the accompanying phenomena during a drop-interface

interaction and also gain insight into the broader perspective of the current study. This chapter will provide a brief review of previous works on the interaction of drops and interfaces in order to understand the context of the current study. The literature survey will first discuss the previous works in studying the spreading of liquids on solid surfaces and will then proceed to discuss the spreading of liquids on liquid substrates. The review will focus on the spreading of liquids arising as a consequence of impact onto a surface.

2.1 Spreading on Solid Substrates

Drop impact and spreading onto a solid surface is a ubiquitous phenomenon and is encountered in many technical applications such as ink-jet printing, spray and coatings industries, forensics etc[173]. A drop impact is characterized by many variables, most important of which is the surface onto which the drop is impacting. The drop may impact a smooth, rough, or a textured surface. The other variables include the angle of impact, size of the impacting drop, velocity of the drop and the liquid properties of the drop. Although the numerous variables during drop impact make it difficult to characterize features across all of them, there exist a few common features do exist during the initial stages of impact. When a drop approaches a surface with considerable velocity, a thin air film trapped between the drop and the surface exerts a pressure on the drop. The pressure is greater at the center of the drop when compared to the periphery. As the drop spreads upon impact, it thins out forming a thin film. At sufficiently small scales, an additional pressure known as the disjoining pressure acts on the thin film causing the formation of a dimple[125, 97]. The small volume of drop is known to shrink to a bubble to minimize surface energy, and attempts have been made to measure the thickness of the thin air disc [142, 101]. Following the initial dynamics, depending on the velocity and the physical properties of the



R Josserand C, Thoroddsen ST. 2016.
Annu. Rev. Fluid Mech. 48:365–91

Figure 2.1: Image showing a review of previous work on the visualization of the dimple. For more information, refer to *Josserand et al.* (2016) [87]

impacting drop, the outcome could result in one of the following - deposition, rebound, corona splashing, prompt splashing, or lamella spreading[87]. In addition to these spreading outcomes, *Yokoi* (2011) and *Driscoll* (2011) observed fingering through experiments and direct numerical simulations [175, 54]. These spreading phenomena on solids, especially fingering and splattering have a tremendous impact in decoding forensic evidence about a victim's position [93]. The dynamics of spreading primarily on solids have been studied extensively, and the existence of the precursor film has been verified.

2.1.1 Morphology of Liquid drop during spreading

The precursor layer, as discussed in chapter 1 has been proposed to eliminate a paradox of singularity at the three phase contact line[20]. Experimentally, the precursor layer has been experimentally investigated by *Kavehpour et al.*[88] using a phase shifting Laser Feedback Interferometer (psLFI). They verified the theoretical predictions of the

logarithmic dependence of the spreading velocity on the capillary number by de Gennes and also the variation of apparent contact angle as predicted by the Hoffman-Tanner-Voinov [88]. Figure 2.2 shows a schematic by Kavehpour *et al.* (2003) illustrating the macroscopic and microscopic features of a spreading drop. Both the macroscopic and microscopic features of the drop were investigated by Kavehpour *et al.*

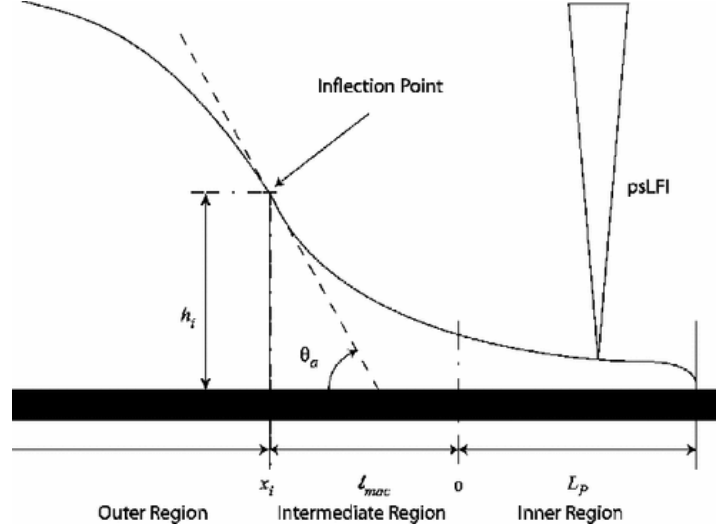


Figure 2.2: The schematic showing the macroscopic and microscopic features of a spreading drop. The precursor layer constitutes a microscopic layer advancing the macroscopic features of a drop while spreading. Used with permission from [88]

2.2 Spreading on Liquid Substrates

Although drop impact on liquid substrates has been studied for over a hundred years now[166], it still retains interest due to rich underlying physics. Worthington[166] was the one of the first researchers to have investigated drop dynamics upon impact on a liquid surface and ever since, multiple articles have been published investigating drop impact on a liquid surface [173, 136]. Similar to drop impact on a solid substrate, the drop impact and the accompanying drop behavior on a liquid substrate can be extremely diverse and involved, and is dependent on the impact velocity, shape of the drop, size of the drop, and the physical properties of the drop, which includes viscosity,

density and surface tension. Recent works have found that the outcome of drop behavior is also directly dependent on the type of substrate[39, 38]. Figure 2.3 shows

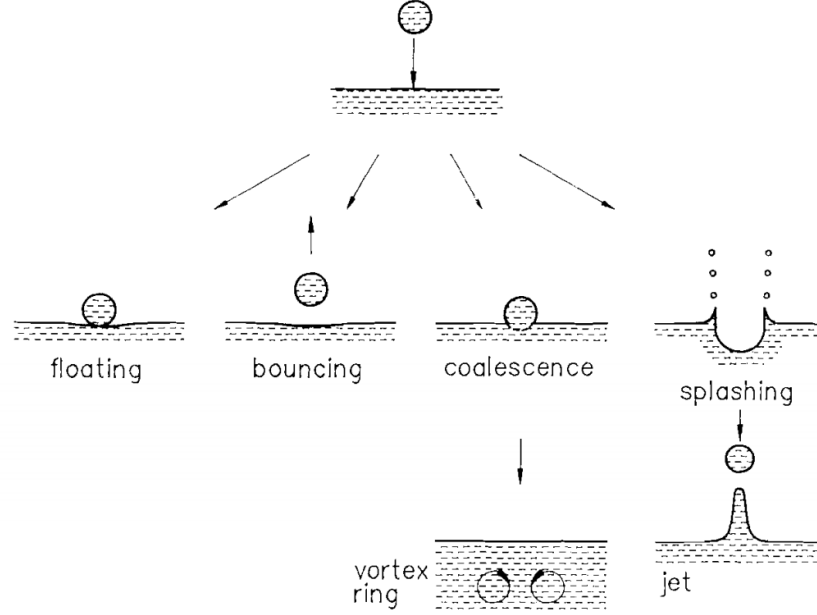


Figure 2.3: The possible outcomes when a drop impacts a liquid surface. The outcomes depend on the physical properties of the drop as well as the impact conditions such as the impact velocity, shape of the drop, and angle of impact. Used with permission from [136]

the possible outcomes when a drop impact a liquid surface. The figure is adapted from [136]. As seen in Figure 2.3, a drop when impacted upon a liquid surface can produce many varied outcomes. The drop can float, bounce or coalesce with the underlying bulk liquid. If the velocity of impact is high enough, the coalescence process also shows a splashing of the bulk liquid and drop. Figure 2.4 shows the splashing of the bulk liquid when a drop impacts onto the surface with a sufficiently high velocity [173]. When the impact velocity is moderate, the drop does not splash and instead produces a jet [173]. As seen in Figure 2.3, when a drop is impacted gently onto the surface of a liquid substrate, it merges with the substrate. If the liquid is chemically identical to the substrate, the merger is termed coalescence. If the drop and substrate are dissimilar, the drop spreads on the substrate [136]. This spreading of oils on merger

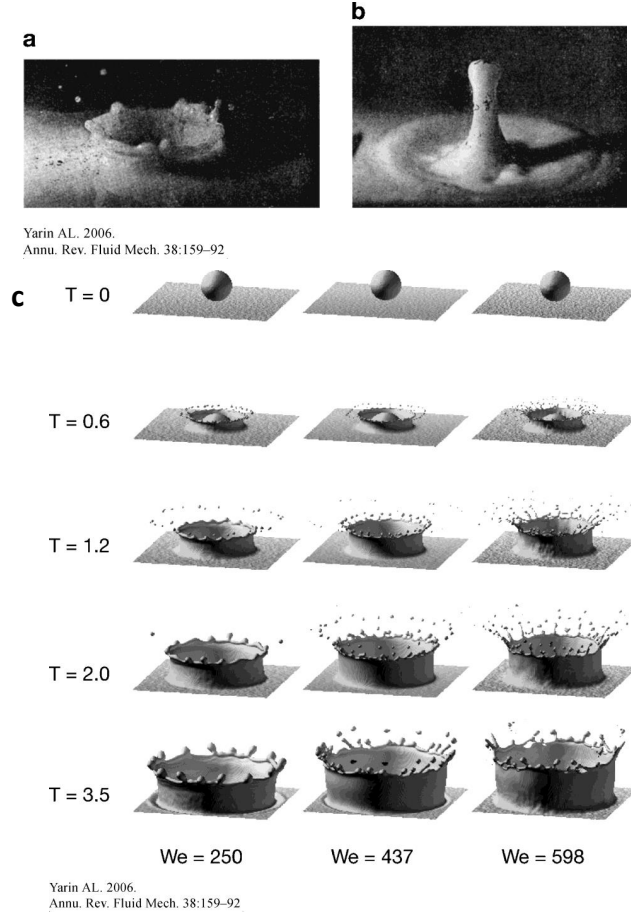


Figure 2.4: The various features of a drop impact on a liquid substrate based on the impact velocity. (a) and (b) show pictures from Worthington’s study on the different kinds of outcomes based on the impact velocity of a drop with the (a) splashing and (b) jetting of the bulk liquid. (c) Shows a direct numerical simulation of a drop impacting a liquid surface. If the viscosity of the bulk liquid is sufficiently low, the crown splash shows a fingering pattern which ejects multiple drops into the ambient air. Adapted with permission from [173]

with a liquid substrate has been studied extensively, and a number of spreading laws have been proposed. A select few are discussed below.

2.3 Spreading Laws on Solids

Largely, drop impact on solid surface has been explored with the intent of understanding the macroscopic spreading, and determining the splash regimes such as lamella splash, corona splash, and crown splash. Over the years, many spreading laws were proposed

to describe the macroscopic spreading of a drop on a solid surface. Some of the spreading laws have been experimentally verified, while others are only a theoretical model. The most commonly used and observed spreading laws are listed below along with the dominant driving and dissipation forces.

2.3.1 Tanner’s Law for Solids

The most widely accepted and experimentally validated model is Tanner’s law which predicts the radius of a small viscous drop spreading as given in [Equation 2.1](#)

$$r(t) = \left[\frac{10\sigma}{9B\mu} \left(\frac{4V}{\pi} \right)^3 \right]^{1/10} \sim t^{1/10} \quad (2.1)$$

Tanner’s law assumes that the driving force is surface tension and that the viscous forces become significant only at a small region near the contact line and are irrelevant in the bulk of the drop [\[152\]](#).

2.3.2 Spreading on a Solid strip

McHale et al., proposed a spreading law which was based on the surface energy balances and considered viscous dissipation at the contact line. They studied the two-dimensional spreading of a viscous strip of oil and the resulting dependence of the growing radius on time was an extension of the law proposed by Tanner as shown in [Equation 2.2](#) [\[108\]](#).

$$d(t) \sim t^{1/7} \quad (2.2)$$

2.3.3 Effect of Surface Roughness

Cazabat and Cohen-Stuart [\[34\]](#) explored the spreading behavior of drops in the presence of surface roughness, and found a good agreement with Tanner’s law when the surface tension forces were used as the driving force and the viscous dissipation was assumed

at the contact line. Furthermore, their study investigated a regime known as the “pancake” regime where the drop thins out during the spreading process and resembles a pancake. They proposed a new law as shown in [Equation 2.3](#) when the drop spread beyond the partial wetting regime to a “pancake” shape. They showed that in this regime, the spreading is slower and that the viscous dissipation occurred in the bulk of the spreading drop with gravity as a major driving force for the spreading.

$$r(t) \sim t^{1/10} \quad (\text{surface tension regime}) \qquad r(t) \sim t^{1/8} (\text{gravity regime}) \qquad (2.3)$$

2.4 Spreading Laws on Liquids

2.4.1 Spreading of Oil Slicks

During the spread of oils, depending on the shape of the drop, different forces are dominant and are responsible for the spreading of the oil drop or oil slick. For example, although gravity acts vertically downwards, it also exerts facilitates a sideways spreading in oil films which are thick enough by creating a pressure difference in the thicker and thinner parts of the spreading drop. As the thickness of the film becomes uniform, the dominance of the gravity force reduces. Secondly, a constant surface tension force near the edge of the spreading film at the three phase contact line works to spread the drop. *Fay and Hoult* [\[59\]](#) provided a comprehensive review of all the possible spreading regimes based on various forces in dominance. Further, they classified the spreading regimes into one-dimensional and axisymmetric for each force in dominance and proposed spreading law coefficients for them. [Table 2.1](#) and [Table 2.2](#) show the spreading laws and the corresponding coefficients under dominant forces. The tables have been adapted from [\[59\]](#).

Table 2.1: Spreading laws for Oil slicks (*Fay and Hoult* (1971))

Dominant Force	One Dimensional	Axisymmetric
Inertial	$l = k_{1i}(\delta g A t^2)^{1/3}$	$r = k_{2i}(\delta g V t^2)^{1/4}$
Viscous	$l = k_{1v}(\delta g A^2 t^{3/2} / \nu^{1/2})^{1/4}$	$r = k_{2v}(\delta g V^2 t^{1/2} / \nu^{1/2})^{1/6}$
Surface Tension	$l = k_{1t}(\sigma^2 t^3 / \rho^2 \nu)^{1/4}$	$r = k_{2t}(\sigma^2 t^3)^{1/4}$

Table 2.2: Spreading laws Coefficients (*Fay and Hoult* (1971))

Dominant Force	One Dimensional	Axisymmetric
Inertial	$k_{1i} = 1.5$	$k_{2i} = 1.14$
Viscous	$k_{1v} = 1.5$	$k_{2v} = 1.45$
Surface Tension	$k_{1t} = 1.33$	$k_{2t} = 2.30$

2.4.2 Spreading on Immiscible Liquid Substrates

Recently, *Rahman et al.* (2018) studied the spreading of a drop on the surface of an immiscible liquid and proposed a spreading law based on the empirical curve fitting of the experimental data. The law proposed by them predicts the spreading of the drops during the later part of the spreading. [133]. Equation 2.4 gives the spreading law proposed by them.

$$\frac{r}{R_e} = 1 - \exp\left(\frac{-\beta t}{\tau}\right) \quad (2.4)$$

where R_e is the equilibrium film radius, τ is the inertial time scale, and β is a time constant. Rahman et al hypothesize that the time constant is a function of the viscous force acting on the drop.

2.4.3 Joos Law

Joos *et al.* [14] predicted the evolution of the radius of the precursor layer in spreading films on liquids. Equation 2.5 shows the prediction of the radius of the precursor layer.

$$r = \sqrt{\frac{4}{3}} \sqrt{\frac{S}{\rho^{1/2} \mu^{1/2}}} \cdot t^{3/4} \quad (2.5)$$

where S is the spreading coefficient of the oil on the substrate, t is the time, ρ is the density and μ is the viscosity of the bulk liquid (water in our case).

2.5 Coalescence on Liquids

The gentle impact of an oil drop on a flat liquid interface may either result in complete coalescence of the drop, where in the oil drop completely spreads on the liquid surface forming thin film or may result in partial merger, leaving a smaller daughter droplet behind to rebound on the interface. Even in drop impacts with moderate and low impact velocities, the impacting drop can generate a cavity which subsequently collapses and creates a jet. The jet travels upwards with a velocity sufficient enough to break off a droplet[111]. This phenomenon where the coalescence of the drop is incomplete is termed as *partial coalescence*. Although initial reports of partial coalescence date back to the 1960s [36], many subsequent attempts were made to explain the mechanism of partial coalescence. Charles and Mason were the first ones to attempt at explaining the mechanism of Partial Coalescence by considering only the viscosity ratio [36, 35]. The concept of partial coalescence has also been explored by studying the bursting of air bubbles at a liquid-air interface [66, 163, 162]. Leblanc studied partial coalescence in detail through which he investigated the stability of the emulsions. Thoroddsen observed that partial coalescence may occur several times in succession to form a cascade of daughter droplets, each smaller than before[155,

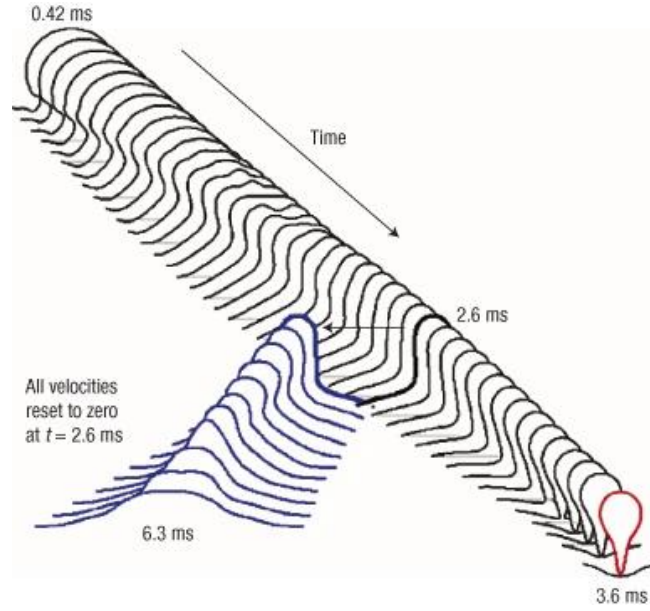


Figure 2.5: The mechanism of partial coalescence as proposed by *Blanchette et al.*[17]. Blanchette proposed that for ethanol drops coalescing with an identical bulk, all velocities reset to zero at 2.6 ms.

[156]. Blanchette, Kavehpour, Mandre have all attempted at explaining the mechanism involved in partial coalescence. Studies also report the effect of electric fields[7, 3, 73, 114] and vibrating surfaces[gilet2009, 68] on the behavior of a drop upon impact. Blanchette et al. [17] studied the mechanism of partial coalescence and identified the role of capillary waves in the process of partial coalescence. Figure 2.5 shows the profile of a coalescing ethanol drop as proposed by *Blanchette et al.* (2006) [17]. They proposed that when an ethanol drop collapses with an identical bulk, the capillary waves determine whether the drop will coalesce completely or partially. At $t = 2.6$ ms, the velocity of the collapsing drop reset to 0, and the drop could take one of two possible paths to result in either partial or complete coalescence. Chen and Mandre studied the mechanism of partial coalescence of identical fluids experimentally and proposed different regimes based on the Ohnesorge and Bond numbers. Figure 2.6 shows the experimental results of Chen and Mandre [39] which show similar results as that of Blanchette et al. While much of the present literature is focused on explaining

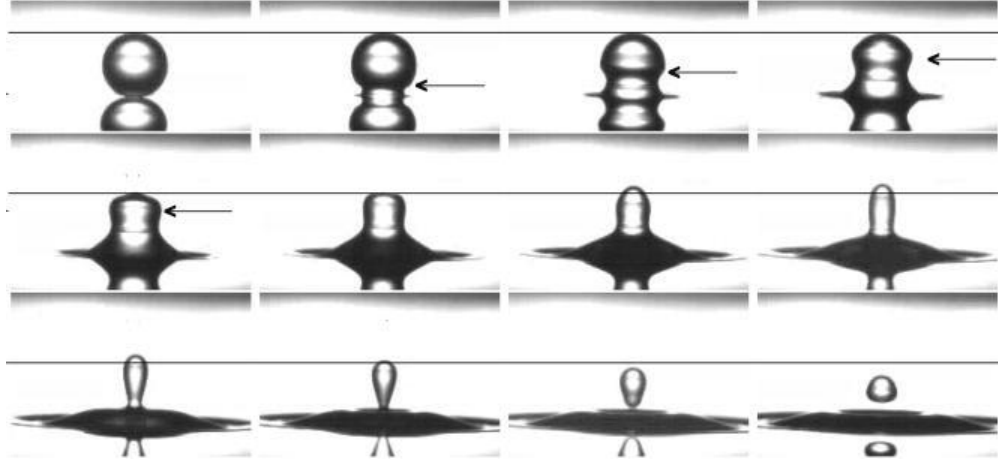


Figure 2.6: Experimental results of Chen and Mandre show the partial coalescence of a water droplet with an identical bulk [39]

the mechanism of partial coalescence and sprading during complete coalescence, the overall dynamics of the drop behavior from the approach of a drop towards the interface to the complete merger of the drop has not been explored. In addition to the spreading, dewetting of liquids on substrates has been explored to great extent.

2.6 Dewetting on Solids

Dewetting on solids has numerous practical applications such as producing corrugated surfaces. Spinodal dewetting is frequently used to create self assembled bead patterns [100]. Recently, *Naffouti et al.* explored templated dewetting (Figure 2.7) to produce nanoscale architectures of monocrystalline silicon on insulator chips [117]. Figure 2.7 shows the different patterns created through Electron Beam Lithography (EBL) where micro features were engrained onto the insulator material. *Trautmann et al.*[158] used modelling to predict the deweting patterns and control the architecture of the dewetting beads on a silicon wafer. These predictions help in designing micro and nano scale insulator chips.

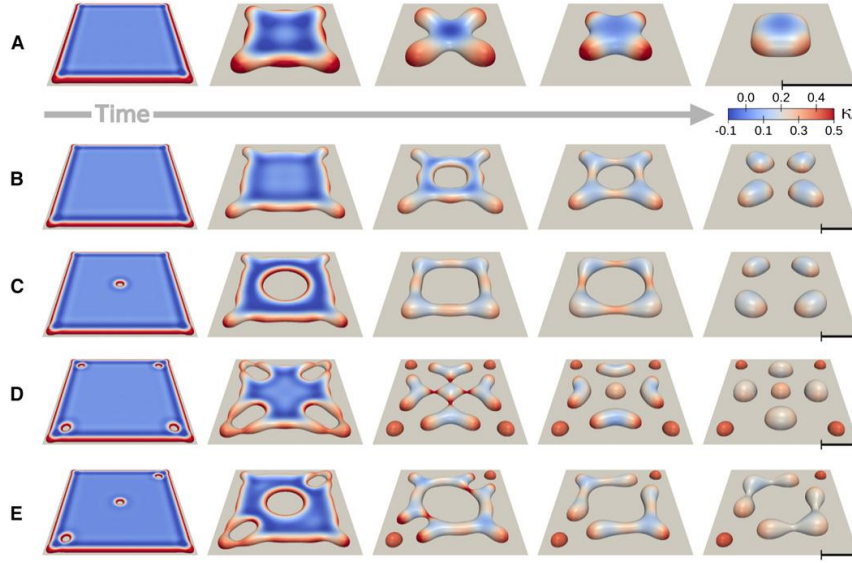


Figure 2.7: The different dewetting patterns achieved through templated solid-state dewetting. [117]

2.7 Dewetting on Liquids

Dewetting of liquids on liquids has been reported by *Wyart et al.*[170] after an investigation of different regimes and cases such as dewetting on thin films, dewetting on stratified liquids etc. *Wyart et al.* used viscous liquids to study the dewetting of liquids as viscous liquids provide advantages like homogenous stratification of liquids, easy measurement of the retracting films through tensiometry etc. They also studied nucleation of the holes in liquid-liquid dewetting and proposed a growth law for the radius of the hole after rupture. *Kostourou et al.* compared the experimental and theoretical results of the dewetting of thin polystyrene films on polymethylmethacrylate (PMMA) and focused on the evolution of the retracting rim[91]. They found that the rates of dewetting increased with an increase in viscosity. Recently, Lolla [102] studied the dewetting of liquids on liquid drops, most relevant to the study of oil spills and reported partial coalescence under the surface of the bulk liquid.

2.8 Computational Studies

Recently, with increased computational capacity, progress has been made in studying drop impact and coalescence through numerical simulations [32]. *Blanchette et al.* were one of the first to explain the mechanism of partial coalescence through simulations. Since then, a number of scenarios have been modeled numerically in order to study detailed features of drop impact and spreading. Recently, *Deka et al.* [49] studied the partial coalescence of two unequally sized drops. Figure 2.8 shows the comparison of the computational and experimental results from the study of partial coalescence of two unequal drops. As can be seen from Figure 2.8, the experimental and numerical

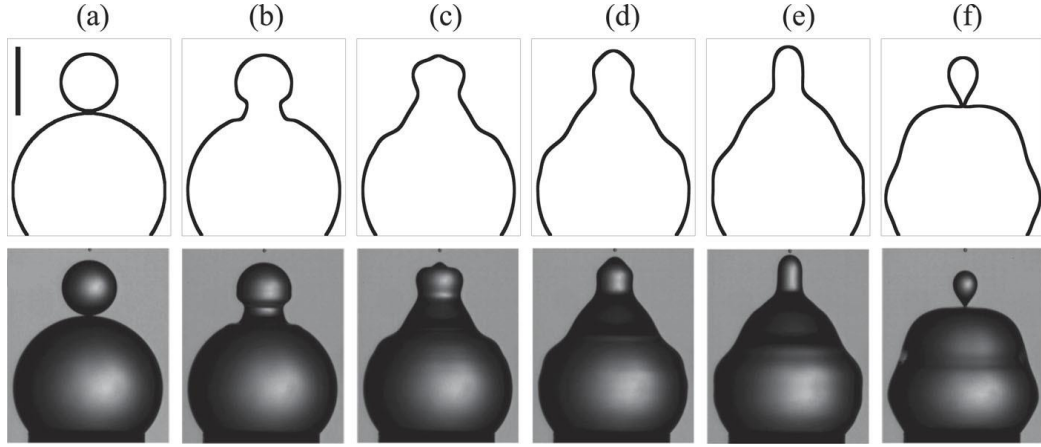


Figure 2.8: The comparison of the experimental and numerical modeling of the partial coalescence of two unequal drops. Used with permission from [49].

results match very accurately, and prove that complex scenarios can be modeled using simulations. Since the scenarios in real life are not as ideal as benchtop experiments, modeling complex scenarios can be a challenge experimentally. To this end, the computational work pertaining to those scenarios can help elucidate the complicated physics taking place. One example of such a work is the modeling of a drop coalescing with an identical bulk in the presence of surfactants by *Dong et al.* [52]. Figure 2.9 shows the results from *Dong et al.*'s study. The velocity profiles in Figure 2.9 give a very detailed description of the behavior of the drop during its coalescence signifying

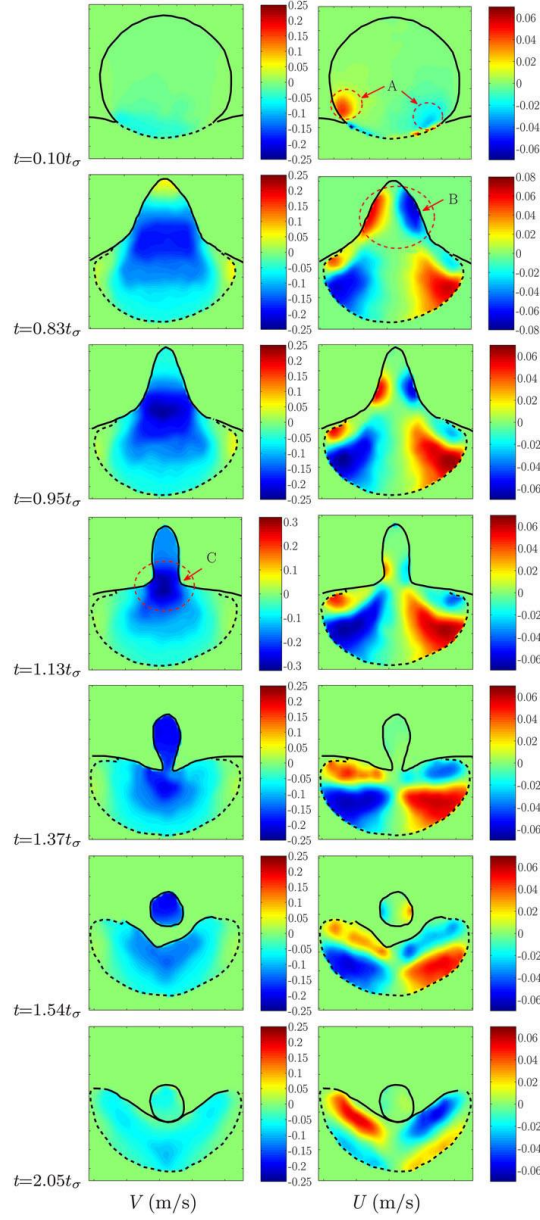


Figure 2.9: Computational results showing the time evolution of a drop coalescing with an identical bulk in the presence of surfactants. "U" and "V" represent the horizontal and vertical velocities respectively. Adapted and reused with permission from [52]

the abilities of a computational model in revealing the intricacies of complex scenarios. Another example of the abilities of a numerical model are seen in Figure 2.10. *Deka et al.* (2019) [48] modeled the coalescence of a compound drop with an interface, and found the effect of the ratio of the two drops in determining the coalescence dynamics of the compound drop.

