

DROPLET IMPACT ON A SOLID SURFACE: ANALYTICAL MODELING
AND EXPERIMENTATION FOR SPREADING PHASE

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A DISSERTATION SUBMITTED TO
THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

GRADUATE PROGRAM IN
MECHANICAL ENGINEERING
YORK UNIVERSITY
TORONTO, ONTARIO

DECEMBER 2024

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Abstract

A normal droplet impacting a flat, stationary, solid surface exhibits symmetric spreading. A key aspect of this symmetric spreading, particularly during deposition at low Weber numbers, is the formation of a rim along the lamella edge. The rim is crucial for predicting maximum spreading, and its dynamics can be captured using a set of ordinary differential equations in numerical calculations. However, establishing a reasonable initial condition remains challenging.

In addition to symmetric spreading, various studies have explored how to disrupt symmetry for industry demands, for example, reducing contact time for anti-icing purposes. However, no attempts to date have been conducted to restore symmetry from asymmetric spreading, such as spreading over an inclined or moving surface, where tangential velocity naturally breaks the symmetry.

To address these issues, this thesis investigates: 1) the rim genesis for a normal impact at low Weber numbers; 2) a model that elaborates how wettability can be manipulated to guide an asymmetric lamella towards a symmetric shape; and 3) experimental validation of this model.

This work demonstrates that rim formation is driven by a developing motion at the lamella edge — the rim region — induced by deceleration due to capillary forces. The dynamic pressure from this motion creates a difference in curvature, and hence the dynamic pressure must be balanced by the Laplace pressure within the rim region. The rim forms when the rim region becomes thicker than the lamella. An analytical model was developed to predict the time when the rim starts to form and the configuration of the droplet at this moment, validated by OpenFOAM simulations and experimental recordings.

Experimental results also support the proposed model for symmetry restoration based on the Taylor-Culick theory, demonstrating that manipulating wettability can accelerate the receding of the stretched contact line to counteract the stretch. A method for fabricating a patch with tunable wettability contrast has been developed for surface design to achieve symmetry restoration. Experimental results confirm the effectiveness of this patch design in correcting asymmetric spreading for water droplets impacting a surface under the following Weber number conditions: $We_n \leq 300$, $We_t \leq 300$, and $0.51 \leq We_n/We_t \leq 2.04$.

Acknowledgements

Before coming here, I had spent nearly the first third of my life in China with no experience studying abroad. I feel fortunate, however, that my first overseas journey has brought me to Canada.

First and foremost, I extend my heartfelt gratitude to my supervisor, Prof. Alidad Amirfazli. His invaluable guidance and unwavering support made this work possible. I am deeply grateful for the freedom he granted me to explore, as well as the encouragement he provided throughout my research journey. His extensive comments on my first conference paper draft were especially impactful, teaching me not only how to properly write a scientific paper, but also how to think in the shoes of readers. I also greatly appreciate Prof. Amirfazli's support in inviting visiting scholars to our lab, including Prof. Lennon Ó Náraigh, Prof. Panagiotis Theodorakis, Prof. Marco Marengo, Mr. Debarshi Debnath, and many others. Their insights into analytical models and simulations helped me recognize the boundaries of my knowledge. In particular, Prof. Ó Náraigh's passion for the mathematics of fluid dynamics left a lasting impression on me. I am also immensely thankful to my supervisory committee members, Prof. Pouya Rezai and Prof. Shooka Karimpour, for their kind support and guidance throughout this tough journey.

I would also like to thank everyone I have had the privilege of meeting here for their companionship. Arriving in Canada alone, I was lucky to be welcomed by kind friends like Milad Shakeri Bonab, Sajad Yazdanparast, Mohammadamin Ghasemzadeh, Gurdeep Saini, and Naijing Jiang. To my current lab mates, I appreciate Ahmed Azzam's calm confidence and Ismail Alkomy's excellent oral skills. Pierre Lesbats was always ready to help. Whenever I asked for 