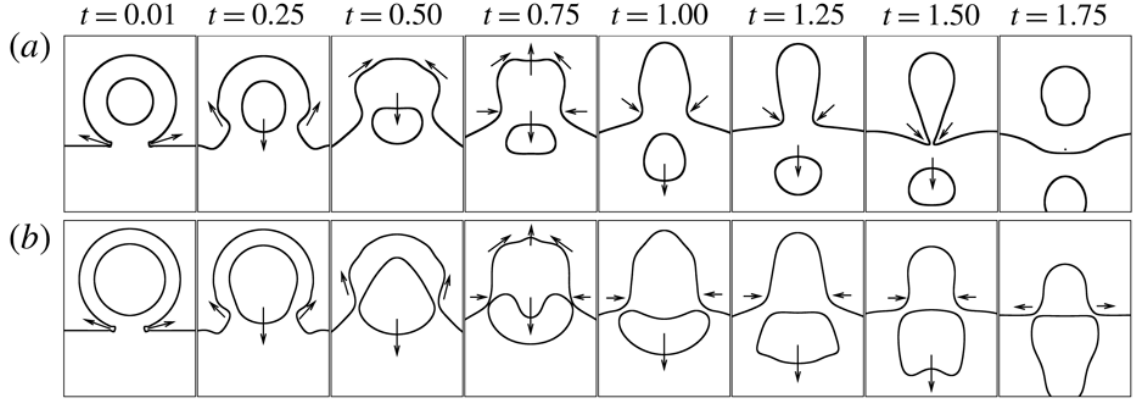


Figure 2.10: The computational results showing the time evolution of a compound drop coalescing with the bulk identical to one of the liquids. The figure shows the dependence of the ratio of the sizes of the two drops in the mechanism of the partial coalescence. used with permission from [48]

Following a literature review of the work related to the current study, we can proceed to establish more defined and specific objectives for the current study. The main objectives of the current investigation lie in the following: (1) Finding the role of capillary waves during the coalescence event and the role of the physical properties of the drop in determining the generation of the daughter droplet. (2) Establishing a regime map clearly demarcating the region of partial coalescence and region of complete coalescence. Establishing a scaling law for each of the various features of the drop as it deforms during coalescence, including the size of the daughter droplet. The various features during drop deformation that will be discussed in detail are: (i) Height of the drop, (ii) Velocity of the tip, (iii) Coalescence time, (iv) Daughter drop, (v) Spreading time and extent of spreading, and (vi) Recoil time. The relation between the strength of capillary waves and various features is also discussed.

Chapter 3

Experimental Methods

This chapter elaborates on the materials and methods used for this study. In order to study the many facets of the interaction of a drop with an interface, three different experiments were conducted:

- **Experiment 1:** Features of drop deformation during partial coalescence
- **Experiment 2:** Spreading characteristics of a drop during partial coalescence
- **Experiment 3:** Spreading characteristics during dewetting

The current chapter is organized as follows - First, in [section 3.1](#), the liquids, dyes, and particles used in the study are described. The next section ([section 3.2](#)) provides a description of the mechanical apparatus used for the experiments along with the methodologies employed in experiments 1 through 3. Following this, [section 3.3](#) describes in detail the features of drop deformation and spreading observed in each phenomenon and highlights the significance of the parameters studied. Lastly, [section 3.4](#) discusses the post-experiment techniques of image analysis used to extract useful information from the captured videos.

3.1 Materials

In order to have a comprehensive understanding of the behavior of various oils during partial coalescence and dewetting, a total of eleven oils were chosen for their physical properties. In tandem with the motivation and objectives of this study, an effort was made to choose oils based on their relevance to practical problems such as oil spills. The following are the oils used for this study:

- **n-Hexadecane** - (ReagentPlus 99%): CAS Number 544-76-3, purchased from Sigma-Aldrich Corporation.
- **Kerosene** (Reagent Grade): CAS Number 8008-20-6, purchased from Sigma-Aldrich Corporation.
- **n-Pentane** (Reagent, 98%): CAS Number 109-66-0, purchased from Sigma-Aldrich Corporation.
- **n-Decane** (Reagent, $\geq 95\%$): CAS Number 124-18-5, purchased from Sigma-Aldrich Corporation.
- **n-Dodecane** (ReagentPlus, $\geq 99\%$): CAS Number 112-40-3, purchased from Sigma-Aldrich Corporation.
- **Tetradecane** ($\geq 99\%$): CAS Number 629-59-4, purchased from Sigma-Aldrich Corporation.
- **Cyclohexane** (ACS Reagent, $\geq 99\%$): CAS Number 110-82-7, purchased from Sigma-Aldrich Corporation
- **Polydimethylsiloxane (PDMS) 0.65 cSt**: CAS Number 107-46-0, purchased from Gelest Inc.

- **Polydimethylsiloxane (PDMS) 1.5 cSt:** CAS Number 9016-00-6/63148-62-9, purchased from Gelest Inc.
- **Polydimethylsiloxane (PDMS) 10 cSt:** CAS Number 9016-00-6/63148-62-9, purchased from Gelest Inc.
- **Polydimethylsiloxane (PDMS) 100 cSt:** CAS Number 9016-00-6/63148-62-9, purchased from Gelest Inc.

The alkanes were chosen for their relative abundance in crude oil and petroleum, and to test for oils with a negative spreading coefficient (n-Hexadecane). Polydimethylsiloxane (PDMS) of varying viscosity was used to study the behavior of oils with a positive spreading coefficient and to understand the role of viscosity during partial coalescence.

In order to select appropriate oils for the study, numerous physical properties like the density (ρ), surface tension (σ_{oa}), interfacial tension of oil and water (σ_{ow}), and their spreading coefficient (S) were taken into consideration. The spreading coefficient is the tendency of a liquid to spread on a liquid or solid surface. It is defined as the difference between the work of adhesion of the two phases and the work of cohesion of the phase under consideration as discussed in [section 1.3](#).

While studying partial coalescence and the spreading of oils on a liquid substrate (Experiments 1 and 2), de-ionized water was used as the bulk liquid. However, while studying the spreading characteristics during dewetting (Experiment 3), the viscosity of the bulk fluid played a major role in determining the outcome of the process, and hence, varying combinations of deionized water and glycerol (CAS number: 56-81-5, ReagentPlus, 99 %) were used as the bulk fluid for **Experiment 3**. The properties of the oils used as drops are shown in table [Table 3.1](#).

The bulk liquids in **Experiment 3** consisted of glycerol and water compounds of varying glycerol concentrations. The method of preparation of these compounds is discussed in [subsection 3.2.2](#). To test for varying viscosity and a wide range

Table 3.1: Properties of the oils used in study

Liquids tested	ρ (kg/m^3)	ν (mm^2/s)	σ_{aw} (mN/m)	σ_{oa} (mN/m)	σ_{ow} (mN/m)	S (mN/m)
Silicone Oil (PDMS)	761	0.65	72	15.9	37.8	18.3
Silicone Oil (PDMS)	853	1.5	72	18	41.7	12.3
Silicone Oil (PDMS)	935	10	72	20	41.3	10.7
Silicone Oil (PDMS)	966	100	72	20.9	40.8	10.3
n-Hexadecane	770	4.25	72	27	52.1	-7.1
Kerosene	810	2.5	72	26.8	34	11.2
n-Pentane	626	0.5	72	15.82	48.15	8.03
n-Decane	726	1.268	72	23.83	51.2	-3.03
Dodecane	746	2.008	72	24.91	51.1	-4.01
Tetradecane	757.88	3.01	72	26.56	50.1	-4.66
Cyclohexane	773.18	1.187	72	26.91	50	-4.91

of Ohnesorge numbers, a total of 5 different compounds were used with glycerol concentrations ranging from 0 - 60 *wt.%* in 20 *wt.%* increments. The physical properties of the bulk fluids are given in [Table 3.2](#).

Table 3.2: Properties of the bulk liquids used in Experiment 3 to study spreading characteristics during dewetting.

Bulk Liquid	Dynamic Viscosity(μ) (Pa-s)	Density(ρ) (kg/m^3)
Water (0% Glycerol)	0.001005	1000
20 % Glycerol	0.00176	1046.9
30 % Glycerol	0.0025	1072.7
40 % Glycerol	0.00372	1099.3
60 % Glycerol	0.0108	1153.8

To visualize the intricate details of the features observed in all experiments, the oils were dyed using either Oil Red O (CAS number: 1320-06-5) or Sudan Blue II (Dye content 98%, CAS number: 17354-14-2), both purchased from Sigma Aldrich Corporation.

3.2 Apparatus

The experiments for this study were carried out using both front lighting reflective photography and the back-lit shadowgraphy depending on the parameters measured. To study all the features of drop deformation during partial coalescence upon a gentle impact of an oils drop onto a liquid surface (**Experiment 1**, side view imaging was used, while top view imaging was used to observe the spreading of the drop in partial coalescence and dewetting (**Experiments 2 and 3**).

3.2.1 Cuvette

A quartz fluorescence cuvette of dimensions $30 \times 30 \times 30$ mm (wall thickness - 1.98 mm) was used to hold the bulk liquid in Experiments 1 and 2. In the process of imaging the drop from the side, (**Experiment 1**) it is crucial to maintain hydrophobicity on the walls of the cuvette so that the bulk liquid does not form a thick meniscus. A very thin interface at the walls of the cuvette allows us to capture the details of drop deformation very close to the interface. In order to achieve hydrophobicity on the walls of the cuvette, a vapor deposition technique was used to coat the walls of the cuvette with a silane (Trichloro [1H, 1H, 2H, 2H - Peflorooctyl] Silane, purchased from Sigma Aldrich Corporation) as described in [subsubsection 3.2.1.1](#).

3.2.1.1 Silanization Process

Prior to silanizing the cuvette, it was cleaned thoroughly using acetone, ethanol, and iso-propanol in succession by placing the cuvette in an immersed bath of the chemical in a sonicator for 5 mins. The process was repeated three times, after which, the cuvette was sonicated in a bath of deionized water. After drying the cuvette with a jet of air, it was placed in a vacuum desiccation chamber along with a microscope slide containing 6-8 drops of $2.5 \mu L$ each of the silane for 8-10 hours.

3.2.2 Glycerol-Water Mixtures

The glycerol-water compounds were prepared by using calculating the desired mass fraction of Glycerol in the mixture. The Glycerol and water were weighed separately using a Mettler Toledo XS64 Excellence XS Analytical Balance (Purchased from Cole-Parmer Instrument Company LLC). Next, the glycerol and water fractions were poured into a beaker and stirred for 90 minutes using a Thermo Scientific Cimatec Stirring Hot Plate and a PTFE Magnetic stirrer Spinbar. In order to ensure accuracy in experiments, the mixtures were freshly prepared for each experimental case, and the degraded mixtures discarded.

3.2.3 High-Speed Imaging

The Photron FASTCAM Mini AX high speed camera, in conjunction with the Photron FASTCAM Viewer software was used to capture the videos for all experiments. All videos were recorded at 4000 f.p.s and at a resolution of 1024×1024 pixels, commensurate with the time scales of the process of partial coalescence and spreading, in order to capture all the distinct features. An exposure time of $5\mu s$ ensured that any initial dynamics occurring during the onset of partial coalescence were captured in detail. The Photron FASTCAM Viewer software was also used to trigger the recording of the high speed camera. High speed imaging requires the use of a strong light source and hence, The Nila Zaila LED light was used as the light source for all experiments. An infinity lens (InfiniProbeTMTS-160) was mounted onto the high speed camera using an F mount to C mount adapter, and was used as the lens for all experiments as it provided a wide range of focus.

3.2.4 Syringe pump

The drops were generated with the help of a Harvard apparatus PHD ULTRATM syringe pump and a HAMILTON, GasTight[®] 1050, 50 ml syringe were used to generate drops. The drops were generated using an infusion rate of $1.67 \mu L$ to minimize any vibrations or disturbance produced from the motor inside the pump. To aide the generation of a consistent drop size for a particular needle, the experimental setup was placed on a vibration damping optical table.

3.2.5 Experiment 1: Features of Drop Deformation in Partial Coalescence

Side view imaging was performed to calibrate We and measure the size of the impacting drop, among other features. A schematic of the experimental setup for the drop impact experiments is shown in [Figure 3.1](#). The syringe was connected to a needle using a transparent PVC tube assembly (purchased from Qosina) of 2 mm ID. The tubing assembly consisted of a male and female luer lock respectively on each end. Blunt head needles of sizes ranging from 14 gauge to 20 gauge were used to generate drops of different sizes.

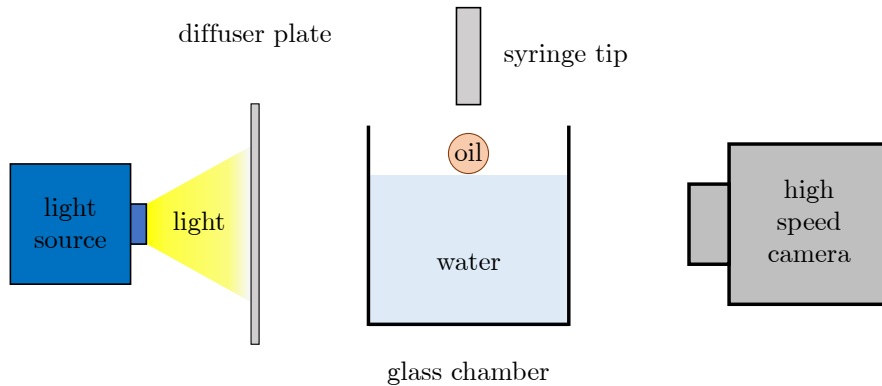


Figure 3.1: Schematic showing the experimental setup for studying the drop deformation features during partial coalescence. The syringe tip is held close enough to the surface of the water to facilitate gentle deposition of oil drops.

3.2.6 Experiment 2: Spreading Characteristics during Partial Coalescence

To study the spreading characteristics of oils during partial coalescence, top view imaging was used as shown in [Figure 3.2](#). Similar to the side view experiments, the top view experiments were executed with backlit imaging to capture the spreading of the drop, however, the orientation of the light source and the camera was slightly different. In this case, the light source was tilted vertically upwards to shine light from the bottom, to obtain a good contrast between the oil drop and the water. Care was taken to select a cuvette of appropriate dimensions ($30 \times 30 \times 30$ mm) such that the size of the cuvette was sufficiently larger than the size of the drop. This was done to ensure that (1) the capillary and menisci effects of the walls do not affect the phenomenon of partial coalescence and (2) the effects of any capillary waves traveling on the surface of the bulk liquid and affecting the process of partial coalescence is minimal. A needle was mounted onto a retort stand and connected to the syringe through a luer lock and PVC pipe assembly. The syringe was mounted onto the syringe pump as described in [subsection 3.2.4](#) to generate drops. In order to capture the spreading of the drop without any obstruction, the needle was moved out of the frame of the high speed camera soon after the drop detached from the needle.

3.2.7 Experiment 3: Spreading during Dewetting

The spreading of oils during dewetting was also studied using the top view imaging technique. However, the orientation of the setup and the apparatus used for drop generation was different. In place of a cuvette, a droplet generator consisting of an aluminum base cuboid and a glass chamber was used to generate drops. Details of the schematic setup and the droplet generator are illustrated in [Figure 3.3](#).

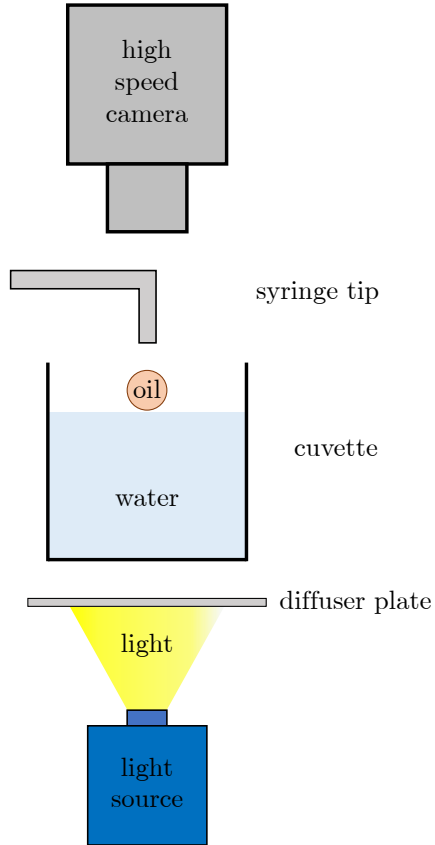


Figure 3.2: Schematic shows the experimental setup for studying the spreading characteristics of oil on water during partial coalescence. The light source, coupled with the diffuser plates provide a strong contrast between the oil drop and the bulk fluid.

3.2.7.1 Drop Generator

The drop generator consists of an aluminum cuboid as a base with an “L” shaped cylindrical channel drilled through it. Both the ends of the channel are drilled, tapped, and threaded to accommodate the fitting of nozzles or luer locks. The top face of the cuboid contains a groove with a gasket for the placing of a glass chamber. It also hosts 4 tall screw stands that act as supports for flanges. To setup the drop generator, a glass chamber (dimensions $30 \times 30 \times 15$ mm) made of boro-silicate glass, is placed in the groove on the aluminum cuboid and the flanges are screwed onto the screw stands such that they hold the glass chamber down, creating a tight seal at the base of the chamber. This ensured that the bulk liquids held in the chamber would not

leak through the gap between the glass chamber and the aluminum cuboid.

To make the drop generator functional, the syringe mounted onto the syringe pump

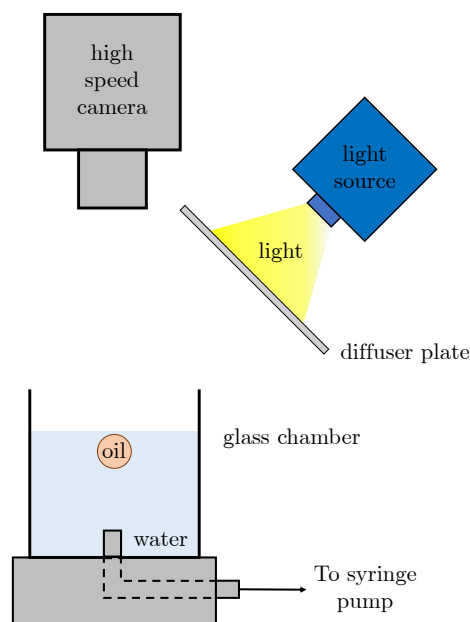


Figure 3.3: Schematic shows the experimental setup used to study the spreading characteristics of oils during dewetting. Front lighting was used to capture the spreading.

was connected to the drop generator using a transparent tube with luer locks on both ends. A nozzle was screwed onto the channel on the top face of the cuboid to generate drops of different sizes. Nozzles of varying sizes were used to control the diameter of the oil drops generated. Since the drop generator was opaque from the bottom, shadowgraphy could not be performed. Instead, the light was placed at an oblique angle from the top and front lighting was used to capture the spreading of oils. The syringe pump was operated as described in [subsection 3.2.4](#) to generate drops of a consistent size. The oils were chosen such that their density was less compared to the density of the bulk liquids. The height of the glass chamber was chosen to be 15 mm to make sure that the drop did not gain momentum due to buoyancy, and impacted the air-water interface gently.

3.3 Parameters Studied

During the partial coalescence of a drop with an immiscible liquid substrate, the drop witnesses many changes to its morphology. As the drop deforms rapidly following the rupture of a thin film of the surrounding fluid, and the subsequent propagation of capillary waves, many distinct features are observed, including the formation of a daughter droplet (secondary droplet). To understand the influence of the transient features on the final outcome, various parameters were studied. The parameters are listed below:

- **Daughter Droplet:** Daughter droplet is the secondary droplet that is left behind as the parent drop merges with the bulk fluid during partial coalescence.

Figure 3.4 shows the radius of the daughter droplet.

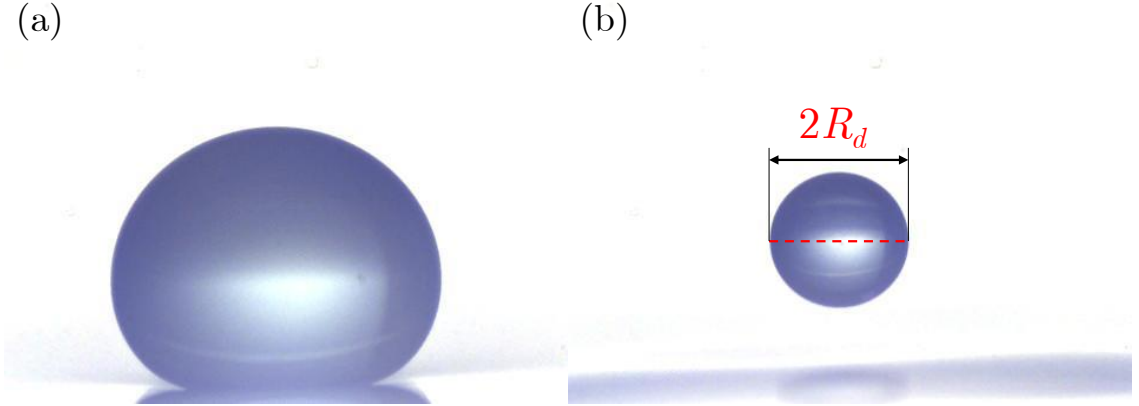


Figure 3.4: (a) Shows the parent drop. (b) Shows the daughter droplet

- **Height of the Drop:** The height of the drop is defined as the distance between the air-bulk liquid interface and the farthest point on the drop. As the capillary waves travel along the surface of the drop, they stretch it upwards and increase the height of the drop. The height of the drop was tracked at every instant to understand the influence of the physical properties of the drop and surrounding bulk fluid on the strength of the capillary waves. Figure 3.5 shows the height of the drop measured at an arbitrary instant during partial coalescence.



Figure 3.5: The height of the deformed drop measured at an arbitrary instant during partial coalescence

- **Maximum Height Attained by the Drop:** Since capillary waves stretch the drop upwards, the maximum height attained by the drop is an indicator of the strength of the capillary waves reaching the apex of the drop. Figure 3.6 shows the maximum height measured

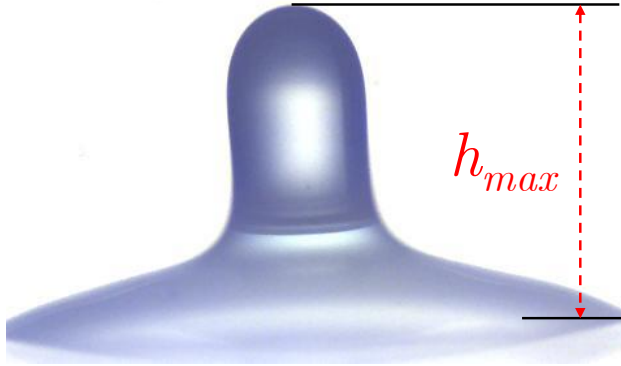


Figure 3.6: The maximum height attained by the drop as the capillary waves stretch the drop upwards.

- **Velocity of the Apex of the Drop:** The formation of a daughter droplet is determined by the rate of vertical and horizontal collapse of the drop. By determining the velocity of the apex of the drop, we can estimate the rate of vertical collapse and eventually predict the formation of a daughter droplet.

The velocity of the apex of the drop is estimated by recording the positions of the apex (X_1, Y_1) and (X_2, Y_2) at two different instances of time t_1 and t_2 respectively, and calculating the velocity using the formula given in [Equation 3.1](#).

$$V_{tip} = \frac{\sqrt{(X_1 - X_2)^2 + (Y_1 - Y_2)^2}}{(t_2 - t_1)} \quad (3.1)$$

- **Coalescence Time:** As the thin film of surrounding fluid separating the drop and the bulk fluid drains out, the drop comes in contact with the bulk fluid and starts to deform with the advent of capillary waves. The coalescence time is thus defined as the time interval between the rupture of the thin film and the complete merger of the oil with the bulk liquid. In case of partial coalescence, the coalescence time is defined as the time interval between the rupture of the film and the pinch off of the daughter droplet. [Figure 3.7](#) shows the instances of time during drop deformation taken into consideration when calculating the coalescence time.

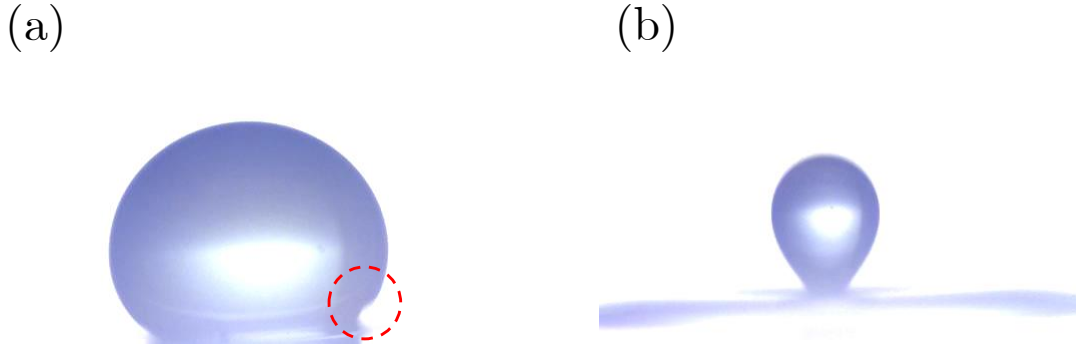


Figure 3.7: The instances of time during the partial coalescence of a drop used for calculating the coalescence time. (a) Shows the time instant at which the air film has drained and the capillary wave propagation is observed. The deformation in the red dotted circle shows the initiation of the capillary waves in the drop. The video frame preceding this is used as the start point for calculating coalescence time. (b) Shows the instant at which the daughter drop pinches off from the parent drop. The video frame succeeding this is taken into consideration when calculating the coalescence time.

- **Collapse Time:** As the capillary waves travel upwards on the surface of the drop, they stretch the drop upwards to a point when the drop attains its maximum height. Following this, the drop collapses vertically, resulting in either partial or complete coalescence. If the horizontal collapse of the drop precedes the vertical collapse, a daughter drop pinches off resulting in partial coalescence. The collapse time in case of partial coalescence is defined as the time interval between the instant that the drop attains its maximum height and the instant the daughter droplet pinches off from the spreading parent drop. In case of complete or delayed coalescence, the collapse time is defined as the time interval between the instant the drop attains its maximum height and the instant the drop completely merges with the bulk liquid. The collapse time of a drop is indirectly proportional to the strength of the capillary waves, and hence measuring the collapse time can give information on the strength of the capillary waves. [Figure 3.8](#) shows the frames of maximum height attained and the complete merger of the drop used to calculate the collapse time of the drop.

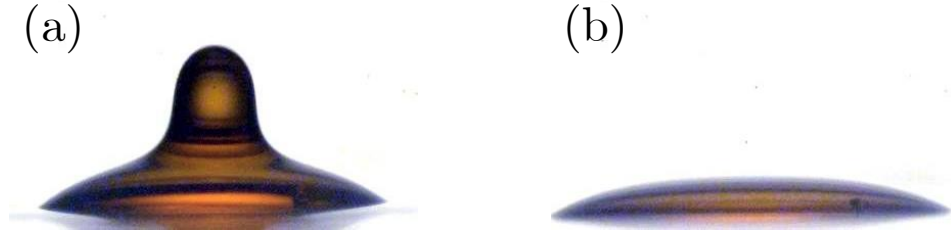


Figure 3.8: The instances of time during a delayed coalescence of a drop used for calculating the collapse time. (a) Shows the time instant at which the drop attains maximum height. (b) Shows the instant at which the drop collapses completely forming a lens on the surface of the bulk liquid.

- **Velocity of the wave front:** The strength of the group of capillary waves traveling on the surface of the drop is dampened by the viscosity of the drop. The velocity of the wavefront is defined as the velocity of the most distinct wave in the group of waves traveling. The velocity of the waves is an indirect measure of the strength of the capillary waves. The velocity of the wavefront is

measured by recording the position of the crest of the most dominant wave at two instances of time and the velocity calculated as given in [Equation 3.1](#).

- **Distance between Waves:** The distance between two most dominant wavefronts in the group of capillary waves is measured. The distance between the wavefronts is a direct indicator of the strength of the waves traveling on the surface of the drop as the waves with lower resistance have pronounced crests and travel with a shorter wavelength. [Figure 3.9](#) shows the measurement of the distance between waves in a drop undergoing partial coalescence.

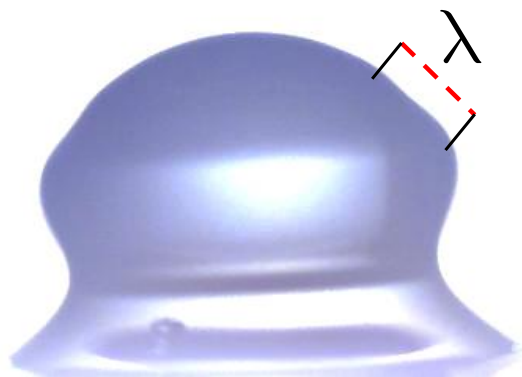


Figure 3.9: The length between successive wavefronts in the group of capillary waves traveling on the surface of the drop.

- **Film Radius of the Spreading Drop:** As the drop begins to merge with the bulk fluid, it starts spreading on the surface of the bulk fluid. Tracking the radius of the film can reveal the behavior of the oils and their extent of spreading especially in the context of oil spills. [Figure 3.10](#) shows the measurements of the radius of the spreading drop at two arbitrary instances of time.
- **Maximum Film Radius:** The spreading characteristics of the drops vary based on the physical properties of the oils. Measuring the maximum radius of

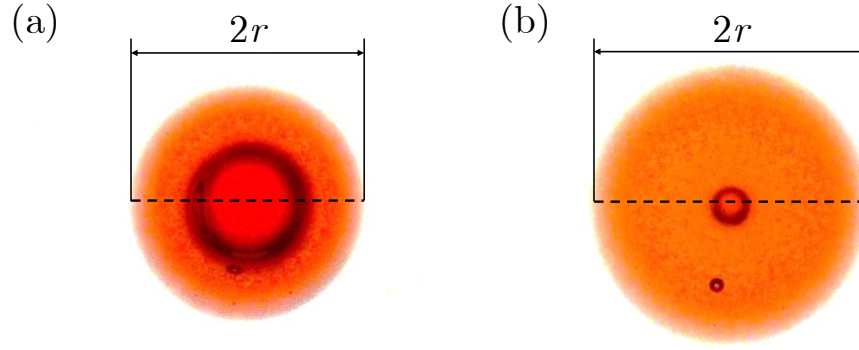


Figure 3.10: The measurement of the radius of the spreading drop at two arbitrary instances of time.

the film during spreading gives us an estimate of the properties of the oil during the transient spreading process. Figure 3.11(a) shows the measurement of the maximum radius of the film as it spreads.

- **Extent of Recoil:** As oils with a lower viscosity spread on the surface of the bulk liquid, they exhibit an oscillatory behavior during the spreading. The extent of recoil is defined as the difference in the maximum and minimum radius of the film after the first recoil event. Figure 3.11 shows the maximum and minimum radius of the film during spreading. The difference between these values is defined as the extent of recoil in this study.

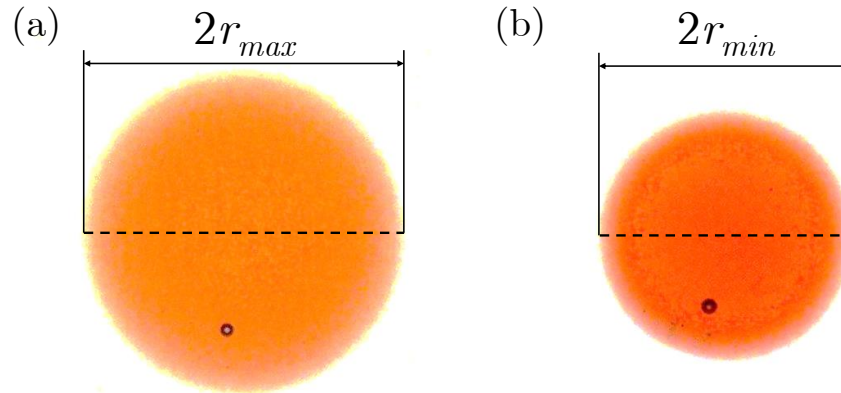


Figure 3.11: Measurement of the (a) maximum (r_{max}) and (b) minimum (r_{min}) radius of the film. The difference between r_{max} and r_{min} is the extent of recoil and the time interval between these two instances is the recoil time.

- **Recoil time:** The recoil time is defined as the time taken by the film to recoil from its maximum size to the minimum size. It is the time interval between the instants of maximum and minimum radius during the first recoil event ([Figure 3.11](#)).

3.4 Image Analysis

Once the videos were captured, they were processed and analyzed using ImageJ software. The process of extracting useful information from raw videos involves roughly 2 steps - (1) Image/Video Processing and (2) Analysis. *ImageJ* is an open source software developed by the National Institute of Health to analyze 2 dimensional and 3 dimensional images. The software takes in a video and converts it into a stack of images. Each image is then analyzed as required. Before a video can be used for analysis, it has to be pre-processed to clearly observe distinguishable features.

3.4.1 Image/Video Processing

Processing an image or video for analysis involves removing the unnecessary parts, whilst enhancing or modifying the visual aspects of the video in order to better visualize the features of interest. All the videos used for this study were imported into ImageJ by dragging them onto the ImageJ user interface. The *ImageJ* user interface containing the toolbar for various functions is illustrated in [Figure 3.12](#). The videos

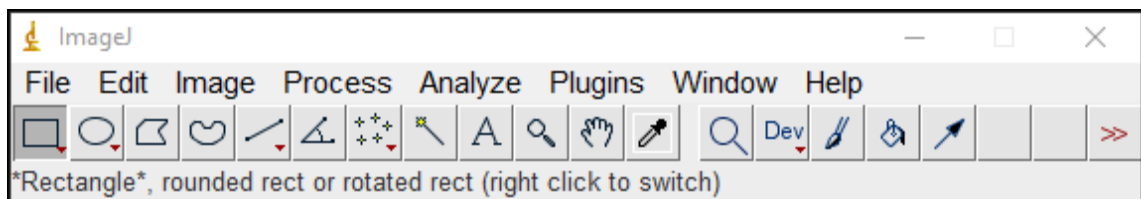


Figure 3.12: The user interface of the ImageJ software. The toolbar contains functions ranging from enhancing the image/video to making measurements.

were imported using the **Virtual Stack** option as it allows the import of large files by storing only parts of it in the RAM of the computer and accessing the rest of the video while processing it. Salient techniques used in processing an image/video are discussed below.

3.4.1.1 Reducing size and length of video

Once the video is imported into the software, it stores the video as a stack of individual frames. In order to reduce the length of the video, the **make substack** option, found in **Image > stacks > tools** is used to generate a substack by omitting/skipping frames from the original stack.

3.4.1.2 Brightness/Contrast

In order to observe the details of drop deformation, it is important to obtain a bright and clear image of the drop. This was achieved through a two-fold process by first enhancing the brightness and contrast using the **Image > Adjust > Brightness/Contrast...** tool. Thereafter, the **Subtract Background** tool, found under the **Process** menu was used to remove the background in the video. The difference in images before and after enhancing the contrast and brightness is shown in [Figure 3.13](#).

3.4.1.3 Binary Images

To automate the process of measuring the radius of the oil film during the spreading of the drop, the videos were converted to a black and white format with the object of interest (oil film) in black and the background (bulk liquid) in white. Once the optimal brightness and contrast was achieved, the **Make Binary** tool in the **Process > Binary > Make Binary** menu was used to convert the video to a black and white format.

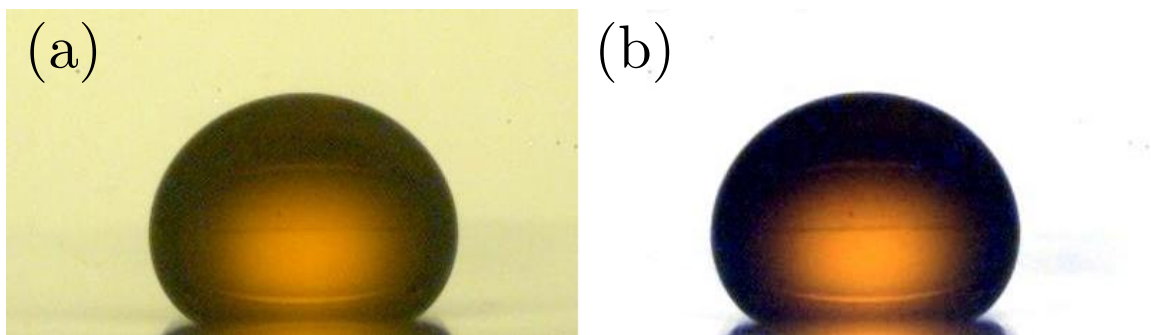


Figure 3.13: Difference between a raw image and an enhanced image used for observing the features of drop deformation during partial coalescence. The **Brightness/Contrast** and **Subtract Background...** tools are used to convert the raw image to a clean enhanced image. (a) The raw image showing an oil drop dyed with red dye. (b) The processed image of a drop after enhancing the brightness and contrast, and subtracting the background.

3.4.1.4 Removing unwanted pixels

Occasionally in the imaging process, few dust or lint particles stuck on lens of the camera would be captured in the videos and would eventually get converted as black points in the binary images. This leads to incorrect measurements of the area of the spreading film. To eliminate these “outlier” points, the **Remove Outliers** tool, found under the **Process > Noise > Remove Outliers** menu was used to convert these “bad pixels” into white background.

3.4.2 Analysis

Analysis consists of measuring the physical properties and characteristics of a phenomenon such as length, time, velocity, geometry etc. and collecting useful information from the measurements. The measurements are made by using common selection tools like **Rectangle**, **Oval/Circle**, **Line**, **Polygon**, etc. available in the toolbar of the *ImageJ* user interface (Figure 3.12). Depending on the type of parameter measured, direct or indirect measurements can be recorded. For example, measurements such as the height of the drop and coalescence time can be measured using the **Line** tool or

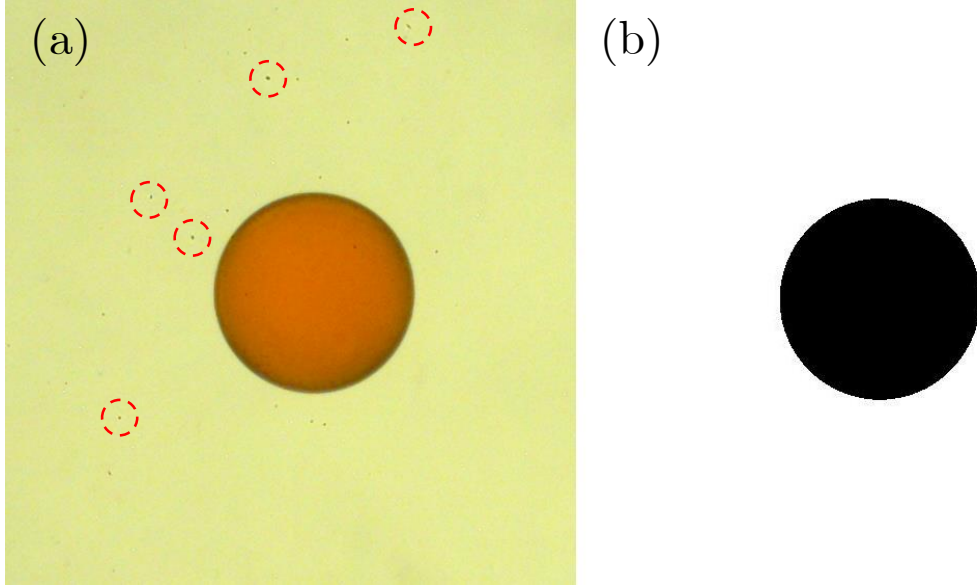


Figure 3.14: Difference between a raw image and binary image used for calculating the radius of the spreading film. The **Make Binary** and **Remove Outliers** tools are used to convert the raw image to a clean binary image. (a) The raw image showing an oil drop dyed with red dye. The small particles in the red dotted circles show dust particles stuck to the lens of the camera whose presence results in incorrect area measurement. (b) The processed image of a drop after converting it to binary and removing any outlier pixels.

by recording the difference in frames respectively. However, a few measurements such as the radius of the daughter drop, the radius of the spreading film, and the velocity of the apex of the drop necessitates the use of indirect measurements. For instance, the radius of the spreading drop is calculated by measuring the perimeter (P) of the film at every instant and the radius (r) of the film is calculated as $r = P/2\pi$.

A sample measurement of the area of the daughter drop is shown in [Figure 3.15](#). The **Oval** tool is used to draw a circle around the daughter drop (shown in black circle ([Figure 3.15\(a\)](#))). Next, the **Analyze** menu is used to measure the perimeter and area of the circle. The results window ([Figure 3.15\(b\)](#)) shows the measurements of the perimeter and area of the circle drawn. Using this data, the radius of the daughter droplet is calculated.

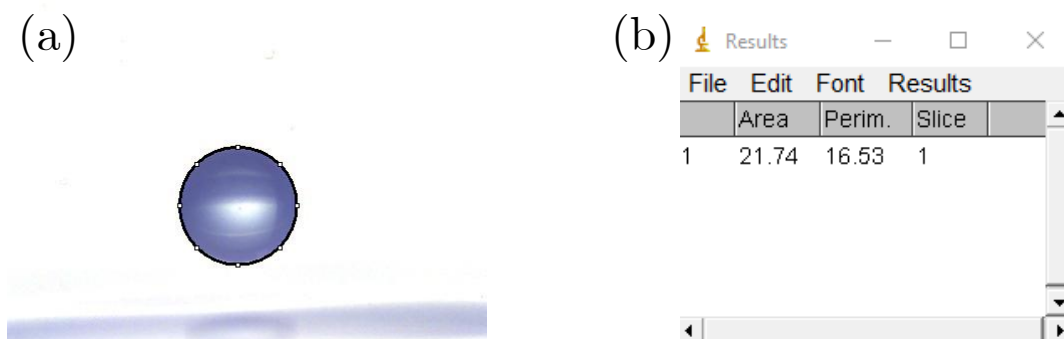


Figure 3.15: A sample measurement of the indirect measurement of the radius of the daughter drop. (a) Shows the selection circle in black drawn around the daughter drop using the **Oval** tool. (b) Shows the results window with the measurements of the area and perimeter of the circle drawn. The data is used to calculate the radius of the circle.

3.4.2.1 Scale Used

The accurate measurement of parameters is made possible only through a reliable scale conversion between the dimensions in pixels and actual length. In order to keep the scale conversion as accurate and consistent as possible, a Carl ZeissTM Microscope eyepiece Reticle available in the lab was used to calibrate the scale for all the experiments described in this study. The reticle provided a very precise measurement of a unit length (10 mm) which was placed in the plane of focus of the camera without disturbing any part of the setup after every experimental case was concluded. A video containing the reticle corresponding to every case was recorded to obtain accurate scale conversion factors. During the process of measuring the parameters in *ImageJ*, the scale was set using the **Set Scale...** option under the **Analyze** menu on the toolbar. A defined length in the scale video was selected using the **Line** tool and the distance in pixels was correlated to the defined length on the reticle. The scale was set to “global” to be able to obtain measurements in actual length for the corresponding case. [Figure 3.16](#) shows the **Set Scale...** window in *ImageJ* used to calibrate the scales for all experiments.

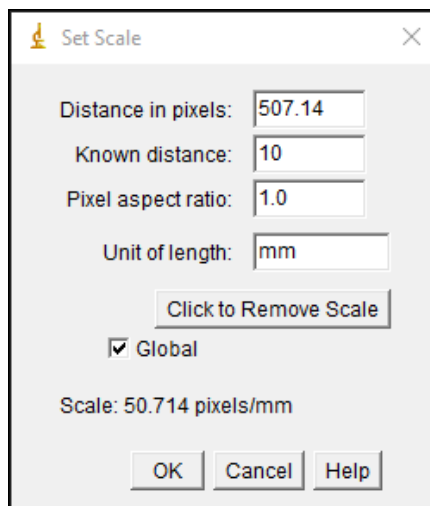


Figure 3.16: The **Set Scale...** window in *ImageJ* used to calibrate the scale for the videos recorded in this study.

Chapter 4

Partial Coalescence: Drop Collapse and Spreading

As established in previous chapters, oil and water interactions form the basis of numerous systems in nature including oil spills, emulsions, and drug delivery. The most elementary of these interactions is the impact of an oil drop with an interface of water and air. This chapter discusses the gentle impact of an oil drop onto a planar surface of water. It contains the experimental results and theoretical validation for **Experiments 1** and **2** described in [chapter 3](#). First, the observed phenomenon is described and a dimensional analysis elucidating the important physical properties is discussed. In later sections, the parameters of drop deformation are discussed and theoretical validations presented.

The impact of a drop of oil on the surface of water consists of three primary stages - (1) the drop descent, (2) drop deformation, and (3) the spreading of the drop. As discussed in [chapter 3](#), the drop descent and deformation were studied in **Experiment 1**, while the spreading of the drop was studied in **Experiment 2**. As a drop of oil is gently brought close to the surface of water, a thin layer of ambient fluid (air in this case) is sandwiched between the drop and the bulk liquid. The drop rests on this thin

layer of air as it becomes thinner due to the weight of the drop. Eventually, the air film between the drop and bulk liquid drains out, establishing contact between the two liquids. Upon contact, the unbalanced surface tension forces in the drop trigger a group of capillary waves along the surfaces of both the drop and the bulk liquid. These capillary waves travel along the phase boundary of the drop and water momentarily before traveling along the interface of the drop and air. Furthermore, another set of waves, although very weak travel along the surface of the water. Depending on the strength of the capillary waves traveling on the surface of the drop, they deform the drop by stretching it upwards, concomitantly inhibiting the merger of the drop with the bulk liquid. The merger of the drop thus can proceed in a single event or in a cascade of self similar events termed as *partial coalescence*.

While the overall mechanism involved in partial coalescence is open for debate, all the investigators agree on the influence of capillary waves. It has been hypothesized that the coalescence process is controlled by the competition between the horizontal and vertical rates of collapse. While it is expected that the vertical collapse will prevail due to the downward pull of the surface tension, partial coalescence is possible only when the rate of horizontal collapse is greater than that of vertical collapse. The vertical collapse is inhibited by the propagation of capillary waves, thus allowing the formation of a daughter droplet. Therefore we can say that the daughter droplet generation is directly dependent on the strength of the capillary waves meeting at the apex of the drop. Since the capillary wave propagation is dependent on the drop and surrounding bulk fluid, we can say that apart from the velocity (V) of the impacting drop and the gravitational force (g), the viscosity of the drop, viscosity of the surrounding bulk fluid, interfacial tension between the drop and the surrounding bulk fluid, density of the drop, density of the surrounding bulk fluid also play an important role in the coalescence event.

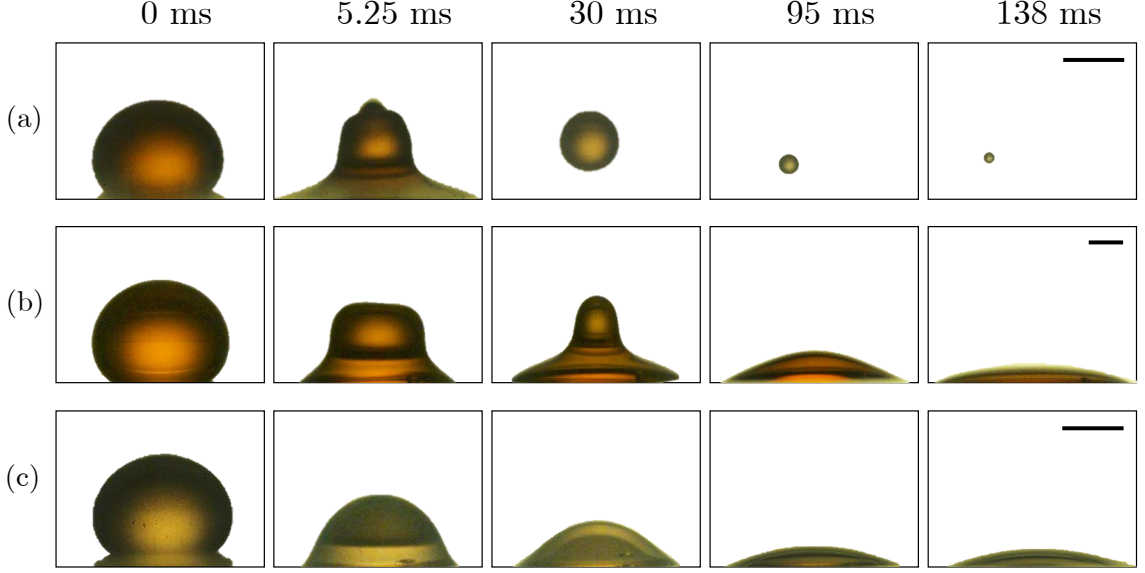


Figure 4.1: Time evolution of oil drops of varying Oh during merger with bulk liquid. Three distinct regimes of (a) partial coalescence, (b) delayed coalescence, and (c) complete coalescence are identified. (a) Shows the case of partial coalescence, where the formation of an upward jet leads to the generation of a daughter droplet ($Oh_p = 0.00422$). (b) Shows the case of delayed coalescence where formation of a jet is observed in the absence of a daughter droplet ($Oh_p = 0.01542$). (c) Shows the case of complete coalescence without jetting. ($Oh_p = 0.6007$).

4.1 Regime Map

Through experiments, upon dewetting of the thin air film, we observe three distinct drop behaviors. These can be referred to as (1) jetting with daughter droplet generation (partial coalescence), (2) jetting without daughter drop (delayed coalescence), and (3) no jetting (complete coalescence). For a drop-bulk fluid system where partial coalescence is observed, the capillary waves that are propagating through the phase boundary are strong enough to inhibit the drop from coalescing completely with water for a sufficient amount of time, thus allowing the formation of a daughter droplet. This is typically observed when the damping effect on the capillary waves are relatively low and the strength of the capillary waves interfering at the apex is high. If the capillary waves that are propagating through the phase boundary are sufficiently damped such that there is no interference at the drop apex, the drop coalesces completely, leading

to the event termed as complete coalescence. However, when the capillary waves undergo damping, but retain sufficient energy to interfere at the apex, we observe the drop undergoing a delayed coalescence. Here, the capillary waves are strong enough to deform the drop, but the damping effect prevents them from inhibiting the vertical collapse of the drop for sufficient amount of time, thus preventing partial coalescence.

Intuitively, from the above discussions one can say that the basic difference between a partial coalescence event and a complete coalescence event is the generation of a secondary daughter droplet. Therefore, we can say that the size of the secondary daughter droplet produced has a finite value for partial coalescence while it is zero for delayed or complete coalescence. Thus, we look to demarcate the regions of partial coalescence and complete coalescence by considering parameters affecting the size of the secondary drop generated. Thus, in order to establish an appropriate regime map describing the drop behavior upon impact, we identify the variables ruling the value of the size of the daughter drop generated.

$$D_d = f(\rho_p, \rho_b, \mu_p, \mu_b, \sigma, D_p, g, V) \quad (4.1)$$

where D_d is the diameter of the daughter droplet generated, ρ_p is the density of the drop, ρ_b is the density of the surrounding bulk, μ_p is the dynamic viscosity of the drop, μ_b is the dynamic viscosity of the surrounding bulk, σ_p is the interfacial tension between the parent drop and the surrounding bulk, D_p is the diameter of the parent drop, g is the acceleration due to gravity, and V is the velocity of the drop as it approaches the surface. It is important to understand that although the drop is impacting onto a “bulk” of water, most of the capillary wave propagation responsible for the drop dynamics occur along the phase boundary of the drop and the surrounding air. Hence, the word *bulk* in this context refers to the air surrounding the drop.

During the gentle deposition of a drop, the velocity of the drop approaching the surface is very low. Additionally, upon impact, a thin air film acts as a cushion for the drop, bringing it to rest before any dynamics take effect. Thus the velocity V has minimal effect on the drop dynamics, allowing us to ignore it. Also, the diameters of all the drops generated were below the capillary length ($< \sqrt{\sigma/\rho g}$) of the liquids and therefore, the gravitational effects on the drop are neglected. Equation 4.1 can thus be rewritten as

$$D_d = F(\rho_p, \rho_b, \mu_p, \mu_b, \sigma_p, D_p) \quad (4.2)$$

Through dimensional analysis, the diameter of the daughter droplet generated can be expressed as a function of non-dimensional terms as given below.

$$\frac{D_d}{\ell} = F(\rho_r, \mu_r, Oh_p) \quad (4.3)$$

Here ℓ is the probable length scale used to non-dimensionalize the diameter of the drop, ρ_r is the density ratio of the drop and the bulk, μ_r is the viscosity ratio of the drop and the bulk, and Oh_p is the Ohnesorge number of the parent drop. Upon close inspection, it is revealed that across the oils tested, the density ratio does not vary significantly, causing ρ_r to have a relatively small effect on the size of the daughter droplet generated. The Equation 4.3 can thus be reduced to

$$\frac{D_d}{\ell} = F(\mu_r, Oh_p) \quad (4.4)$$

Thus upon plotting the viscosity ratio against Oh_p , we establish a regime map as shown in Figure 4.2, demarcating regions of partial coalescence, delayed coalescence, and complete coalescence. Region 1 represents the regime of partial coalescence, where both the μ_r and Oh_p are relatively low. In this region, the strength of the capillary waves are sufficiently high, delaying the vertical collapse of the drop and allowing

the generation of a daughter droplet. At higher μ_r and Oh_p , delayed coalescence is observed, represented by the plots in region 2. In this regime, the capillary waves manage to deform the drop, but are not strong enough to inhibit the vertical collapse entirely. Region 3 represents the regime of complete coalescence, where the capillary wave propagation is sufficiently damped. The plots in this region represent drops with relatively high μ_r and Oh_p .

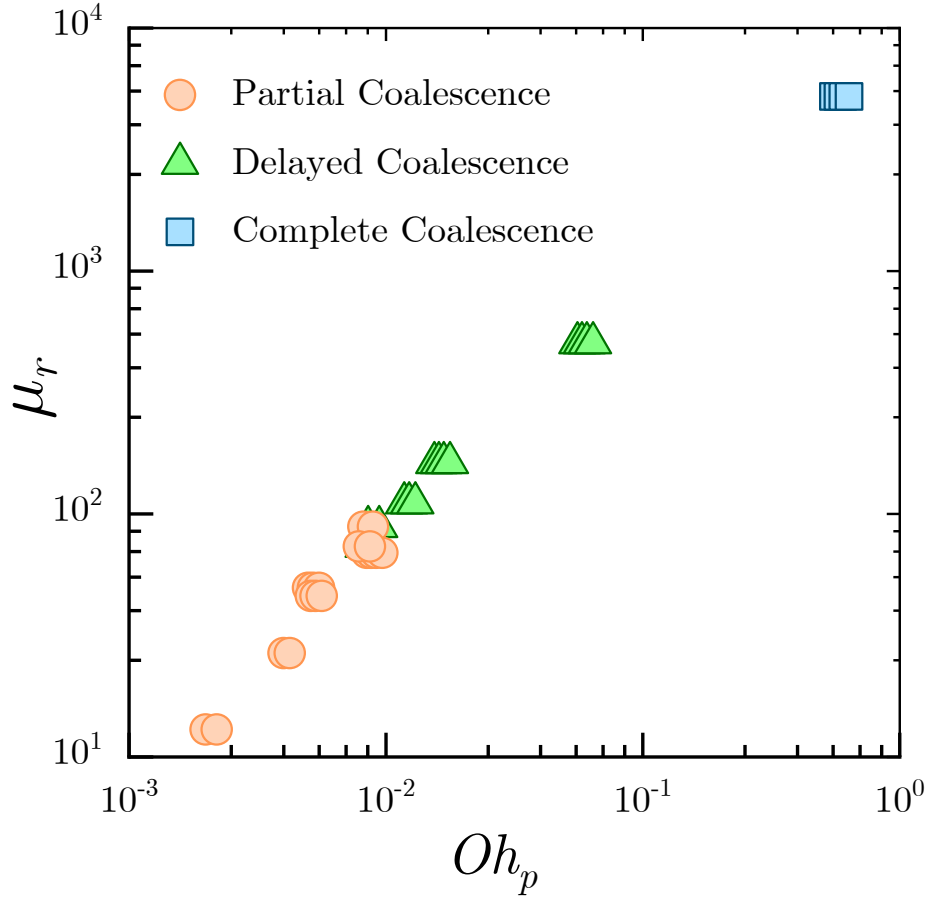


Figure 4.2: The regime map demarcates the regions of partial coalescence, delayed coalescence, and complete coalescence as a function of the viscosity ratio ($\mu_r = \mu_p/\mu_b$) and the parent drop Ohnesorge number (Oh_p).

While replacing the air with a more viscous and denser fluid might cause the plots to spread out, it will not have any effect on the demarcating regions on the regime map.

4.2 Length, Time, and Velocity Scaling

As the thin air film, sandwiched between the drop and bath, dewets, capillary waves are initiated into the system resulting in the deformation of the drop as these waves propagate through the phase boundary. We set out to investigate various features of the drop deformation as the drop is coalescing with the liquid bath. To further characterize the drop deformation features, we aim to propose scaling laws for each feature by comparing them to drop properties. Since it has already been established that the physical properties of the drop can be represented by Oh_p (drop), thus, there is a need to propose appropriate length, time and velocity scales to non-dimensionalize the respective length, time and velocity features to establish the appropriate scaling laws. Taking X as the drop deformation feature under study, using dimensional analysis, we identify variables that have a direct impact on drop deformation and capillary wave propagation.

$$X = F(\rho_p, \rho_b, \mu_p, \mu_b, \sigma_p, D_p) \quad (4.5)$$

Using dimensional arguments, the feature X is expressed in non-dimensional terms as

$$\frac{X}{\ell} = F(\rho_r, \mu_r, Oh_b) \quad (4.6)$$

where ℓ is the appropriate length, time or velocity scale, and Oh_b represents the Ohnesorge number of the bulk fluid. The above expression can be further reduced to represent the physical properties of the drop, and can be expressed as:

$$\frac{X}{\ell} = F(Oh_p) \quad (4.7)$$

Hence, the feature X can be expressed as a function of Oh_p . Using different scaling methods, the length, time, and velocity scales can be obtained as shown in [Table 4.1](#).

Table 4.1: Time, Length, and velocity scales using different scaling methods

Scaling used	Time scale (t_μ)	Length scale (l_μ)	Velocity scale (v_μ)
Inertio-capillary	$\sqrt{\rho R^3/\sigma}$	R	$\sqrt{\sigma/\rho R}$
Visco-inertial	$\rho R^2/\mu$	R	$\mu/\rho R$
Visco-capillary	$\mu R/\sigma$	R	σ/μ
Inertio-visco-capillary	$\mu^3/\rho\sigma^2$	$\mu^2/\rho\sigma$	σ/μ

During the pinch off of the daughter droplet, the length scales are of the order of $\mathcal{O}10^{-9}$. Thus we choose the scaling that yields the length scale which is of the same order of the length scales observed during pinch off. These scales are obtained by using the *inertio-visco-capillary* scaling. Hence, the parameter X can be non-dimensionalized using the scaling parameter ℓ and expressed as a function of μ_r and Oh_d as shown below

$$\frac{X}{\ell} = f(\mu_r, Oh_p) \quad (4.8)$$

The parameter scales obtained using the visco-inertio-capillary scaling are given below.

$$l_\mu = \frac{\mu_p^2}{\rho_p \sigma_p} \quad t_\mu = \frac{\mu_p^3}{\rho_p \sigma_p^2} \quad v_\mu = \frac{\sigma_p}{\mu_p} \quad (4.9)$$

4.3 Height of the Drop

On close observation of the coalescence event, one can say that the behavior of the drop, including the possibility of the generation of a daughter droplet is highly dependent on the vertical collapse. As the capillary waves travel upwards on the surface of the drop, they deform the drop. At a certain point when they meet at the apex, they stretch the drop upwards, and the drop attains its maximum height. Hence, the maximum height of the apex of the drop can indicate the strength of the capillary waves. Stronger the wave propagation, higher the apex of the drop. Since the capillary waves are damped due to viscosity, it is expected that with an increase in viscous

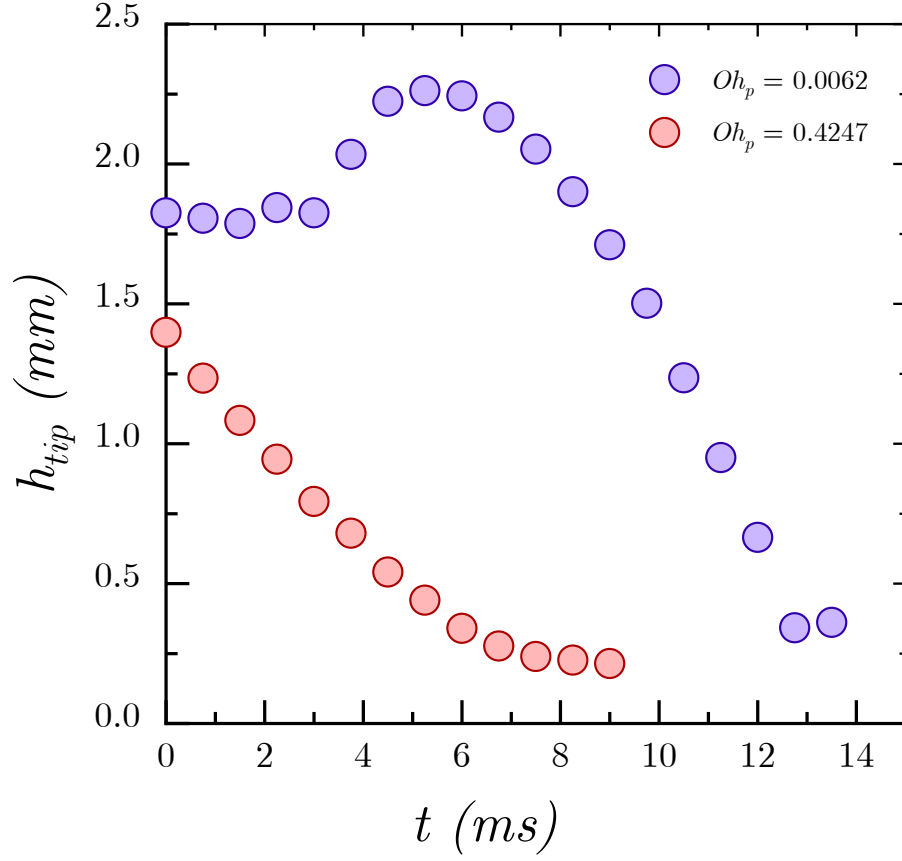


Figure 4.3: The time rate of change of the height of the drop. The drop with a comparatively lower viscosity $Oh_p = 0.0065$ shows an initial increase in height due to marginally damped capillary wave propagation along the surface of the drop. The drop with higher viscous effects ($Oh_p = 0.4247$) shows a monotonic decrease in the height due to strong damping of the capillary waves.

effects, the maximum height of the drop will decrease. Thus, in order to characterize the behavior of the drops, we measure the height of the apex of the drop from the interface, and also note the maximum height of the drop. Using the length scale obtained from the inertio-visco-capillary scaling, the maximum height of the drop is non-dimensionalized, and plotted against Oh_p , as shown in [Figure 4.4](#). Upon plotting the scaled H_{max} against Oh_p , we observe that the data collapses onto a line, giving a relationship between the maximum height of the drop and the physical properties of the drop. As is observed in [Figure 4.4](#), with an increase in Oh_p , the maximum height of the drop decreases. Theoretically, the maximum height (H_{max}) of the drop is of the

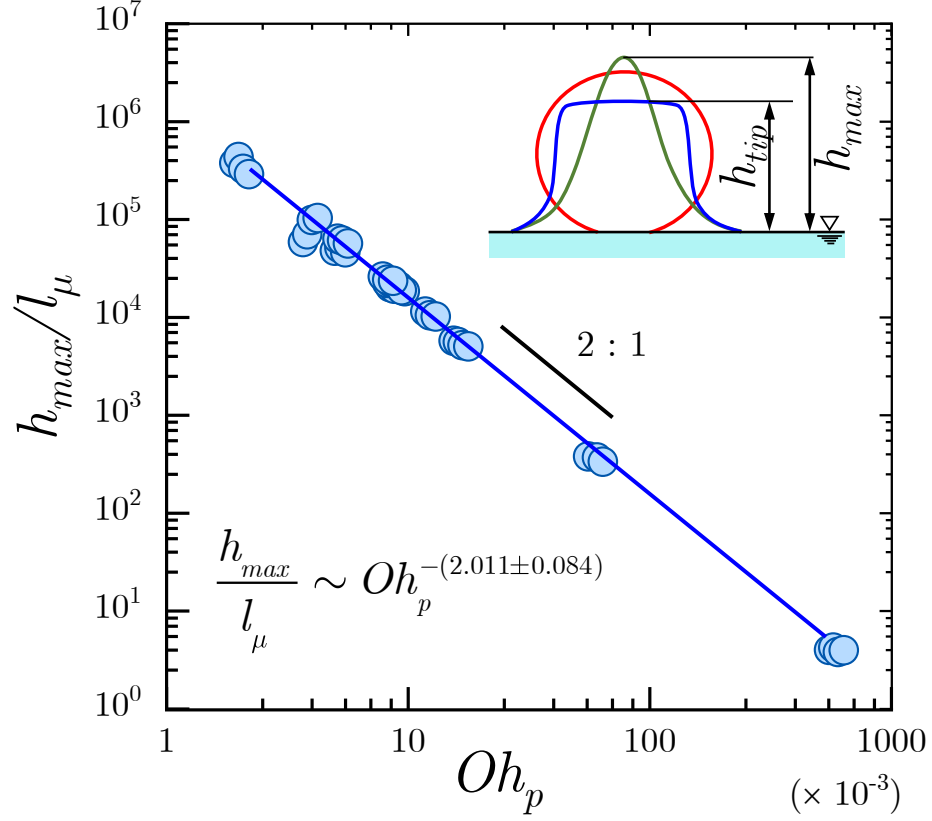


Figure 4.4: The maximum height attained by the drop scaled against the Oh_p and non-dimensionalized using the inertio-visco-capillary length scale.

order of the diameter of the parent drop ($H_{max} \sim D_p$). Non-dimensionalizing H_{max} with the length scale, we obtain a relationship between H_{max} and Oh_p which matches with the experimental values as shown below

$$\frac{H_{max}}{l_\mu} \sim \frac{D_p}{l_\mu} \sim \frac{\rho_p \sigma D_p}{\mu_p^2} \sim Oh_p^{-2} \quad (4.10)$$

4.4 Velocity of the wavefront

As the draining air film thins out and eventually ruptures, the contact between the oil drop and the bulk water induces capillary waves along the surface of the oil drop as well as the bulk liquid. The traveling capillary waves deform the drop and ultimately

determine the outcome of the process as explained at the beginning of this chapter. The velocity of the wavefront as described in [section 3.3](#) is a direct representation of the strength of the capillary waves traveling towards the apex of the drop. It is expected that with a higher damping effect, the velocity of the waves reduce and consistently, the strength of the waves are also reduced. [Figure 4.5](#) plots the velocity of the wavefront as a function of the Oh_p and is non-dimensionalized using the inertio-visco-capillary velocity scale. The variation of velocity in [Figure 4.5](#) is counter-intuitive as it shows

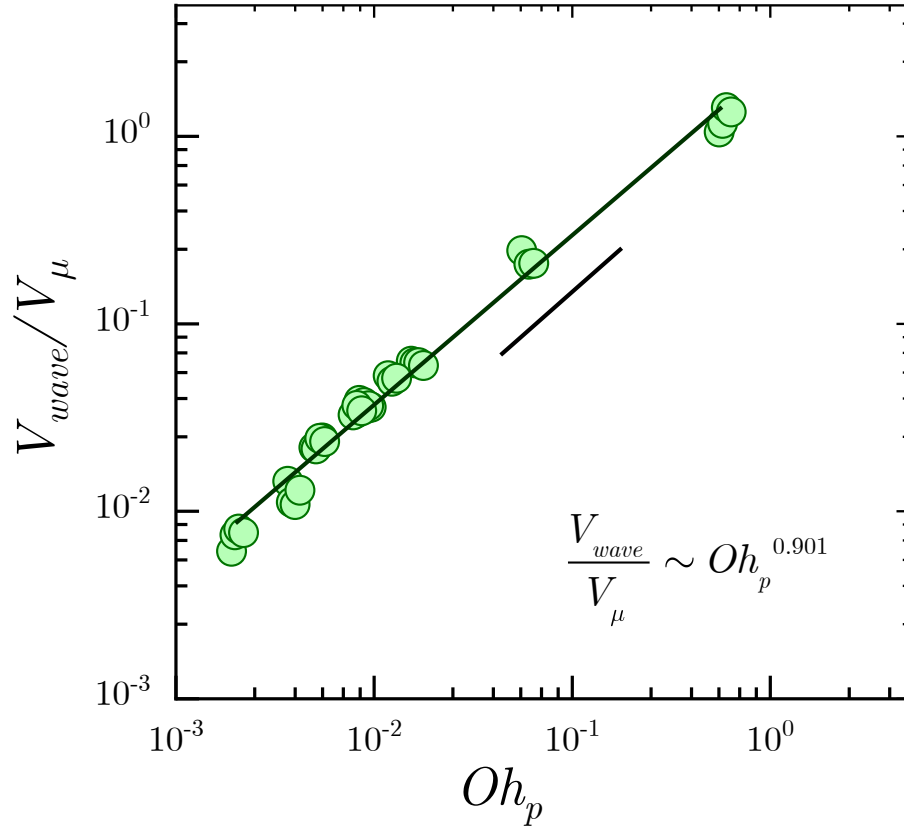


Figure 4.5: The velocity of the wavefront scaled against the Oh_p of the drop, non-dimensionalized using the inertio-visco-capillary velocity scale.

an increasing trend with an increase in Oh_p . The reason for an increasing trend is not the inherent velocity, instead lies in the velocity scale considered for scaling. As discussed in [section 4.2](#) the velocity scale is obtained when the inertial, viscous, and capillary forces are in balance. The capillary number (Ca), which gives the relative

importance of the viscous and surface tension forces is used to obtain an expression for the velocity scale as shown in Equation 4.11 through Equation 4.12

$$Ca = \frac{\mu_p V_{wave}}{\sigma_p} \quad (4.11)$$

where v is the velocity of the wavefront, μ_p is the viscosity of the parent drop, σ_p is the surface tension of the drop. When the viscous and surface tension forces are in balance, the $Ca \sim 1$. The velocity scale resulting from such a balance depends only on the physical properties of the liquid as given in Equation 4.12.

$$Ca = 1 = \frac{\mu_p V_{wave}}{\sigma_p} \implies V_{wave} = \frac{\sigma_p}{\mu_p} \quad (4.12)$$

The velocity scale obtained in Equation 4.12 shows a high dependence on the viscosity of the drop, and hence bears a range of values spanning 3 orders of magnitude. Due to this, the value of the velocity scale (V_μ) decreases sharply with an increase in the viscosity of the drop. The decrease in the value of V_μ far exceeds the decrease in the velocity of the wavefront, and as a result, the non-dimensional velocity (V_{wave}/V_μ) increases in magnitude with an increase in Oh_p .

4.5 Velocity of the Apex of Drop

As the capillary waves travel on the phase boundary of the drop and the ambient fluid, they deform the drop and delay the vertical collapse. When the capillary waves meet at the apex of the drop, constructive interference of the waves leads to the formation of a jet. As the jet collapses, the velocity of the apex of the drop (V_{tip}) during the vertical collapse affects other features such as the size of the daughter droplet, coalescence time, and spreading rate of the drop. In order to characterize the influence of the velocity of the apex of the drop on the concomitant features observed during drop

deformation, a non-dimensional form of the velocity is scaled against Oh_p . As the

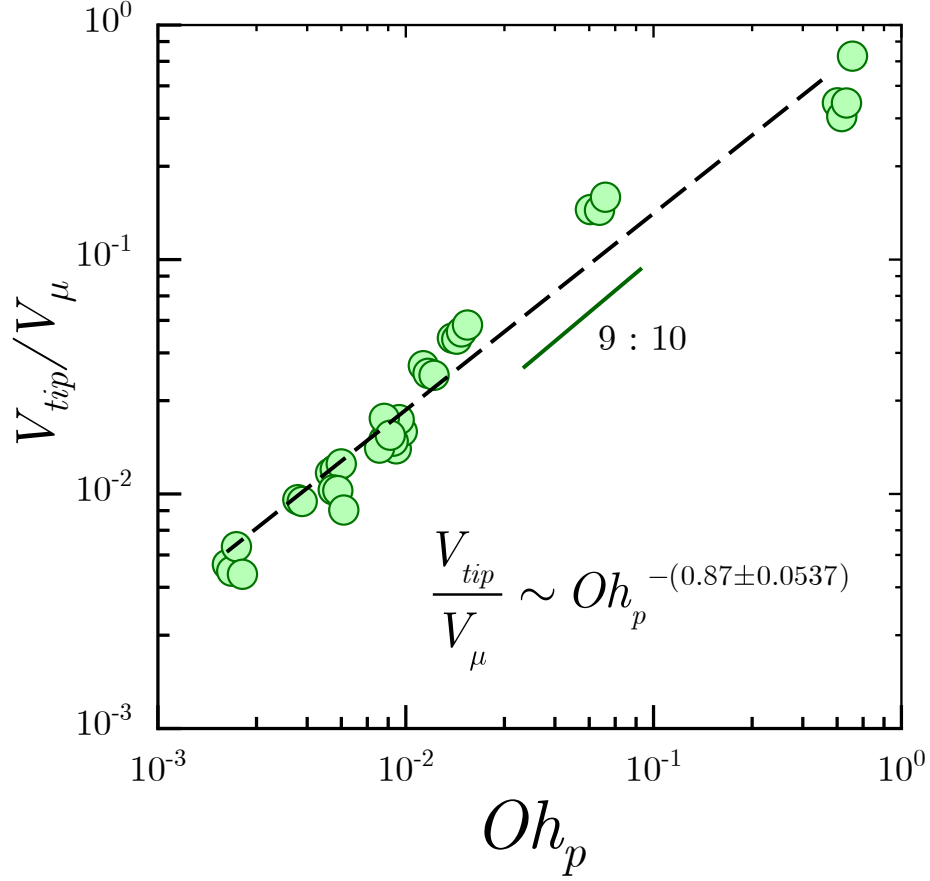


Figure 4.6: The velocity of the apex of the drop scaled against the Oh_p and non-dimensionalized using the inertio-visco-capillary velocity scale.

capillary waves impart a vertical velocity to the drop, they stretch the drop to form a jet. The diameter of the jet thus formed (D_{cy}) is of the order of the parent drop diameter ($D_{cy} \sim D_p$). The competing forces during the stretching of the drop are the inertial and surface tension forces. We can express the resulting inertio-capillary force balance as follows in [Equation 4.13](#)

$$\rho_p V_{tip}^2 \sim \frac{\sigma_p}{D_{cy}} \implies V_{tip} \sim \sqrt{\frac{\sigma_p}{\rho_p D_{cy}}} \implies V_{tip} \sim \sqrt{\frac{\sigma_p}{\rho_p D_p}} \quad (4.13)$$

During the pinch off of the daughter drop however, the inertial, viscous, and capillary forces are all in balance, and hence we use the velocity scale obtained using the

inertio-visco-capillary scaling to non-dimensionalize the velocity of the apex. The non-dimensional velocity can thus be resolved as [Equation 4.14](#)

$$\frac{V_{tip}}{V_\mu} \sim \sqrt{\frac{\sigma_p}{\rho_p D_{cy}}} \cdot \frac{\mu_p}{\sigma_p} \sim \frac{\mu_p}{\sqrt{\rho_p \sigma_p D_p}} \sim Oh_p \quad (4.14)$$

4.6 Daughter Drop

If the capillary waves are strong enough to delay the vertical collapse of the drop, it causes the formation of a daughter droplet, resulting in partial coalescence. In some cases, this process continues as a cascade of events, with the daughter drop collapsing and producing a secondary daughter drop. If the vertical collapse happens before the

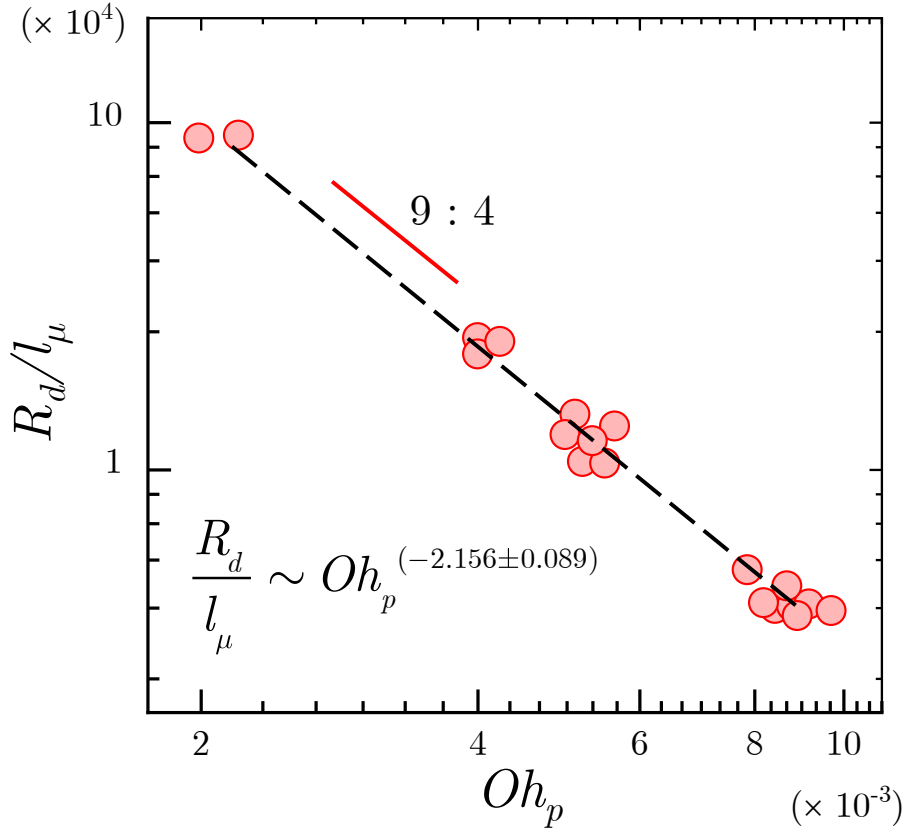


Figure 4.7: The radius of the daughter droplet as a function of the Oh_p non-dimensionalized using the inertio-visco-capillary length scale.

horizontal collapse, the process results in complete coalescence. In the event that a daughter drop is generated, the size of the daughter drop can be accurately predicted based on the Oh_p of the drop. The relation between the radius of the daughter drop and the Oh_p of the parent drop is shown in [Figure 4.7](#). The radius of the daughter drop is found to scale as $Oh_p^{-7/3}$. This is validated by the inertio-visco-capillary scaling obtained. From the calculation of the tip velocity, we can estimate the scaling of the daughter drop with Oh_p . The volume of the drop contained in the cylinder formed during jetting pinches off and forms the daughter droplet. Thus from the conservation of mass, we can conclude that the volume of the daughter droplet is the volume of the cylinder just before pinch off. Equating them, we obtain the scaling for the daughter droplet with respect to Oh_p . The diameter of the cylinder (d) is found to scale with Oh_p as $d/l_\mu \sim Oh_p^{-2.5}$. Also consider that the length of the cylinder (l_{cy}) can be approximated using the velocity of the apex of the drop (V_{tip}) and the collapse time (t_{coll}) as $l_{cy} = V_{tip} \times t_{coll}$. Now, considering the conservation of volume just before pinch off, the volume of the cylinder ($\mathbb{V}_{cy}$) is given by $\mathbb{V}_{cy} = (\pi d^2/4) \times l_{cy}$. Since the volume of the cylinder is equal to the volume of the daughter drop, equating them results in [Equation 4.15](#)

$$\pi \frac{d^2}{4} V_{tip} \cdot t_c \sim \pi \frac{D_d^3}{6} \quad (4.15)$$

Using known scalings for the diameter of the cylinder, velocity of the apex of the tip, and the collapse time, we obtain the scaling for the daughter drop as shown in [Equation 4.16](#)

$$(l_\mu^2 \cdot Oh_p^{-5})(V_\mu \cdot Oh_p)(t_\mu \cdot Oh_p^{-3}) \sim D_d^3 \implies \frac{D_d^3}{l_\mu^3} \sim Oh_p^{-7} \implies \frac{D_d}{l_\mu} \sim Oh_p^{-7/3} \quad (4.16)$$

where the relation between the length scale, velocity scale, and time scale can be written as $l_\mu \sim V_\mu \cdot t_\mu$.

4.7 Coalescence Time

As the drop comes in contact with the bulk liquid and starts to spread, it also begins to lose its shape due to the capillary waves traveling on the surface. The final outcome is the formation of a convex lens on the surface of the bulk liquid. The time interval between the initial rupture of the drop causing deformation and the formation of the convex lens is considered as the time taken for full coalescence. In the event a

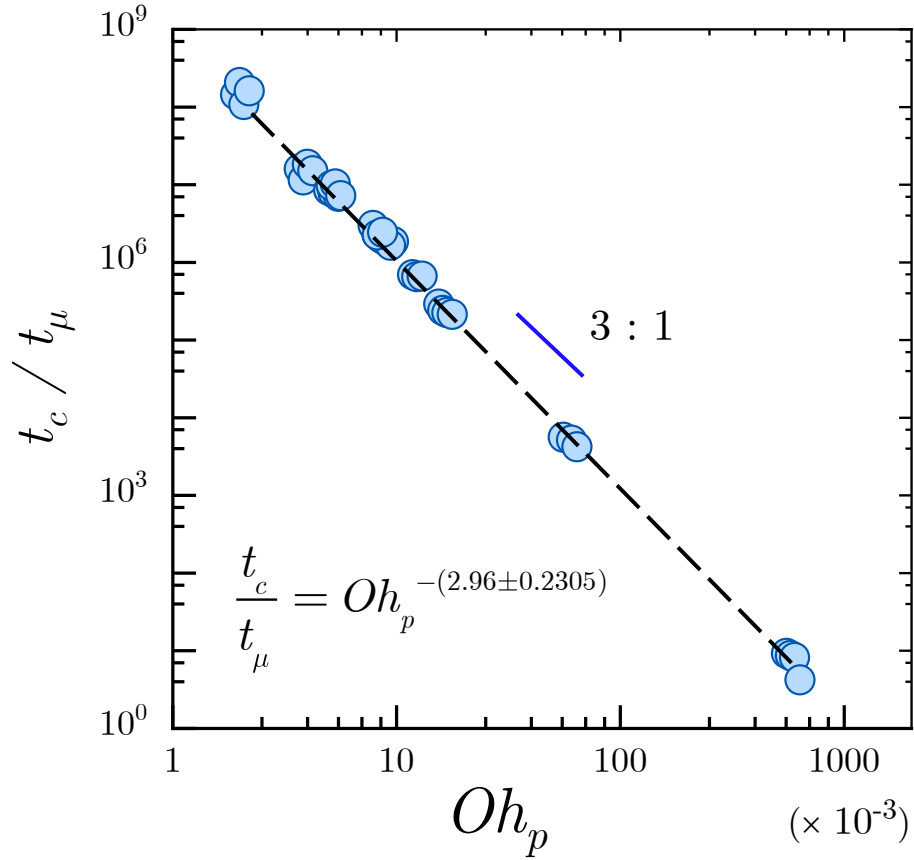


Figure 4.8: The coalescence time of the drop as a function of the Oh_p and non-dimensionalized using the inertio-visco-capillary timescale.

daughter droplet form or a cascade of daughter droplets form, time of coalescence is considered as the time at which the last daughter drop in the cascade collapses. The coalescence time (t_c) for the drops has been measured and plotted in [Figure 4.8](#). The coalescence time scales with the Oh_p of the drop as $t_c/t_\mu \propto Oh_p^{-3}$. Theoretically, the

coalescence time can be expressed as in [Equation 4.17](#).

$$t_c = \frac{H_{max}}{V_{tip}} \quad (4.17)$$

Using the scaling relations obtained for H_{max} and V_{tip} , we obtain the expression below

$$t_c = \frac{l_\mu Oh_p^{-2}}{V_\mu Oh_p} = t_\mu Oh_p^{-3}$$

4.8 Spreading Characteristics

As the drop collapses on the surface, the area of contact of the drop with the bulk liquid increases with time. Based on the viscosity of the drop, the radius of the spreading drop changes differently. The radius of the drop in contact with the water was measured at every instant and the tracking of the radius is shown in [Figure 4.9](#). It can be observed that for the oil with lower viscosity ($Oh_p = 0.026$), the radius of the drop initially increases to a maximum value, and then recoils to a minimum value before increasing again. The oscillation of the drop ultimately dampens and the film reaches a stable radius. On the contrast, the liquid with high viscosity ($Oh_p = 0.502$) does not show this tendency to spread and contract. It monotonically spreads to a stable radius and remains constant thereafter.

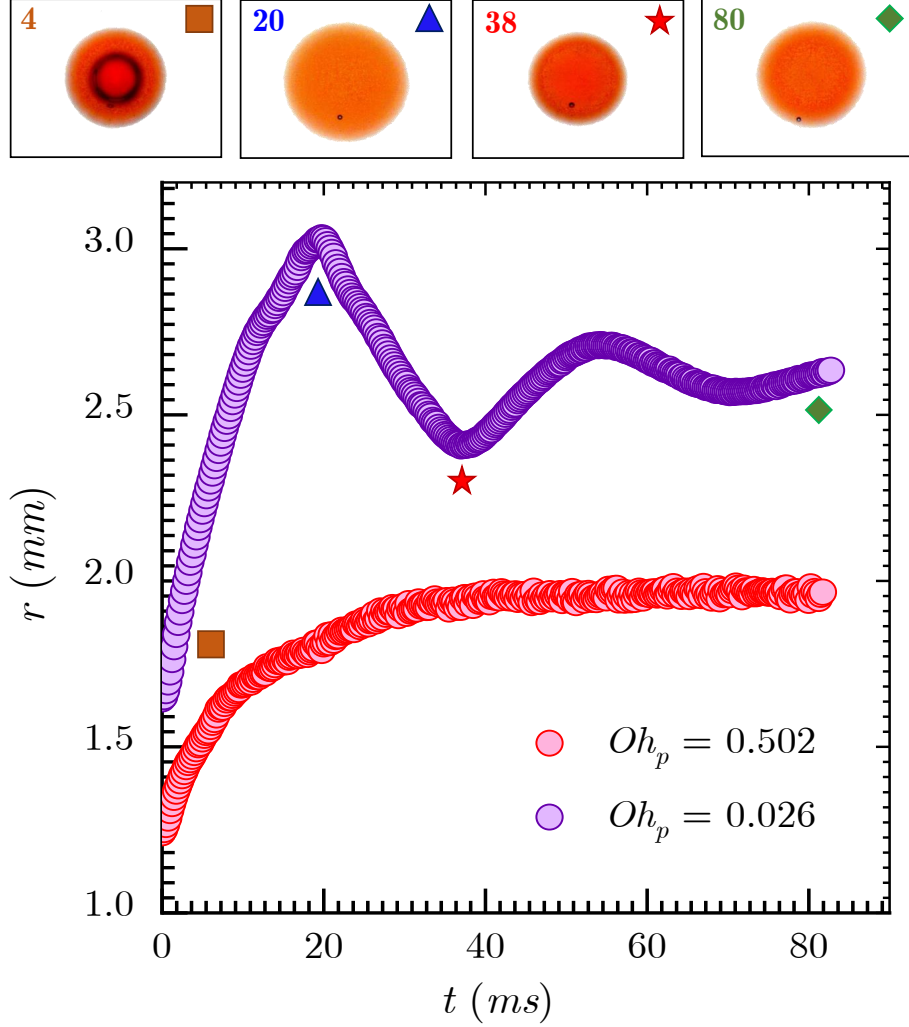


Figure 4.9: (a) Shows the time variation of the radius of the spreading film. Oils with low Oh_p exhibit an oscillatory behavior while oils with relatively high Oh_p exhibit a monotonic increase. (b) shows the scaling of the recoil time (t_{rec}) normalized using the time scale multiplier, with the Oh_p of the drop.

4.9 Maximum Radius

The maximum radius attained by the drop plays a major role in determining the extent of oil film coverage in the case of oil spills. To characterize the behavior of oils in the context of oil spills, the maximum radius attained by the drops is calculated and plotted in Figure 4.10. The maximum radius, non-dimensionalized using the inertio-visco-capillary length scale is scaled against the Oh_p and shows a decreasing trend. The non-dimensional maximum radius scales as $r_{max}/l_\mu \sim Oh_p^{-2 \pm 0.092}$.

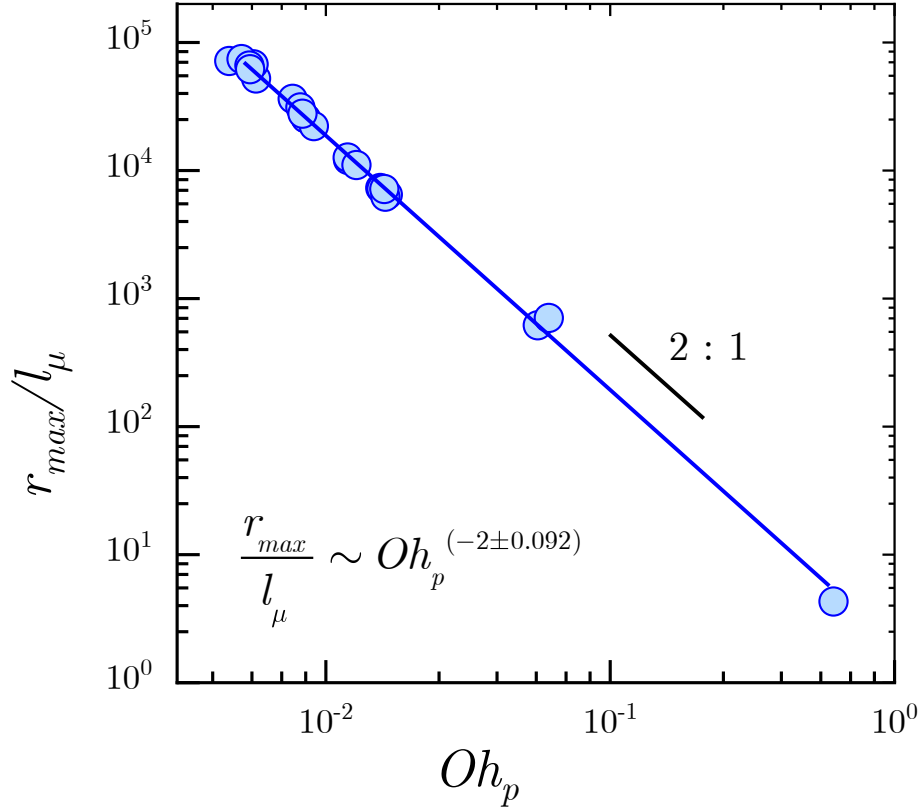


Figure 4.10: The maximum radius of the spreading film as a function of Oh_p non-dimensionalized using the inertio-visco-capillary scaling.

4.10 Recoil Dynamics

The recoil dynamics have been studied and the results are shown in [Figure 4.9](#). The maximum and minimum radius of the drop ie. the radii at the first spreading and recoiling iteration have been measured. It is found that the difference of the radii (normalized with the length scale multiplier) scales with the Oh_p of the drop as $\Delta R/l_\mu \sim Oh_p^{-1.74}$. It is also noted that the normalized time of recoil, measured as the time interval between the instances of maximum and minimum radii of the drop scales with Oh_p of the drop as $t_{rec}/t_\mu \sim Oh_p^{-5/2}$. The extent of recoil and the time of recoil influences many parameters such as the final size of the lens formed, and also the spreading of the drop. In applications such as polymerization of oil drops, controlling the time and extent of recoil is vital.

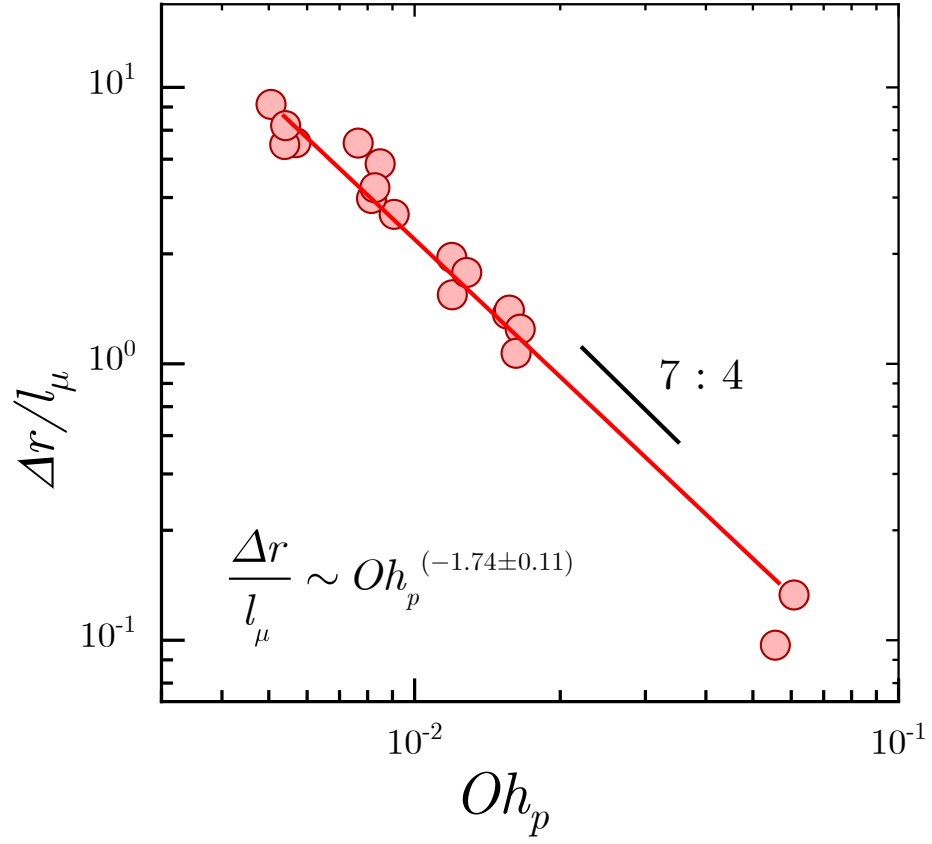


Figure 4.11: The extent of recoil ($r_{max} - r_{min}$) as a function of the Oh_p , non-dimensionalized using the inertio-visco-capillary length scale.

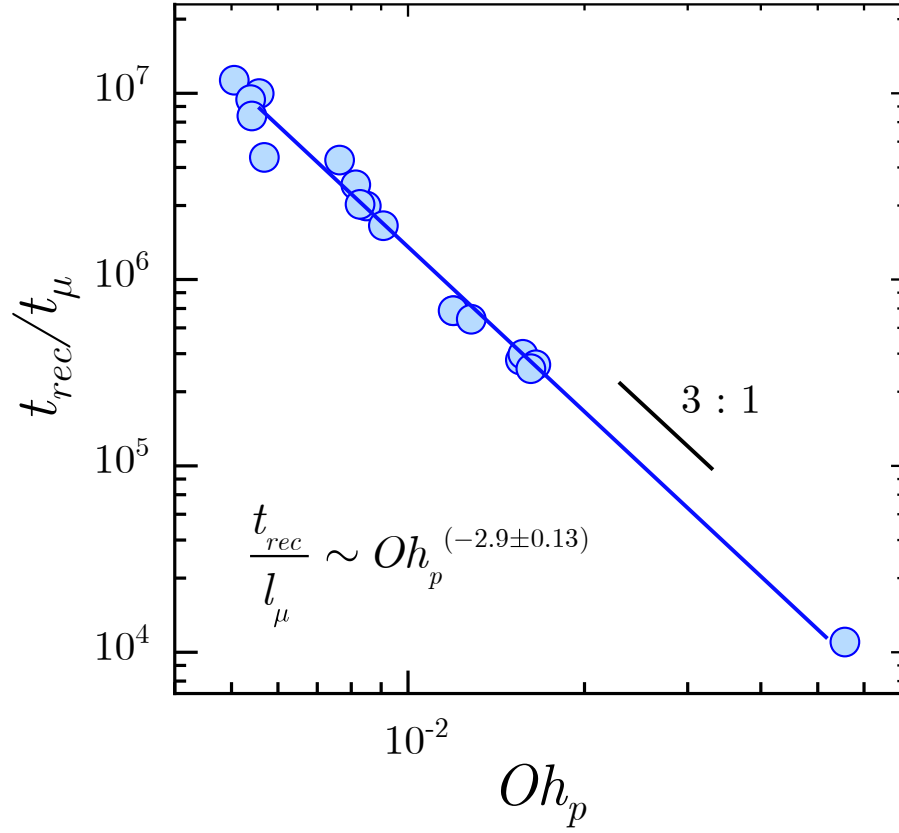


Figure 4.12: (a) Shows the time variation of the radius of the spreading film. Oils with low Oh_p exhibit an oscillatory behavior while oils with relatively high Oh_p exhibit a monotonic increase. (b) shows the scaling of the recoil time (t_{rec}) normalized using the time scale multiplier, with the Oh_p of the drop.

4.11 Theoretical Model for Oil Spreading on Water

As discussed in the previous sections, the spreading behavior is highly dependent on the physical properties of the oils. It is observed that drops with a higher Oh follow a monotonic increase in the contact area as they spread while drops with comparatively low Oh show a non-monotonic behavior. This behavior is analogous to and can be characterized using the forced response of a second order mechanical system.

Consider a mechanical spring-mass damper system with a block of mass m , spring with a spring constant k and a damper with a viscous damping coefficient c as shown in [Figure 4.13](#). Let us assume that an initial step force of magnitude F_0 acts on the mass. Assuming that the system has an initial displacement X_0 and an initial velocity V_0 , the equation of motion of the system can be expressed as [Equation 4.18](#)

$$m \frac{d^2 X}{dt^2} + c \frac{dX}{dt} + kX = F_0 \quad (4.18)$$

with initial conditions $V(0) = V_0$ and $X(0) = X_0$. Dividing [Equation 4.18](#) by m , we

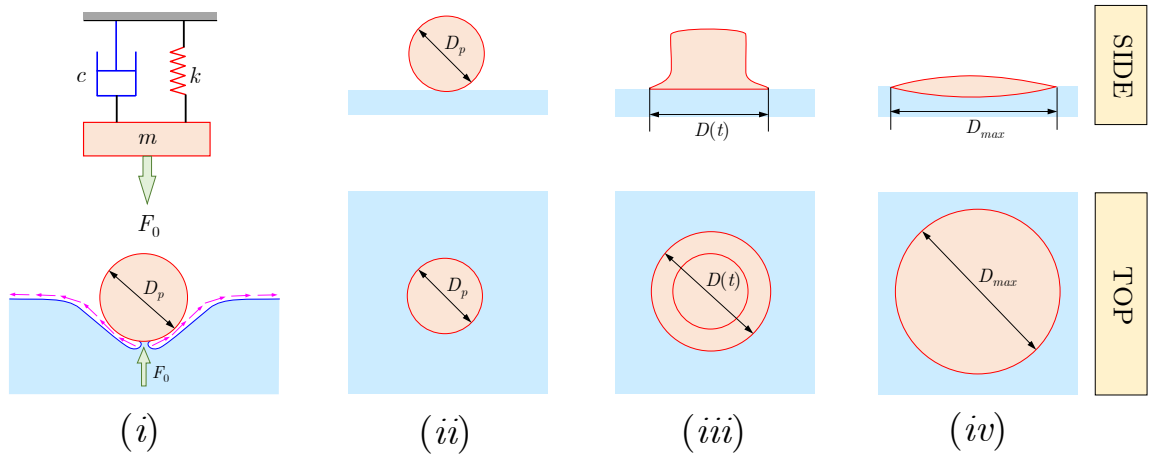


Figure 4.13: Schematic shows the modeling of the spreading of the oils as a second order mechanical system. The spreading is analogous to a spring-mass damper system.

obtain the equation of motion for the second order mechanical system in terms of its

oscillatory features like the natural frequency ω_n viscous damping ratio ζ as given in [Equation 4.19](#)

$$\frac{d^2 X}{dt^2} + 2\zeta\omega_n \frac{dX}{dt} + \omega_n^2 X = \frac{F_0}{k}\omega_n^2 \quad (4.19)$$

where the undamped natural frequency of the system is given by $\omega_n = \sqrt{k/m}$ and the viscous damping ratio is defined as $\zeta = c/c_{cr}$. Here, c_{cr} is the critical damping value given by $c_{cr} = 2\sqrt{km}$. This spring-mass damper system is analogous to the case of a spreading drop where the mass of the drop is equivalent to the mass of the block, the spring force is provided by the surface tension, and the viscosity of the spreading liquid is responsible for the viscous damping force. As the thin air film between the drop and bulk liquid drains bringing the drop in contact with the surface, a step force of magnitude F_0 acts on the drop. Let the diameter of the oil drop in contact with the bulk liquid be $D(t)$ at any instance of time t . The velocity of the expanding film is thus given as $V = dD/dt$ at any instant t . The equation of motion for the case of an oil drop spreading on a liquid substrate can be expressed as [Equation 4.20](#)

$$m \frac{d^2 D}{dt^2} + c \frac{dD}{dt} + kD = F_0 \quad (4.20)$$

with an initial diameter $D(0) = D_p$ equal to the diameter of the parent drop, and initial velocity $V(0) = 0$. The mass of the drop m , the coefficient of viscous damping force c , the spring coefficient (surface tension) k , and the initial step force F_0 can be expressed with dimensional consistency as follows in [Equation 4.21](#)

$$m = \frac{\rho_p \pi D_p^3}{6} \quad c = \mu_p D_p \quad k = \sigma_p \quad F_0 = \sigma_p D_p \quad (4.21)$$

Here, we consider the inertio-visco-capillary length and time scales as appropriate dimensional scales to transform the equation of motion into a non-dimensional form since during the spreading of the drop, the inertial, viscous, and capillary forces are in balance. Using these length and time scales, a non dimensionalized form of the

equation of motion can be obtained as shown in Equation 4.22 with the appropriate scales as shown in Equation 4.23.

$$\frac{\pi \rho_p D_p^3}{6 t_\mu^2 \sigma_p} \frac{d^2 \tilde{D}}{d\tilde{t}^2} + \frac{\mu_p D_p}{t_\mu \sigma_p} \frac{d\tilde{D}}{d\tilde{t}} + \sigma_p D_p \tilde{D} = \tilde{F} \quad (4.22)$$

$$\tilde{D} = \frac{D}{l_\mu} \quad \tilde{t} = \frac{t}{t_\mu} \quad (4.23)$$

where the right hand side (R.H.S) of Equation 4.22 represents a non-dimensional form of the initial step force acting on the drop as it comes in contact with the drop. The non dimensional form of the equation of motion can be further reduced with the consideration of an appropriate time scale. Considering the inertio-visco-capillary timescale as defined in Table 4.1 ($t_\mu = \mu_p^3 / \rho_p \sigma_p^2$), the equation of motion is reduced to Equation 4.24

$$Oh_p^{-6} \frac{d^2 \tilde{D}}{d\tilde{t}^2} + Oh_p^{-2} \frac{d\tilde{D}}{d\tilde{t}} + \tilde{D} = \tilde{F} \quad (4.24)$$

which shows a dominant influence of the Ohnesorge number of the parent drop (Oh_p). The solution to the second order Ordinary Differential Equation (ODE) in Equation 4.18 consists of homogenous and particular parts as given in Equation 4.25.

$$X = X_h + X_{par} = Ae^{st} + \frac{F_0}{k} \quad (4.25)$$

where X_h is the homogenous solution while X_{par} is the particular solution. The homogenous part of the solution is given by the exponential function Ae^{st} while the particular solution ($F_0/k = X_{ss}$) signifies the state achieved by the system if the initial step force F_0 is applied very slowly. Substituting Equation 4.25 into Equation 4.19,

we obtain the characteristic equation of the system as shown in [Equation 4.26](#)

$$s^2 + 2\zeta\omega_n s + \omega_n^2 = 0 \quad (4.26)$$

The roots of this polynomial are given in [Equation 4.27](#)

$$s_{1,2} = -\zeta\omega_n \mp \omega_n \sqrt{\zeta^2 - 1} \quad (4.27)$$

Since the roots of the characteristic equation depends on the value of the viscous damping ratio ζ , the solution to the equation of motion can now be rewritten as given in [Equation 4.28](#).

$$X(t) = A_1 e^{s_1 t} + A_2 e^{s_2 t} + \frac{F_0}{k} \quad (4.28)$$

where A_1 and A_2 are constants determined from the initial conditions in displacement and velocity. Based on the values of the damping ratio ζ , three distinct cases for the response of the mechanical system can be defined as follows

- Underdamped response: $0 < \zeta < 1$; $c < c_{cr}$
- Critically Damped response: $\zeta = 1$; $c = c_{cr}$
- Overdamped response: $\zeta > 1$; $c > c_{cr}$

Based on the defined cases, the solutions for the underdamped and overdamped responses can be derived by adding the homogenous and particular solutions.

4.11.1 Underdamped System

For the underdamped system, the solution is given by [Equation 4.29](#)

$$X(t) = e^{-\zeta\omega_n t} (C_{1u} \cos(\omega_d t) + C_{2u} \sin(\omega_d t)) + X_{ss} \quad (4.29)$$

where the particular solution ($X_{ss} = F_0/k$) is given by the steady state achieved if the initial force is applied very slowly. ω_d is the damped natural frequency given by $\omega_d = \omega_n \sqrt{1 - \zeta^2}$. The constants C_{1u} and C_{2u} are based on the initial conditions as given in [Equation 4.30](#). At $t = 0$, the initial conditions are given by $V(0) = V_0$ and $X(0) = X_0$.

$$C_{1u} = (X_0 - X_{ss}) \quad C_{2u} = \frac{V_0 + \zeta \omega_n C_{1u}}{\omega_d} \quad (4.30)$$

4.11.2 Overdamped System

For the overdamped system, the solution is given by [Equation 4.31](#)

$$X(t) = e^{-\zeta \omega_n t} (C_{1o} \cosh(\omega_o t) + C_{2o} \sinh(\omega_o t)) + X_{ss} \quad (4.31)$$

where the term ω_o is a term which gives the overdamped equivalent frequency. It is not a frequency of the system as in the overdamped case, since the response is not oscillatory. The term is given by $\omega_o = \omega_n \sqrt{\zeta^2 - 1}$. The constants C_{1o} and C_{2o} are given in [Equation 4.32](#)

$$C_{1o} = (X_0 - X_{ss}) \quad C_{2o} = \frac{V_0 + \zeta \omega_n C_{1o}}{\omega_o} \quad (4.32)$$

Using the solutions for the underdamped and overdamped cases, the corresponding constants in the ODE representing the drop spreading in [Equation 4.24](#) are substituted and the theoretical model is plotted. The constants in [Equation 4.24](#) used in the solutions are given in [Equation 4.33](#)

$$\omega_n = Oh_p^3 \quad c_{cr} = 2Oh_p^{-3} \quad \zeta = \frac{Oh_p}{2} \quad (4.33)$$

The theoretical solution is given by the solid line in [Figure 4.14](#), while data points represent the experimental data. It is evident from [Figure 4.14](#) that the theoretical

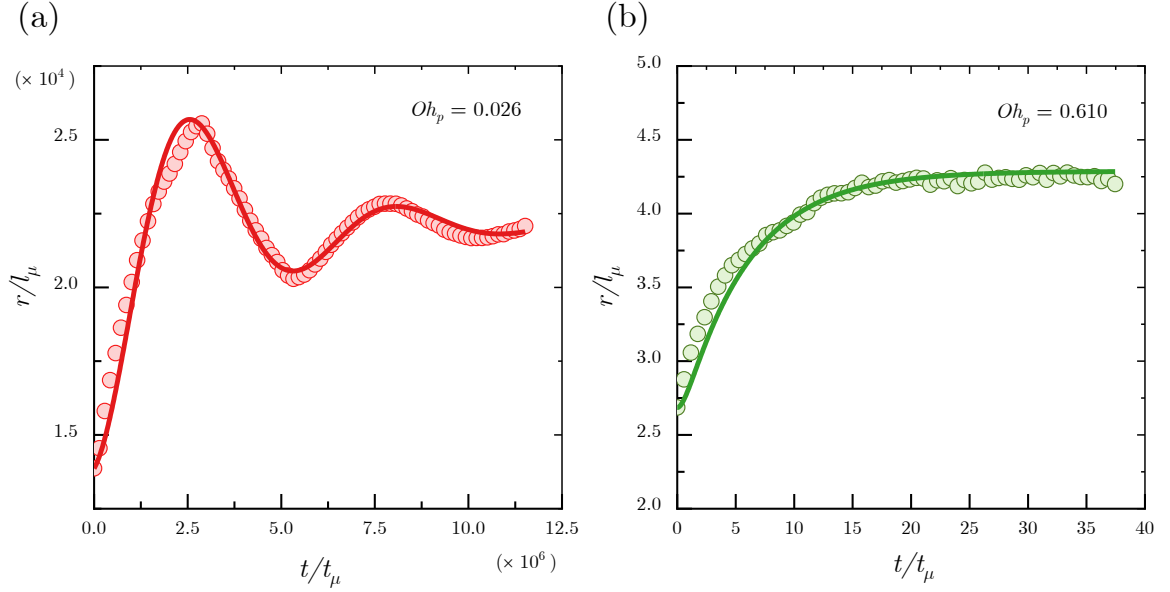


Figure 4.14: Time evolution of the radius of the oil films during spreading. (a) shows an oscillatory behavior in the case of an oil with comparatively low Oh (0.0085) corresponding to an underdamped mechanical system, while (b) shows monotonic spreading in the case of an oil with comparatively higher oh (0.610) corresponding to an overdamped mechanical system. The radius and time have been non-dimensionalized using the inertio-visco-capillary length and time scales respectively. The experimental data shows a match with the theoretical model.

model developed using the equation of motion for a second order mechanical system describes accurately the behavior of the drop during spreading.

In order to obtain a good match between the theoretical model and the experimental results, a fitting constant is appended into the solution of the theoretical model. The fitting constants added were of the order $\mathcal{O} 1$. The prefactor fitting constant was multiplied to the natural frequency of the system ω_n . The corrected natural frequency is given by $\omega_n^* = j \times \omega_n$. The values of j range from 1.32 - 5.88.

Chapter 5

Spreading during Dewetting

The coalescence of an oil drop with the surface of water as discussed in [chapter 4](#) represents a case of oil-water interaction commonly observed in tanker spills etc. A second scenario frequently observed during an underwater oil spill is the impact of a drop onto an air-water interface following a rise in the bulk liquid. This scenario can be modeled by introducing a rising oil drop in a bulk liquid and gently impacting it at the liquid-air interface. The spreading of oils following such an impact are representative of the behavior of oils undergoing a similar impact during an oil spill in the ocean. This chapter elaborates on the spreading characteristics of various oil drops upon impact onto the interface of liquid and air.

5.1 Background

Although drop impact on liquid substrates has been studied extensively in the context of an oil spill, comparatively less studied is the impact and subsequent spreading of an oil drop when introduced below the surface of a liquid. Recently, Lolla [\[102\]](#) investigated the dynamics of drop deformation during the impact of a drop beneath the surface of the bulk liquid and reported partial coalescence. The drop deformation features observed during the partial coalescence of an oil drop with a dissimilar liquid

as discussed in [chapter 4](#) are very similar to the dynamics during the impact and emergence of an oil drop introduced below the interface. When a drop gently impacts the air-liquid interface from below, it exerts a force vertically upwards due to buoyancy. This anti-gravity force causes the thinning of a small volume of bulk liquid trapped between the drop and the ambient air. Eventually, the thin film reaches microscopic scales and ruptures, forcing the bulk liquid to dewet the drop, inducing capillary waves along the interface of the oil drop and bulk liquid. These capillary waves stretch the drop downwards causing a *reverse jetting* analogous to the upward jet discussed in [chapter 4](#). Similar to the results of **Experiment 1**, the outcome of the dewetting process depends greatly on the strength of the capillary waves reaching the apex of the drop. Consequently, this means that the viscous resistance offered to the capillary waves by the drop and the bulk liquid ultimately determine the outcome. In the case of drop impact from the top, the ambient air is considered to be inviscid and hence the only resistance offered to the capillary waves is by the inherent viscosity of the drop. On the contrary, in the case of dewetting, the viscous resistance offered by the bulk liquid is of greater significance when compared to the drop. Accordingly, the *Ohensorge* number of the bulk (Oh_{bulk} or Oh_b) is defined, taking the properties of the bulk liquid into consideration. The Oh_b is defined as the ratio of viscous forces to the inertial and surface tension forces as given in [Equation 5.1](#)

$$Oh_b = \frac{\mu_b}{\sqrt{\rho_b \sigma R_p}} \quad (5.1)$$

where μ_b , ρ_b are the viscosity and the density of the bulk respectively, σ is the interfacial tension of the oil and water, and R_p is the radius of the parent drop. The *Ohnesorge* number of the bulk fluid and the drop can be related using the viscosity and density

ratios of the drop and bulk fluid as shown in [Equation 5.2](#)

$$Oh_b = \frac{\sqrt{\rho_r}}{\mu_r} Oh_p \quad (5.2)$$

where ρ_r is the ratio of the densities of the drop and bulk liquid ($\rho_r = \rho_p/\rho_b$), and μ_r is the ratio of dynamic viscosities of the drop and bulk liquid ($\mu_r = \mu_p/\mu_b$).

Thus it is appropriate to express the features of drop deformation and spreading as a function of the bulk *Ohnesorge* number (Oh_b). Before the various features are scaled with the Oh_b , the mechanism of spreading is discussed in [section 5.2](#).

5.2 Mechanism of Drop Spreading in Dewetting

As the film of bulk liquid thins under the force of buoyancy as discussed in [section 5.1](#), the rupture induces capillary waves along the interface of the drop and bulk liquid. At the interface of the bulk liquid and the ambient air, the ruptured film retracts over the drops surface, dewetting it to expose it to the ambient air. [Figure 5.1](#) shows the different stages in the spreading of the drop during dewetting. [Figure 5.1\(a\)](#) shows

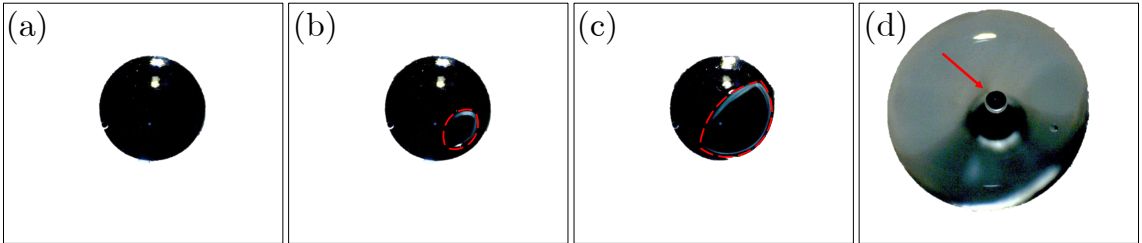


Figure 5.1: The different stages of dewetting and subsequent spreading of a drop during impact from bottom. (a) Shows the drop when it approaches the air-bulk liquid interface and thins the film of bulk fluid. (b) The rupture of the thin film takes place when the film thins to microscopic scales. The rupture area is shown in the red dashed ring. (c) The ruptures film dewets the drop as it spreads on the surface. The retracting film is shown in the red dashed ring. (d) The spreading of the drop after the bulk liquid has dewet the drop. The dynamics under the surface such as the pinching off of the daughter droplet can also be observed.

the drop as it approaches the interface of air and bulk liquid and thins the film of bulk liquid trapped. As the film thins to microscopic scales, the rupture causes the onset of the dewetting of the film as shown in [Figure 5.1\(b\)](#) where the red dashed ring shows the region of rupture. Following this, the film dewets the oil drop exposing it to the ambient air as shown in [Figure 5.1\(c\)](#) with the dashed red curve showing the periphery of the dewet region of the drop. Once the film completely dewets the drop, a three phase contact line is established on the edge of the spreading oil film and the drop spreads on the surface of the bulk liquid. From the top, the drop features below the surface such as the pinch off of the daughter droplet can be seen in [Figure 5.1\(d\)](#). The daughter droplet can be seen as a small black circle shown using the red arrow.

5.3 Spreading Characteristics during Dewetting

After understanding the mechanism of dewetting and spreading of the drop, we can proceed to understand the different spreading characteristics based on their physical properties. As the drop starts to spread on the surface of the bulk liquid, the contact area of the drop with the surface increases. To understand the behavior of the spreading film, the radius was tracked at every instant and plotted in [Figure 5.2](#). On observing the time variation of the radius of the spreading films during dewetting, one notices two distinct cases as shown in [Figure 5.2](#). If the viscous resistance offered by the bulk liquid is comparatively low, then the spreading film shows an oscillatory behavior as the film contains greater energy during the spreading. The greater energy results in the spreading of the film to a certain maximum radius, following which the restoring force namely the surface tension acts to retract the film to a stable radius. This behavior is observed in drop-bulk liquid systems with comparatively less dominant viscous forces, represented by a lower Oh_b ($Oh_b = 0.0025$). On the contrary, if the viscous resistance offered by the bulk liquid is relatively high, then the

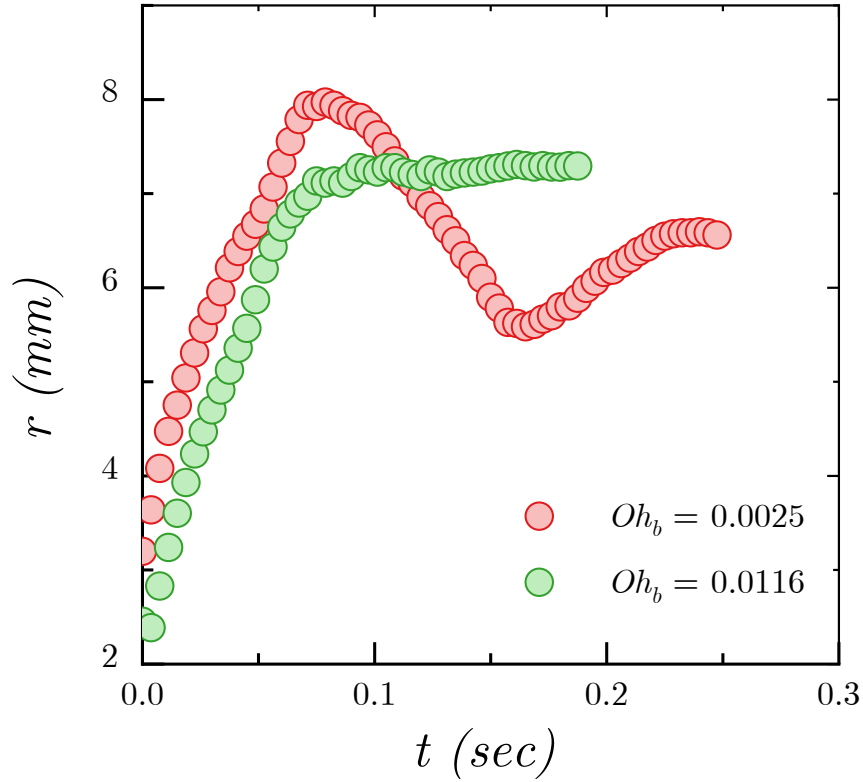


Figure 5.2: The time variation of the radius of the spreading during dewetting. The drop and bulk system with lower viscous resistance ($Oh_b = 0.0025$) shows an oscillatory spreading behavior as it recoils and subsequently spreads to a stable film, while the drop and bulk system with higher viscous resistance ($Oh_b = 0.0116$) shows a monotonic spreading behavior.

energy of the spreading film is diminished greatly after the dewetting event. Under such circumstances, the drop spreads monotonically as it expends a majority of its kinetic energy in overcoming the viscous forces. This behavior of monotonic spreading corresponds to drop-bulk liquid systems with comparatively higher Oh_b as seen in [Figure 5.2](#) ($Oh_b = 0.0116$). These spreading behavior are similar to the spreading behavior observed in drops gently deposited on the surface of water as discussed in [chapter 4](#). They show analogous behavior to a second order mechanical system such as the spring mass damper system with the drops with a lower and higher Oh_b showcasing an underdamped and overdamped response respectively.

5.4 Maximum Radius of Spreading Film

After identifying the different modes of spreading during dewetting, the following steps involve characterizing the features during the spreading using the physical properties of the drop. As discussed in [section 5.3](#), the drops show different spreading behavior depending on the physical properties of the bulk liquid they are introduced in. To understand the extent of spreading of the drops especially in the context of underwater oil spills, the maximum radius of the spreading film is recorded and a non-dimensional form of the maximum radius is plotted against the Oh_b in [Figure 5.3](#). As expected,

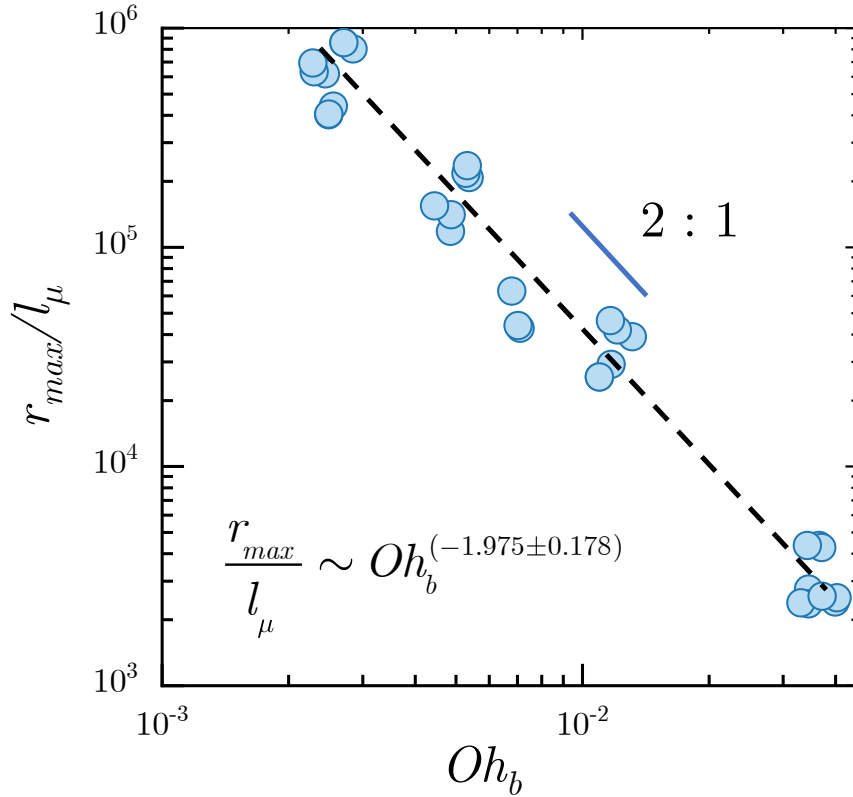


Figure 5.3: The maximum radius of the spreading film as a function of Oh_p non-dimensionalized using the inertio-visco-capillary scaling.

the maximum radius shows a decreasing trend with an increase in Oh_b . This confirms the high influence of the physical properties of the bulk liquid, more importantly the viscosity, in determining the extent of spreading of the oil drops. The data collapses onto a master curve when plotted against the Oh_b and the maximum radius is found

to scale as $r_{max}/l_\mu \sim Oh_b^{-1.97 \pm 0.178}$.

It is important to note that the dimensional scales obtained through the inertio-visco-capillary scaling, as discussed in [chapter 4](#) is used to non-dimensionalize the salient features in dewetting. Although the dimensional analysis used it the same, the appropriate length scale (l_μ), time scale (t_μ), and velocity scale (V_μ) as given in [Equation 5.3](#) are obtained .

$$l_\mu = \frac{\mu_b^2}{\rho_b \sigma} \quad t_\mu = \frac{\mu_b^3}{\rho_b \sigma^2} \quad V_\mu = \frac{\sigma}{\mu_b} \quad (5.3)$$

where μ_b and ρ_b are the viscosity and density of the bulk liquid respectively, and σ is the interfacial tension of the bulk liquid and the drop.

5.5 Recoil Dynamics during Dewetting

As discussed in [section 5.3](#), the drop and bulk liquid systems with relatively lower Oh_b show an oscillatory behavior, first spreading to a maximum radius and subsequently retracting to a minimum radius due to the restoring surface tension force. The recoil dynamics displayed by such oils have implications on the final spreading radius of the oil drop. The recoil dynamics are useful in predicting the extent of spreading of drops during an oil spill as well as in determining the radius of the oil lens in applications such as polymerizing the oil film to form optical lenses. To study the recoil dynamics of the drops during dewetting, two salient parameters, the extent of recoil, and the time taken for recoil are investigated and characterized using the Oh_b . [Figure 5.4](#) shows the extent of recoil ($\Delta r/l_\mu \sim Oh_b^{(-2.74 \pm 0.086)}$) scaled against the Oh_b . As expected, with increasing viscous effects signified by an increase in Oh_b , the extent of recoil, calculated as the difference between the maximum and minimum radius of the spreading film, shows a decreasing trend. This is indicative of the damping effect provided by the intrinsic viscosity of the bulk liquid.

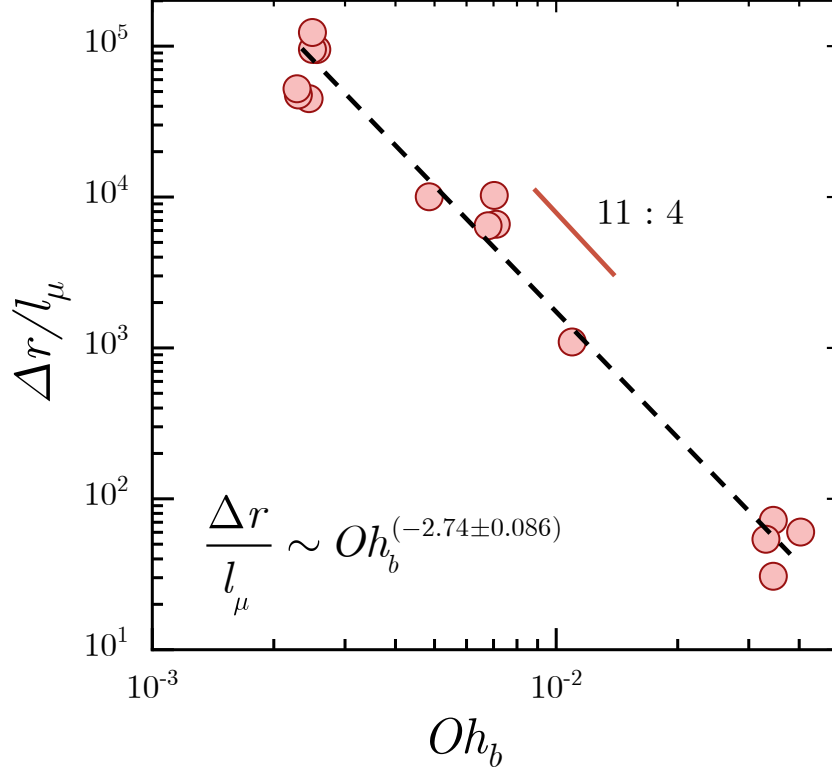


Figure 5.4: The maximum radius of the spreading film as a function of Oh_p non-dimensionalized using the inertio-visco-capillary scaling.

Another facet of the recoil behavior studied is the time taken for the drop to recoil. The recoil time (t_{rec}), defined as the time taken by the drop to recoil from its maximum size to its minimum size during the first recoil, is scaled against the Oh_b and plotted in Figure 5.5. The recoil time, like the extent of recoil, shows a decreasing trend with an increase in the Oh_b . The data follows a master curve which is represented by the relation $t_{rec}/t_\mu \sim Oh_b^{-4.386 \pm 0.26}$.

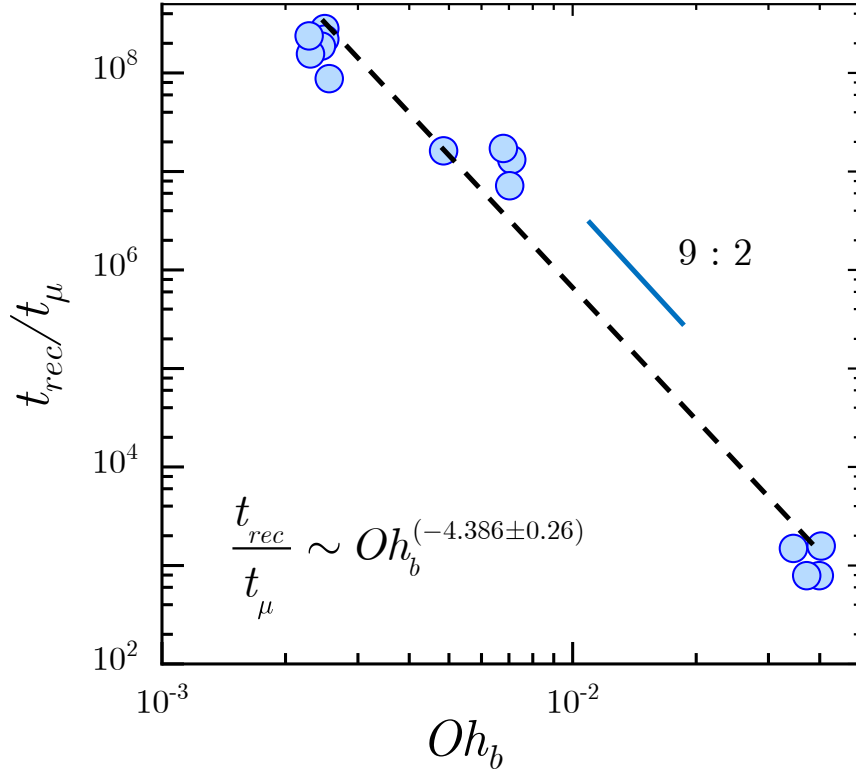


Figure 5.5: The maximum radius of the spreading film as a function of Oh_p non-dimensionalized using the inertio-visco-capillary scaling.

5.6 Comparison of Spreading during Partial Coalescence and Dewetting

It is observed that the spreading behavior of the drops during dewetting is similar to the spreading behavior of the drops during partial coalescence. To note any differences between the spreading of the drops, the time variation of the radii of two similar drops, one undergoing partial coalescence and the other dewetting, are plotted simultaneously in [Figure 5.6](#). Although the behavior is oscillatory in both of them, the obvious differences lie in the radius and time of the process. While the initial radii of both the drops are comparable, the maximum radius and ultimately the stable film radius attained by the drop during dewetting are far greater than the corresponding radii of

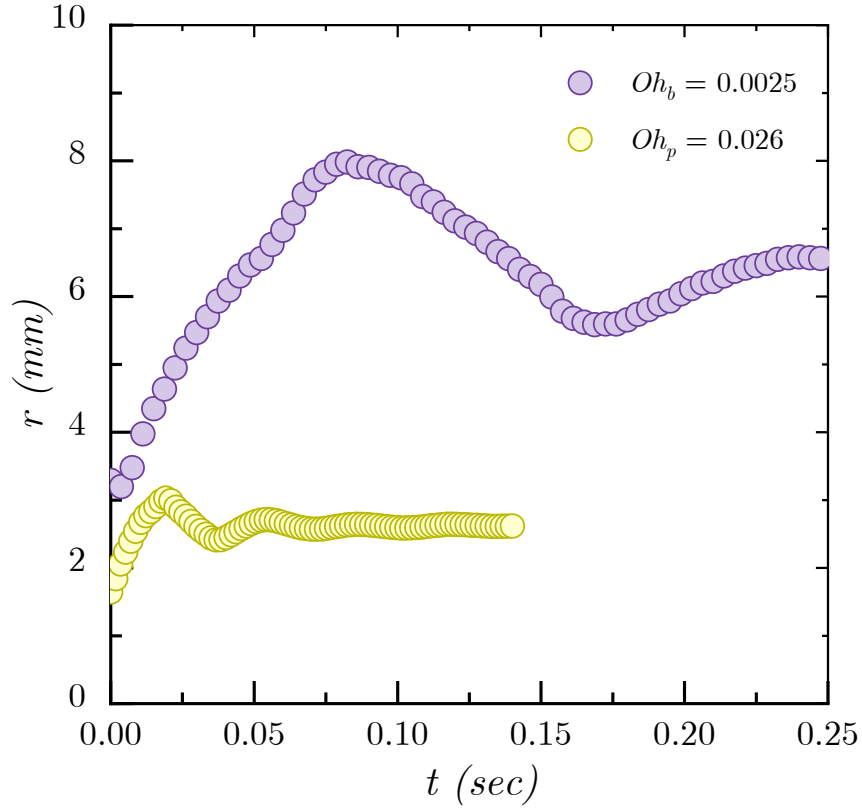


Figure 5.6: The time variation of the radius of the spreading of drops during dewetting (purple) ($Oh_b = 0.0025$) and partial coalescence (yellow) ($Oh_p = 0.026$). Both systems show an oscillatory behavior due to their relatively low *Ohnesorge* numbers, however the time taken to form a stabilized film is different.

the drop spreading during partial coalescence. This leads to a very important difference between the spreading characteristics under partial coalescence and dewetting. If an oil drop is introduced below the surface of water in an ocean, the spreading of the drop upon rupture and emergence would be greater than a drop introduced above the surface of the water. It can thus be hypothesized that the spreading of oil drops during an underwater oil spill will be greater than the spreading of the drops during a tanker spill occurring above the surface of water. The drops however, would reach a stable film radius faster if the drop is introduced above the surface.

Chapter 6

Material Synthesis

Similar to the dynamics of drop deformation discussed in [chapter 4](#), an oil drop impacted gently onto an air-liquid interface from below undergoes several transformations to its profile. When a drop with density lower than the bulk liquid is brought close to the interface of air and bulk liquid, the drop exerts a force on the interface due to buoyancy. Subsequently, the film of bulk liquid sandwiched between the drop and ambient air thins to microscopic scales, following which, it ruptures to dewet the drop. This rupture leads to an onset of capillary waves along the interface of the drop and bulk liquid, much alike the waves discussed in [chapter 4](#). As the capillary waves deform the drop, they are opposed by the viscous forces of both the drop and bulk liquid. Depending on the viscous effects of the drop and bulk liquid, the dewetting process can either result in the generation of a secondary drop known as a daughter droplet or in the complete spreading of the drop on the surface. In oils with low viscosity, the generation of the secondary droplet results in a cascade of dewetting events until the full volume of oil spreads on the surface of the bulk liquid. This chapter explores various methods to control these dewetting events to arrest the process of partial coalescence (see [section 6.1](#)), as well as examines methods to encapsulate distinct drops by controlling the dewetting process ([section 6.2](#)).

6.1 Production of Armored Drop via Dewetting

The most reliable technique to arrest a drop under water without altering its inherent properties like surface tension is by coating the drops with an armor of particles. The “armored” drops, also known as pickered or particle-stabilized drops play a vital role in applications such as particle encapsulation, emulsion stabilization, and flotation devices[2]. When the drops of oil are coated with particles, they jam the interface and create a barrier between the oil and surrounding bulk. The following sections elucidate the methods and mechanism employed in arresting the partial coalescence and stabilizing armored drops at the interface of an air-water interface.

6.1.1 Methods

The control of dewetting events was achieved using hydrophilic Bentonite clay particles (CAS: 1302-78-9, purchased from Sigma Aldrich Corporation). The particles were dispersed in the oil (n-Hexadecane) in different concentrations ranging from 0.5% *w/w* to 6% *w/w* by first weighing the particles on a Mettler Toledo XSR analytical balance. Next, the clay particles were mixed with the oil using a Scientific Industries Vortex Genie 2 Vortex mixer. The mixture was later sonicated for 5 minutes to disperse the clay particles and to deagglomerate any lumps of clay. The dispersion mixtures were prepared freshly for each experiment to maintain accurate particle concentration during the experiments. A glass cuvette of dimensions $30 \times 30 \times 30$ mm was used to hold the bulk water. Drops of the dispersed mixture were generated under water using a NE97 ‘J’ shaped needle purchased from KRÜSS Scientific.

6.1.2 Arrest of the Dewetting Cascade

The mechanism of arresting an oil drop by impeding the cascade of dewetting events is illustrated in [Figure 6.1](#). As the oil drop containing the dispersed particles rises

up the water column, the hydrophilic nature of the clay particles promote them to move to the interface of oil and water (Figure 6.1(a)). At the interface, the drop thins the layer of bulk liquid by exerting a force due to buoyancy, ultimately rupturing the film. Concurrently, the rupture induces capillary waves which travel the interface of the oil and water to deform its profile and stretch it downwards, leading to a pinch off of the daughter droplet. With the spreading of the oil drop on the surface of the water, most of the clay particles are released into the bulk water and are stranded at the interface of the spreading oil film and water (see Figure 6.1(b)). The first dewetting event also reduces the surface area of the oil drop significantly providing more particle coverage on the surface of the drop. If the initial particle concentration in the parent drop is high enough, the clay particles self assemble on the surface after the first dewetting event. In the event that the particle concentration in the

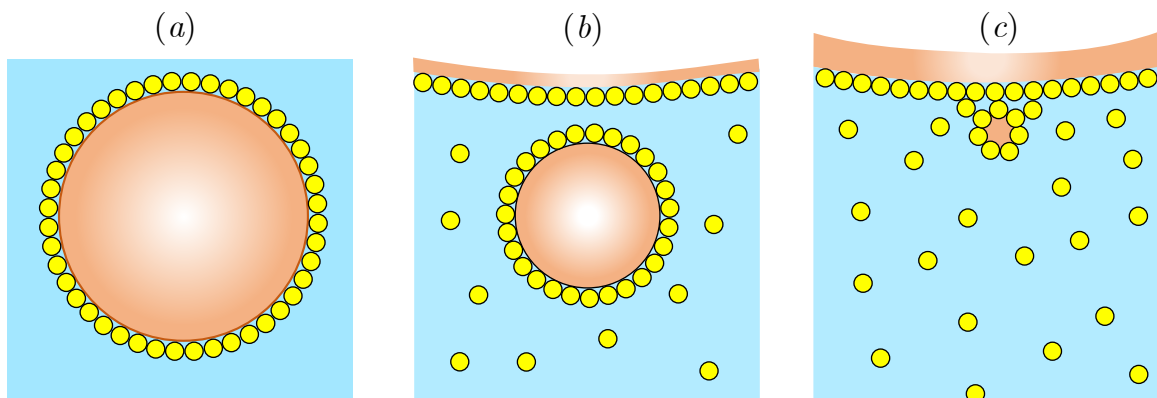


Figure 6.1: The schematic representation of the formation of a stable armored drop during the cascade of dewetting events. (a) Represents the parent drop with low surface coverage of hydrophilic particles. (b) The relatively increased surface coverage of the particles after the first dewetting event. (c) The formation of a stable armored drop with a dense particle coverage on the surface of the drop. Following successive dewetting events, some particles disperse into the bulk liquid and are found at the interface of the bulk liquid and air.

parent drop is not sufficient to cover the surface of the first generation of daughter drop, further dewetting events take place until the surface area of the drop reduces substantially to allow for the self assembly of the particles on the interface of oil and water. The self assembly of the particles at the surface jams the interface and creates

a semi permeable barrier between the oil phase and the water phase. Simultaneously, following successive dewetting events at the air-water interface, the number of clay particles suspended near the air-water interface increases greatly, resulting in a layer of particles between the air-water interface and the oil drop (Figure 6.1(c)). The layer of clay particles at the air-water interface and the self assembled particles on the surface of the drop contribute to the suspension of the armored drop under the surface of water.

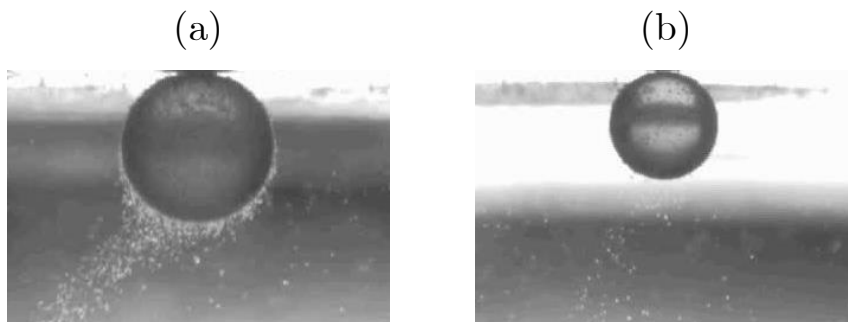


Figure 6.2: The arrest of the dewetting cascade results in a stable armored droplet. (a) shows a stable armored drop obtained after 1 dewetting event using a 5% w/w particle concentration. (b) shows the stable armored drop in the case of 3% w/w particle concentration. The stable armored is obtained after 2 dewetting events.

6.1.3 Effect of Particle Concentration

From the discussion in subsection 6.1.2, it is clear that adding particles to the oil alone does not ensure the arrest of the oil drop under the surface of water. The amount of particles added to the oil greatly determines the outcome of events following the first dewetting event. To investigate the effect of particle concentration on the number of dewetting events and the size of the stable armored drop, various concentrations of particles were tested. Parent drops of a constant size were loaded with particles in different weight percentages ranging from 0.5% w/w to 6% w/w and the number of dewetting events and the radius of the armored drops were measured.

Figure 6.3 shows the effect of particle concentration (ϕ) on the number of dewetting

events taking place before a stable armored drop is obtained. Figure 6.3 also illustrates the ratio of radii of the final armored drop to the initial parent drop. As is expected,

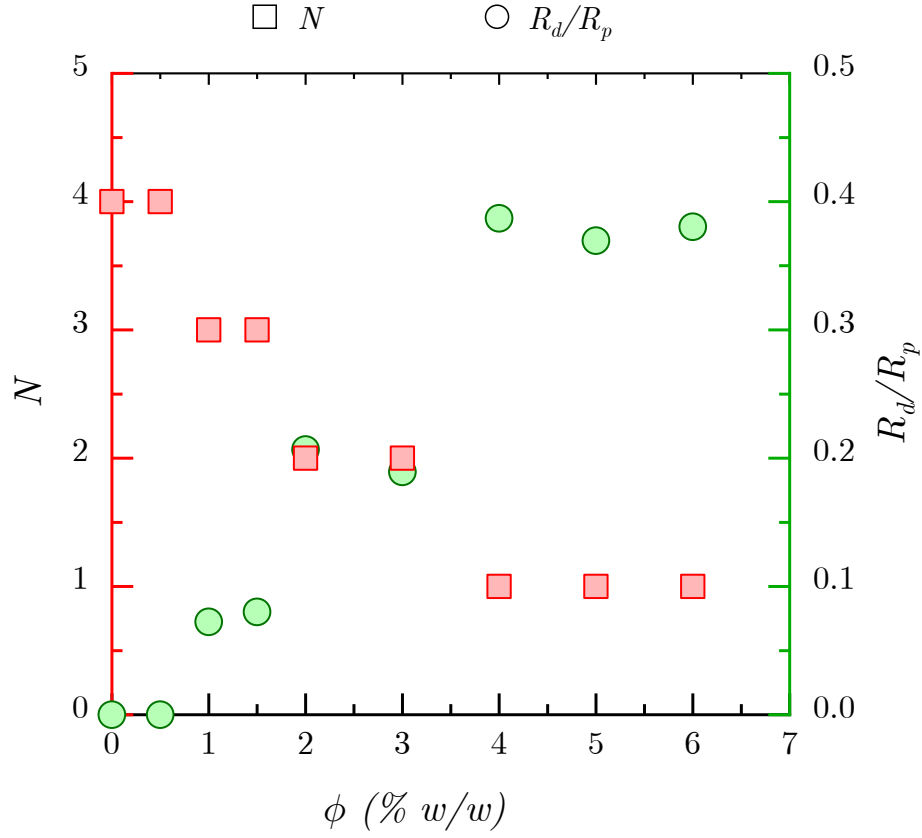


Figure 6.3: The number of dewetting events needed for stable armored drop (squares), and the ratio of radii of stable armored drop to the parent drop (circles) as a function of particle concentration (ϕ) in the parent drop.

with an increase in the initial particle concentration, stable armored drops are obtained in fewer dewetting events, consequently resulting in drops of larger size (evident from the ratio R_d/R_p). It is important to note however, when reading the graph in Figure 6.3, that the data points representing dewetting events (N) corresponding to particle concentrations of 0% and 0.5% w/w do not signify a stable armored drop, but instead are representative of cases where the cascade of dewetting events lead to a complete spreading of the oil drop on the surface of water. Armored drops of desired size can thus be obtained by controlling the amount of particles added to the parent drop.

6.1.4 Visualization of Particle Self Assembly

As described in [subsection 6.1.2](#), as the drop ascends in the bulk liquid, the clay particles move towards the oil-water interface owing to their hydrophilic nature. A stable armored drop is thus formed when the clay particles completely cover the surface of the drop and jam the interface. In order to identify the nature of particle coverage at the interface and to understand the morphology of the self assembled particles, a number of imaging techniques were used to visualize the particles as elaborated in further sections.

6.1.4.1 Particle Adsorption at oil-water interface

To verify the adsorption of the clay particles at the surface of the oil drop, an inverted pendant drop approach was chosen. A pendant oil drop of n-Hexadecane with a particle concentration of 3%w/w was generated using a ‘J’ shaped needle inside a volume of water, but was not allowed to detach the needle tip. After 30 minutes, the volume of the drop was retracted back into the needle, resulting in a ‘crumpling’ like behavior of the drop. [Figure 6.4](#) shows the adsorption of the clay particles on the surface of the inverted pendant drop during the retraction process. As the clay

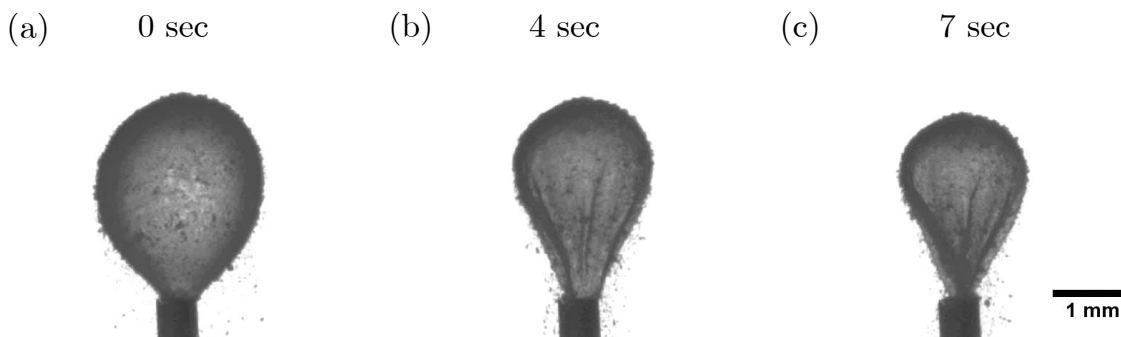


Figure 6.4: The adsorption of the clay particles at the interface of oil and water. As the oil drop is retracted back into the syringe, the shell of clay particles tries to retain its shape thereby showing a crumpling effect. (a) Shows the drop morphology at the start of the retraction process, and (b) and (c) show the changing morphology of the pendant drop at 4 and 7 seconds respectively.

particles self assemble at the oil-water interface, they strongly bond to each other forming a shell on the surface. During the retraction of the oil into the syringe, the particles prefer to retain this shell structure as opposed to desorbing from the surface, causing a crumpling of the shell due to the reduced volume. This retraction test exhibits the strong adsorption characteristics of the Bentonite clay particles at the oil-water interface, confirming the choice of particles for preparing armored droplets.

6.1.5 Confocal Laser Scanning Microscopy

The crumpling test in [subsubsection 6.1.4.1](#) presents a method to confirm the self assembly of the clay particles on the exterior of the drop. However, it does not reveal the interior of the drop. To obtain a full picture of the interior and exterior of the drop, the armored drop was visualized under a Confocal Laser Scanning Microscope (CLSM). A confocal fluorescence microscope permits the investigation of the interior of liquids and semi-permeable surfaces without any damage to the sample owing to its non invasive excitation laser beam. The sample under a fluorescent microscope must however contain fluorophores, compounds which emit light upon light excitation. To be able to visualize the drop and the behavior of the clay particles under a fluorescent microscope, the particles were labeled with *Rhodamine-B* (red) fluorescent dye, while the bulk water was dyed with Fluorescein (green) dye. The oil drop was unlabeled to make sure that any particles inside the drop were visualized under the microscope. A drop of n-Hexadecane with 4%w/w particle concentration was generated inside a microwell and allowed to dewet to form a stable armored drop. The microwell was then placed under a Zeiss Laser Scanning Confocal Microscope (LSM) 710 META and excited using a laser beam. The *Rhodamine-B* was excited using a wavelength of 561 nm and the fluorescein was excited using a wavelength of 488 nm. [Figure 6.5](#) shows the confocal microscope image of the hexadecane drop in water bulk. It is evident from the ring of red particles in [Figure 6.5](#) that the particles

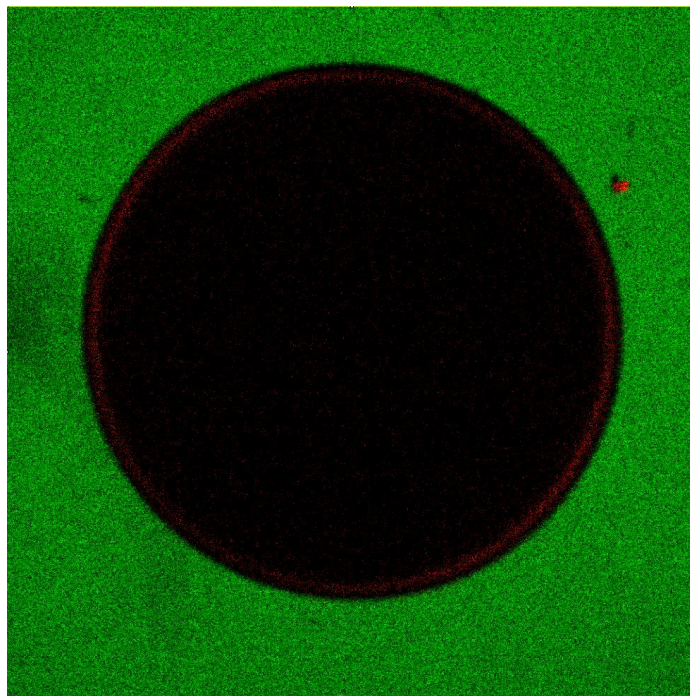


Figure 6.5: The confocal fluorescence microscope image of the armored drop. To image the armored drop, the hydrophilic particles were labeled using *Rhodamine B* dye while the bulk water was stained with *Fluorescein* dye

are adsorbed at the interface of oil and water without any trace of the particles inside the drop. [Figure 6.5](#) also shows a lump of clay particles (top right corner) that are released into the bulk liquid during the first dewetting event. The process of staining the clay particles is discussed in [subsubsection 6.1.5.1](#).

6.1.5.1 Staining process of Bentonite clay particles

Bentonite clay particles are inherently not fluorophores, and hence need to be stained with a fluorescent dye to be able to visualize under a confocal microscope. *Rhodamine-B* dye was selected to stain the Bentonite particles as *Rhodamine-B* has been found to organically bond to Bentonite clay particles. Sodium Bentonite stained with *Rhodamine-B* has been used as a tracer material in studying water contamination in rivers [51, 144]. To bentonite particles were stained by sorbing *Rhodamine-B* onto the surface of the clay particles. First, 10 gm of Bentonite particles were added to 400 ml of water and sonicated for 30 min to disperse them in the liquid. Next, 0.25

gm of *Rhodamine-B* was added to the dispersed solution and additional water was added to increase the volume of the final solution to 800 ml. The mixture was then sonicated for 60 min to ensure the dye and clay particles mixed properly. Next, it was stirred on a shaker/stirrer at 100 rpm for 180 minutes. Following the stirring,

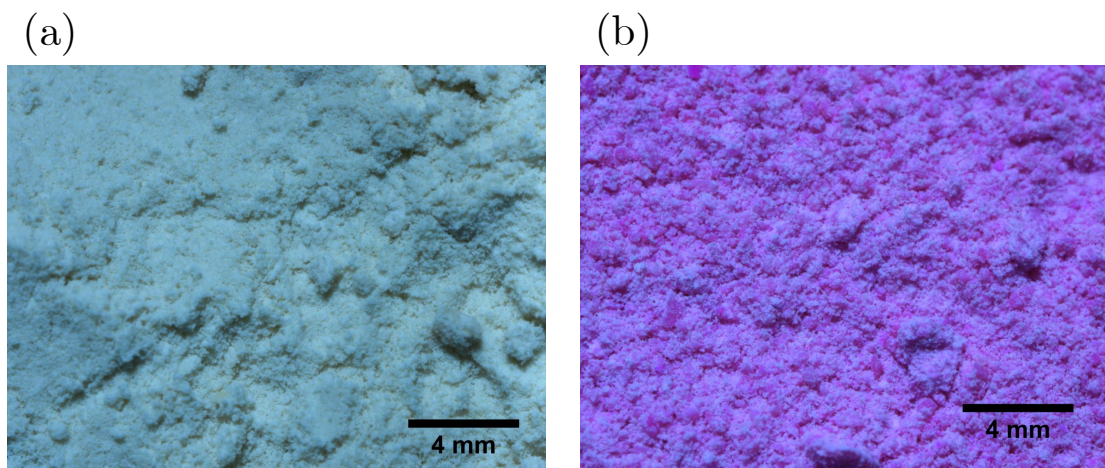


Figure 6.6: The bentonite particles imaged (a) before staining, and (b) after staining with *Rhodamine-B* fluorophore.

the mixture was allowed to settle by placing in a cool dry place for 6 hours. After 6-8 hours of not disturbing the beaker, it was observed that the supernatant liquid was clear and colourless, and a vivid red-purple powder was visible at the bottom of the beaker. The excess supernatant was decanted and the powder transferred to new container. The powder was then thoroughly rinsed repeatedly using a 50:50 mixture of saturated NaCl and ethanol and then with water. The rinsed powder, which now had a pink-purple tint to it was dried at room temperature in a vacuum desiccator. Occasionally, lumps of clay were gently separated by hand. Finally, the particles were ground to a fine powder with the help of a pestle and mortar to ensure uniform size distribution. [Figure 6.6](#) shows the particles (a) before and (b) after they were labeled with the *Rhodamine-B* fluorophore.

6.2 Other Applications of Dewetting

The generation of a secondary daughter droplet after the first dewetting event presents possible mechanisms to produce emulsions or encapsulate drops under the surface of water. To utilize the phenomenon of daughter droplet generation in producing emulsions, a coaxial nozzle was used to generate a water-in-oil double emulsion droplet which would rise up and dewet the interface of the bulk liquid and air. Depending on the volume ratio of the oil phase to the aqueous phase, the dewetting results in either a w/o/w double emulsion drop, or in a poly-dispersed o/w emulsion system. [Figure 6.7](#) shows the different scenarios of drop encapsulation and emulsion formation achieved through controlled dewetting. In order to differentiate between the two liquid phases, the oil was dyed using *Sudan Blue II*, while the water was dyed using *Rhodamine-B*. As seen in [Figure 6.7](#), when the volume of water inside the parent oil drop is comparatively less, the dewetting causes the water drop to be trapped in the daughter drop, resulting in a double emulsion ([Figure 6.7\(a\),\(b\)](#)). On the contrary, when the volume of water is comparatively very high in the parent drop, the drop rises up to the surface of the bulk liquid and forms a lens due to the weight of the water in the drop. eventually, the oil film holding the water ruptures and due to a Rayleigh-Taylor type instability, the film fragments, leaving polydispersed drops of oil beneath the surface of water[[98](#), [99](#)]. Thus by controlling the volume of water and oil impacting the surface of the bulk liquid-air interface, both polydispersed and double emulsions can be produced. Through the mechanism used in the first case ([Figure 6.7\(a\)](#)) to produce a double emulsion a very accurate volume ratio of the two components in a double emulsion can be maintained. The inner phase (water) can be controlled using a definite flow rate during production while the outer phase (oil) can be controlled by controlling the number of dewetting events taking place. The second case discussed ([Figure 6.7\(b\)](#)) pertains to an interesting scenario found in the oceans. Consider an oil slick covering the surface of the water during an oil spill. In

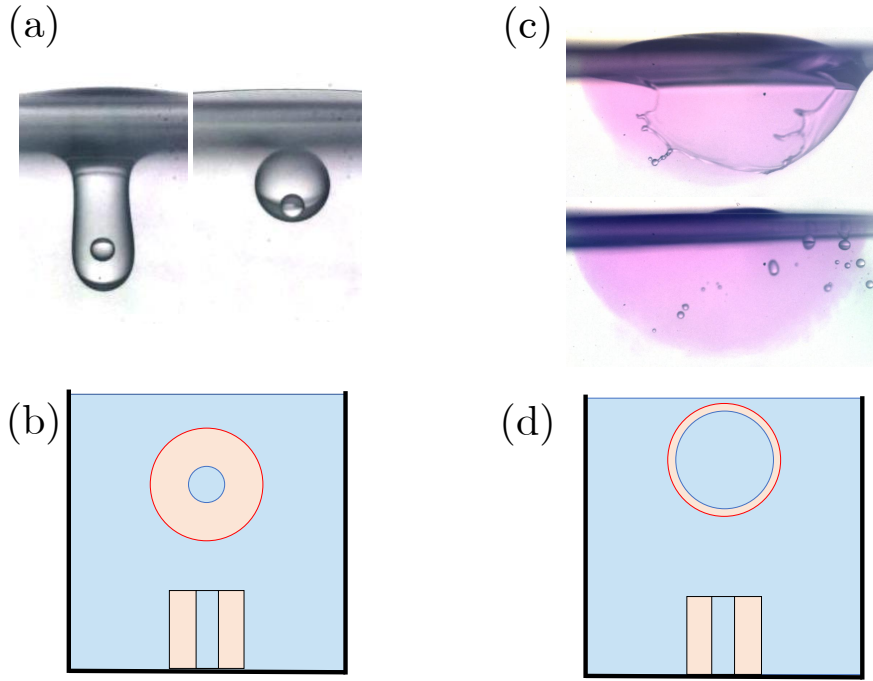


Figure 6.7: The different scenarios is drop encapsulation and emulsion formation. (a) Drop encapsulation after an event of dewetting achieved through a small water-oil ratio in the parent drop. (c) A polydispersed emulsion formed through the rupture of a thin film of oil when the parent drop comprises of a large water-oil ratio. (b) and (d) Show the schematics of a parent drop with a low water-oil ratio and a high water-oil ratio corresponding to cases (a) and (c) respectively.

the event of a raindrop impacting the surface of the oil slick at this point, the merger of the rain drop with the bulk ocean water will involve the thinning and fragmentation of the oil slick, trapping polydispersed drops of oil under the surface of water. This mechanism, previously unexplored shows an additional mechanism through which the oceans could be contaminated.

Chapter 7

Summary and Conclusions

7.1 Summary

The motivation for this study, as outlined in [chapter 1](#) proceeds from the complex interaction of oil drops and water in the context of phenomenon such as oil spills. The primary objective of the present work was understanding the behavior of an oil drop upon interaction with a liquid-air interface. Eleven Oils were chosen for their relative importance in crude oil and three different experiments were conducted. The following summarizes the salient features of the present work

- Drop deformation was studied in Experiment 1, which consisted of gently depositing a drop of oil onto the surface of water. The outcome of the process was found to have high dependence on the physical properties of the drop which were quantified using the Oh_p of the parent drop. Three different regimes partial coalescence, delayed coalescence, and complete coalescence were identified and characterized on a regime map using the Oh_p and the viscosity ratio (μ_r) of the drop and the ambient fluid.
- Experiment 1 also revealed the mechanism of partial coalescence as detailed in [chapter 4](#), with the role of capillary waves being studied. It was observed

that as the thin air film between the drop and the bulk liquid drained, capillary wave are triggered at the points of contact of the drop and the surface of water, and travel along the surface of the drop, stretching the drop upwards against gravity. It was found that the strength of the capillary waves reaching the apex of the drop determined majority of the dynamics taking place during the process of partial coalescence including the formation of a daughter droplet. The traveling capillary waves deform the drop and stretch the drop upwards against gravity if and when they meet at the apex of the drop. The stretching results in the thinning of the jet at the base of the drop and leads to a pinch off due to increasing surface energy. The pinch off results in the generation of a secondary droplet known as the daughter droplet which eventually impacts onto the air-water interface, repeating the previous process in a cascade of events ultimately leading to complete coalescence of the initial parent drop.

- However, since the viscosity of the drop dampens the strength of the capillary waves, not all drops partially coalesce with the bulk liquid. In the case of drops with relatively higher viscosity, it was found that the capillary waves are damped sufficiently before they reach the apex of the drop, and fail to deform the drop, resulting in complete coalescence. In moderately viscous drops, the capillary waves are found to deform the drop to form a jet, but are not adequately strong enough to cause a pinch off at the base of the drop. The resulting regimes are identified as (i) partial coalescence, (ii) delayed coalescence, and (iii) complete coalescence.
- The various features observed during partial coalescence were quantified and scaled against the Oh_p of the drop using the dimensional scales obtained using the dimensional analysis. The features quantified are: (1) height of the drop, (2) maximum height attained by the drop, (3) velocity of the apex of the drop, (4)

coalescence time, and (5) radius of the daughter droplet.

- Next, the spreading characteristics of a drop during the gentle impact onto the surface of water was studied in Experiment 2 ([chapter 4](#)). The same eleven oils tested in Experiment 1 were used for Experiment 2 in order to correlate the features in both cases. It was observed that similar to drop deformation features in experiment 1, the spreading of the drop was highly dependent on the Oh_p of the drop. In drops with relatively lower Oh_p , an oscillatory behavior of spreading and shrinking was observed, while drops with relatively higher Oh_p showed a monotonic increase in area. Various features of the spreading film, namely (1) radius of the film, (2) maximum radius of the film, (3) extent of recoil, and (4) time of recoil were quantified and scaled against the Oh_p of the drop.
- The spreading of the film during gentle impact of an drop was found analogous to the forced response of a second order mechanical system to a step force. To verify the analogy, a second order differential equation representing the equation of motion of a spring-mass-damper system was used to solve for the radius of the spreading film, considering the viscous and surface tension forces to be analogous to the damping and spring force respectively. The resulting analytical solution to the equation of motion of a 2nd order mechanical system matched accurately with the experimental results. It was found that drops with lower Oh_p showing an oscillatory behavior correspond to the case of an underdamped 2nd order mechanical system while the drops with a higher Oh_p with a monotonic spreading behavior are analogous to an overdamped 2nd order mechanical system.
- In Experiment 3 ([chapter 6](#)), three oils, n-Pentane, n-Hexadecane, and Polydimethylsiloxane (PDMS) 1.5cSt were used to investigate the spreading characteristics of the oils during dewetting. In order to test for a range of conditions,

different combinations of glycerol-water mixtures ranging from 0% glycerol to 60% glycerol were used as the bulk liquids. The features of spreading, namely (1) radius of the spreading film, (2) maximum radius of the film, (3) extent of recoil, and (4) recoil time were quantified. The parameters were scaled against the Oh_b of the bulk liquid using the obtained dimensional scales from the dimensional analysis.

- Lastly, the controlling of dewetting events was investigated in [chapter 6](#). Bentonite clay particles were used for their hydrophilic nature to arrest the cascade of dewetting events of the oils upon gentle impact at the liquid-air interface. Various concentrations of the clay particles ranging from 0% to 6% w/w in oil were tested to arrest the dewetting. It is shown that with the increase in concentration of particles in the oil phase, the number of dewetting events occurring before the the drop is arrested reduces. The implications of this are that by controlling the particle concentration in the oil, one can control the size of the daughter droplet arrested under the surface of the liquid.

7.2 Future Work

Following a comprehensive understanding of the salient features of drop deformation and spreading during partial coalescence, along with the spreading trends of oils during dewetting, the current work can be extended to more complex systems and the the influence of additional parameters to the system can be studied. The recommended future work is as follows:

- The current study uses an ambient fluid that can be treated as inviscid (air) to study the features of dewetting. By replacing the ambient fluid with one possessing finite viscosity, the effects of the physical properties of the ambient fluid on the spreading characteristics of the oils can be explored.

- To explore the applications of dewetting, a complex system such as a compound drop as found in double emulsions can be introduced into the bulk liquid, and the parameters can be studied. Such a study can provide insight into applications like targeted drug delivery and mass transport.
- The current study did not use any additional compounds or particles in either of the fluids. Compounds such as surfactants, which have a definite effect on the critical properties of the fluids such as surface tension can be added to the system and their effects explored.
- The bulk liquid used in this study to study the spreading of oils during partial coalescence (water) has a viscosity that is comparably lower than the viscosity of the oils. The effects of the physical properties of the bulk liquid on the spreading of the drops can be explored.
- Although with the advent of the high speed camera, the most intricate features of the drop deformation can be visualized, many microscopic features such as the dynamic contact angles during spreading and the dimensional scales during the pinch off can only be explored through computer simulations.
- During the process of dewetting, a *reverse jet* in the downward direction is observed. However, when an air bubble is introduced beneath the surface of a liquid, the dewetting results in an upward jet due to the inviscid nature of air. The transition from a *reverse jet* to an upward jet can be explored as it can provide insight into fundamental questions regarding the nature of capillary waves, and their interference at the apex of the drop.
- In the current work, newtonian fluids are used to study various features of partial coalescence and dewetting, however real scenarios of oil spills may contain non-newtonian fluids like asphalt etc. The study of the behavior of non-newtonian

fluids during partial coalescence, particularly spreading characteristics can be explored.

- This work focuses on the dynamics during a gentle impact of an oil drop onto the surface of water and eliminates any inertial effects. The inertial effects of a drop impact can be explored.

Appendices

Appendix A

Dimensional Scales

When solving problems in fluid mechanics, a complex system can be better understood when the quantities under consideration can be made scale invariant. In order to obtain the fundamental scales (length, time and velocity) to non-dimensionalize the quantities, an understanding of the dominant forces is critical. Once the dominant forces in the system are identified, the balance of the forces shed light on the **length**, **time** and **velocity** scales to be used in the system.

Considering specifically the case of free surface flows, the most relevant forces are *inertial*, *viscous*, *capillary*, and *gravitational* forces. Different force balances can be chosen based on the dominant forces in the system and corresponding dimensional scales can be obtained. It is interesting to note that the mathematical balance of the dominant forces give rise to the prominent non-dimensional numbers associated with various fluid mechanics systems such as drop formation, jet flow etc.

A.1 Definitions

Inertial Force Newton's second law of motion (conservation of momentum) dictates that the stress induced on a fluid element due to the inertial force is given by the time rate of change of momentum. For scaling analysis, it is sufficient to express the

inertial force as the proportionate inertial stress acting on a fluid element as given by $F_{in} = \rho u^2$.

Viscous Force According to Newton's equation for viscosity, the viscous stress is defined as the product of viscosity and the velocity gradient ($F/A = \mu(\Delta U/\Delta x)$ where A is the area). Consequently, the Viscous force for scaling analysis can be considered as $F_{vi} = \mu u/R$.

Capillary Force The Laplace equation gives the capillary pressure at the interface of two fluids ($\Delta P = \sigma/R$). Subsequently, the capillary force per unit area considered for scaling analysis is $F_{ca} = \sigma/R$.

Gravitational Force In the case of a liquid drop, the gravitational force acting on a drop of radius R is $F_{gr} = \rho g R$. It is important to note that for scaling arguments, it is always the stress or pressure equivalent (Force per unit area) that are considered.

A.2 Force Balances

The major forces which act on a drop/jet in different scenarios compete with each other to either stabilize or destabilize the system. The dimensional scales thus arising out of these force balances determine the scales at which these phenomenon take place. The force balances and corresponding scales are given as follows:

Inertia - Capillary force Balance Considering a balance between the inertial and capillary (surface tension) forces yields [Equation A.1](#). Subsequently, the velocity

scale is resolved in [Equation A.2](#).

$$\frac{\sigma}{R} \sim \rho u^2 \quad (\text{A.1})$$

$$\vartheta_{ic} = \sqrt{\frac{\sigma}{\rho R}} \quad (\text{A.2})$$

Considering the motion of a drop in a fluid medium, when the inertial and capillary forces are in balance, the length scales are typically the order of the characteristic length, in our case, the radius ‘R’ of the drop. The timescale is given by the ratio of the length scale and the velocity scale.

$$\ell_{ic} = R \quad (\text{A.3})$$

$$\therefore \tau_{ic} = \frac{\ell_{ic}}{\vartheta_{ic}}$$

$$\tau_{ic} = \sqrt{\frac{\rho R^3}{\sigma}} \quad (\text{A.4})$$

The non-dimensional number which relates the inertial and capillary forces is the Weber number (We). when the inertial and viscous forces perfectly balance each other, the We mathematically tends to unity. This is illustrated in [Equation A.5](#).

$$\frac{\sigma}{R} \sim \rho u^2 \implies \frac{\rho u^2 R}{\sigma} = We \sim 1 \quad (\text{A.5})$$

Inertia - Viscous force Balance The balance between inertial and viscous forces gives the relation in equation [Equation A.6](#). Solving for the velocity gives the velocity scale as shown in [Equation A.7](#).

$$\rho u^2 \sim \frac{\mu u}{R} \quad (\text{A.6})$$

$$\vartheta_{iv} = \frac{\mu}{\rho R} \quad (\text{A.7})$$

Similar to the inertio-capillary balance, the length scale is considered to be the order of the drop radius ‘R’. Additionally, since we know that the timescale can be expressed as the ratio of the length scale and the velocity scale, the length and time scales can be expressed as [Equation A.8](#) and [Equation A.9](#) respectively.

$$\ell_{iv} = R \quad (\text{A.8})$$

$$\tau_{iv} = \frac{\rho R^2}{\mu} \quad (\text{A.9})$$

The relative dominance of the inertial and viscous forces is famously characterized using the Reynold’s number (Re) of the system. In the event of an equal influence of the inertial and viscous forces, the Re is 1. Using the force balance in [Equation A.6](#), the relation for Re can be obtained as shown in [Equation A.10](#).

$$\rho u^2 \sim \frac{\mu u}{R} \implies \frac{\rho u R}{\mu} = Re \sim 1 \quad (\text{A.10})$$

Viscous - Capillary force Balance Here, the viscous and capillary forces are balanced ([Equation A.11](#)) and the velocity scale is found in [Equation A.12](#). The length scale is considered to be the radius of the drop ([Equation A.13](#)) and the time scale is derived in [Equation A.14](#).

$$\frac{\mu u}{R} \sim \frac{\sigma}{R} \quad (\text{A.11})$$

$$\vartheta_{vc} = \frac{\sigma}{\mu} \quad (\text{A.12})$$

$$\ell_{vc} = R \quad (\text{A.13})$$

$$\tau_{vc} = \frac{\mu R}{\sigma} \quad (\text{A.14})$$

When the viscous and capillary forces are in perfect balance, the Capillary number (Ca) mathematically takes the value of unity. This can be verified by considering the velocity scale obtained using the force balance as demonstrated in [Equation A.15](#).

$$\vartheta_{vc} = \frac{\sigma}{\mu} \implies \frac{\mu u}{\sigma} = Ca \sim 1 \quad (\text{A.15})$$

Inertia - Viscous - Capillary force Balance When the inertial, viscous, and capillary forces have equal influence on the system, the length, velocity, and time scales can be estimated using the force balances, as shown in [Equation A.16](#) through [Equation A.19](#).

$$\rho u^2 \sim \frac{\mu u}{R} \sim \frac{\sigma}{R} \quad (\text{A.16})$$

Solving for the velocity from the viscous and capillary force balances, we obtain the velocity scale ([Equation A.17](#)).

$$\vartheta_{vc} \sim \frac{\sigma}{\mu} \quad (\text{A.17})$$

Substituting this velocity in the inertial and viscous force balance, we obtain the length scale ([Equation A.18](#)).

$$\rho \frac{\sigma^2}{\mu^2} \sim \frac{\mu}{R} \frac{\sigma}{\mu} \implies \ell_{vc} \sim \frac{\mu^2}{\rho \sigma} \quad (\text{A.18})$$

Using the relation between time, velocity and length as in previous arguments, we obtain the time scale in [Equation A.19](#).

$$\tau_{ivc} = \frac{\ell_{ivc}}{v_{ivc}} \implies \tau_{ivc} \sim \frac{\mu^3}{\rho\sigma^2} \quad (\text{A.19})$$

The dimensional scales obtained using the inertio-visco-capillary balance become significant when the system has an equal influence of the inertial, viscous, and the surface tension forces. The Ohnesorge number (Oh) gives the relative importance of the inertial, viscous, and surface tension forces in the system. When the inertial, viscous, and capillary forces are in perfect balance in the system, the Oh , as defined in [Equation A.20](#), takes the value of 1.

$$\ell_{ivc} = \frac{\mu^2}{\rho\sigma} \implies \frac{\mu^2}{\rho\sigma R} = Oh \sim 1 \quad (\text{A.20})$$

Capillary - Gravity force Balance In the context of fluid dynamics, If the capillary and gravitational forces are the dominant forces in the system, the resulting dimensional scales can shed light on the geometry of the drop. For example, the length scale resolved using the capillary-gravity force balance is the capillary length of the drop.

$$\frac{\sigma}{R} \sim \rho g R \quad (\text{A.21})$$

Solving for the radius/length scale, we obtain the capillary length in [Equation A.22](#)

$$R \sim \sqrt{\frac{\sigma}{\rho g}} \sim \ell_{cg} \quad (\text{A.22})$$

The non-dimensional number which characterizes this capillary-gravity force balance is the Bond number (Bo) given by [Equation A.23](#).

$$\frac{\sigma}{R} \sim \rho g R \implies \frac{\rho g R^2}{\sigma} = Bo \sim 1 \quad (\text{A.23})$$

When the capillary and gravitational forces are in balance, the $Bo \rightarrow 1$. A simple demonstration of this occurs when a drop resides on a surface. At $Bo \ll 1$ (by virtue of a small radius ‘ R ’), the drop exhibits a near spherical shape. As the radius of the drop increases (with an increase in volume), the gravitational effects play a more dominant role characterized by a higher Bo and the spherical drop changes shape to form a puddle.

Inertia - Gravity force Balance When the inertial and an external force (in most cases gravity) are the most dominant on a system, the dimensional scales are obtained by their balance as given in [Equation A.24](#)

$$\rho g R \sim \rho u^2 \quad (\text{A.24})$$

The dimensional scales are given by [Equation A.25](#) through [Equation A.27](#).

$$v_{ig} \sim \sqrt{gR} \quad (\text{A.25})$$

With an assumption that the length scale is of the order of the radius of the drop (R), we can estimate the time scale.

$$\ell_{ig} \sim R \quad (\text{A.26})$$

$$\tau_{ig} = \frac{\ell_{ig}}{v_{ig}} \implies \tau_{ig} \sim \sqrt{\frac{R}{g}} \quad (\text{A.27})$$

The non-dimensional number describing the inertio-gravity balance is the Froude number (Fr) which usually gains significance in flows. Although not used very commonly, Fr is used in naval architecture. Froude number is given by [Equation A.28](#).

$$\rho g R \sim \rho u^2 \implies \frac{u^2}{g R} = Fr \sim 1 \quad (\text{A.28})$$

Appendix B

Precursor layer on Liquid Substrates

The precursor layer continues to spread at a rate given by Joos law [14]. The radius of the spreading precursor (r) is as given in Equation B.1.

$$r = \sqrt{\frac{4}{3}} \sqrt{\frac{S}{\rho^{1/2} \mu^{1/2}}} \cdot t^{3/4} \quad (\text{B.1})$$

where S is the spreading coefficient of the oil on the substrate, t is the time, ρ is the density and μ is the viscosity of the bulk liquid (water in our case).

However, considering the microscopic precursor layer as shown in Figure B.1, the height (or width) of the layer at any point on the precursor layer is given by $h(x)$. The normal stress balance at the interface leads to the *Young-Laplace Equation*: as given in Equation B.2.

$$\rho g z = \sigma \vec{\nabla} \cdot \hat{\mathbf{n}} \quad (\text{B.2})$$

where $\vec{\nabla} \cdot \hat{\mathbf{n}}$ represents the curvature of the free surface. Therefore, the force due to surface tension is given by $\sigma \vec{\nabla} \cdot \hat{\mathbf{n}}$. Let us define the free surface of the drop as

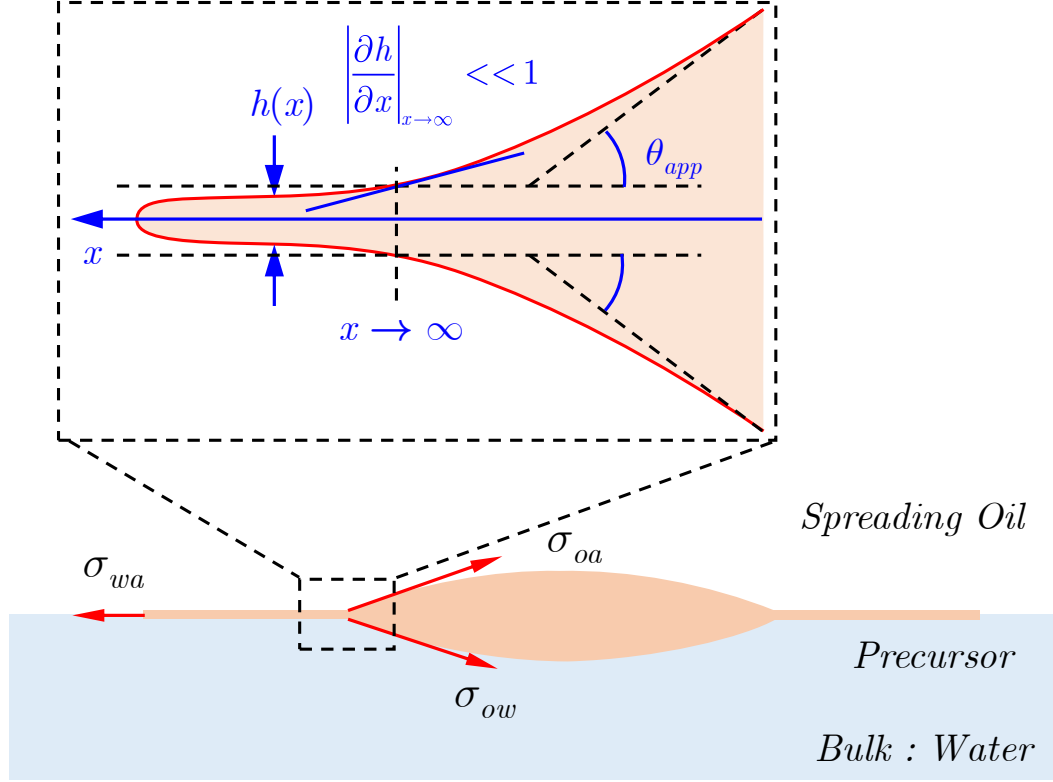


Figure B.1: The precursor layer spreading in the case of an oil drop spreading on water ($S > 0$). The height $h(x)$ represents the height of the layer at every point x on the layer.

$z = h(x)$, where the height of the lens at any point is a function of the horizontal position of the point. We can thus define a function $f(x, z) = z - h(x)$ such that the value of $f(x, z)$ is zero on the surface. The normal to the surface is given by the vector $\mathbf{n}$ as defined in Equation B.3.

$$\mathbf{n} = \frac{\nabla f}{|\nabla f|} \quad (\text{B.3})$$

The curvature of the free surface given by $\vec{\nabla} \cdot \hat{\mathbf{n}}$ can thus be expressed as in Equation B.4.

$$\vec{\nabla} \cdot \hat{\mathbf{n}} = \frac{-\frac{\partial^2 h}{\partial x^2}}{\left(1 + \left\{\frac{\partial h}{\partial x}\right\}^2\right)^{3/2}} \quad (\text{B.4})$$

As $x \rightarrow \infty$, $\partial h / \partial x \ll 1$ and $\partial^2 h / \partial x^2 \rightarrow 0$. Therefore, at the leading edge of the precursor layer, the surface tension force can be neglected. However, at a finite distance x from the center of the film, where the macroscopic curvature of the spreading drop becomes noticeable, the curvature has a finite value. At this point, the surface tension forces becomes significant and we define an apparent contact angle θ_{app} with respect to the substrate.

Appendix C

Solution of Second order mechanical system using Laplace transform

The solution of a second order mechanical system can be obtained using Laplace transforms. This chapter illustrates the solution for the response of a second order mechanical system with a spring, mass, and damper. Consider the equation of motion of a body of mass m , when it is subjected to an initial step force F_0 and when the system consists of a spring of spring constant k , and a damper with damping coefficient c as given in [Equation 4.18](#). Considering also the initial conditions $V(0) = V_0$ and $x(0) = x_0$, the equation of motion can be rewritten as [Equation 4.19](#) with the standard notations for damping ratio $\zeta = c/c_{cr}$, $\omega_n = \sqrt{k/m}$, and critical damping value $c_{cr} = 2\sqrt{km}$.

The Laplace transform of a function $f(t)$ is given by $\mathcal{L}\{f(t)\}$ or $\mathcal{F}(s)$ and is

defined in [Equation C.1](#).

$$\mathcal{L}\{f(t)\} = \mathcal{F}(s) = \int_0^{\infty} f(t)e^{-st} dt \quad (\text{C.1})$$

Rewriting [Equation 4.19](#) using Newton's notation for time derivatives, and noting the distinct terms in the equation, we obtain [Equation C.2](#).

$$\underbrace{\ddot{x}}_A + \underbrace{2\zeta\omega_n\dot{x}}_B + \underbrace{\omega_n^2 x}_C = \underbrace{\frac{F_0}{k}\omega_n^2}_D \quad (\text{C.2})$$

Taking the Laplace transform of [Equation C.2](#), we can convert the response of the system from the time domain to the frequency domain. The Laplace transform of Term A is given by [Equation C.3](#).

$$\mathcal{L}\{\ddot{x}\} = s^2\chi(s) - sx(0) - x'(0) \quad (\text{C.3})$$

where $\chi(s) = \int_0^{\infty} x(t)e^{-st} dt$, and the terms $x(0)$ and $x'(0)$ are terms obtained from the initial conditions. Subsequently, the Laplace transforms of terms B, C, and D follow as [Equation C.4](#) through [Equation C.6](#)

$$\mathcal{L}\{2\zeta\omega_n\dot{x}\} = 2\zeta\omega_n[s\chi(s) - x(0)] \quad (\text{C.4})$$

$$\mathcal{L}\{\omega_n^2 x\} = \omega_n^2 \cdot \chi(s) \quad (\text{C.5})$$

$$\mathcal{L}\left\{\frac{F_0}{k}\omega_n^2\right\} = \frac{G_0}{s} \quad (\text{C.6})$$

Writing the Laplace transform of [Equation C.2](#) with all terms, we obtain [Equation C.7](#)

$$s^2\chi(s) - sx(0) - x'(0) + 2\zeta\omega_n[s\chi(s) - x(0)] + \omega_n^2 \cdot \chi(s) = G_0/s \quad (\text{C.7})$$

Solving for $\chi(s)$, we obtain an intermediate expression [Equation C.8](#)

$$\chi(s) = \frac{sx(0) + 2\zeta\omega_n x(0) + G_0/s}{s^2 + 2\zeta\omega_n s + \omega_n^2} \quad (\text{C.8})$$

To solve the above equation, the method of separation of variables is used. To simplify the terms during the separation of variables, [Equation C.8](#) can be written as [Equation C.9](#)

$$\chi(s) = \frac{a_1 s^2 + a_2 s + a_3}{s(s + A)(s + B)} \quad (\text{C.9})$$

where the terms a_1, a_2, a_3, A and B are as follows:

$$\begin{aligned} a_1 &= x(0) = D_p \\ a_2 &= 2\zeta\omega_n x(0) \\ a_3 &= G_0 \\ A, B &= \frac{-2\zeta\omega_n \pm \sqrt{4\zeta^2\omega_n^2 - 4\omega_n^2}}{2} \end{aligned}$$

where D_p is the diameter of the parent drop. Separating the variables, the [Equation C.9](#) reduces to [Equation C.10](#) with terms b_1, b_2 and b_3 .

$$\chi(s) = \frac{b_1}{s} + \frac{b_2}{s + A} + \frac{b_3}{s + B} \quad (\text{C.10})$$

equating [Equation C.9](#) and [Equation C.10](#), we obtain the expressions for b_1, b_2, b_3, A

and B as follows

$$\begin{aligned}
b_1 &= \frac{G_0}{\omega_n^2} \\
b_2 &= D_p - \frac{G_0}{\omega_n^2} - \frac{1}{A - B} \left[D_p(2\zeta\omega_n - B) + G_0 \left(\frac{2\zeta}{\omega_n} + \frac{1}{\omega_n^2} \right) \right] \\
b_3 &= \frac{1}{A - B} \left[D_p(2\zeta\omega_n - B) + G_0 \left(\frac{2\zeta}{\omega_n} + \frac{1}{\omega_n^2} \right) \right] \\
A, B &= -\zeta\omega_n \pm \omega_n \sqrt{\zeta^2 - 1}
\end{aligned}$$

Hence considering the terms in [Equation C.10](#), and applying an inverse Laplace transform on the terms, we obtain the response of the system $x(t)$ in the time domain as shown in [Equation C.11](#).

$$x(t) = b_1 + b_2 e^{-At} + b_3 e^{-Bt} \quad (\text{C.11})$$

Since the damping ratio of an underdamped system $\zeta_u < 1$, one of the coefficients A, B will be imaginary. Thus the response in [Equation C.11](#) can be written as a combination of *sine* and *cosine* functions as elaborated in [chapter 4](#).

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4. V. Kulkarni, V. Y. Lolla, S. R. Tamvada, N. Shirdade, and S. Anand,
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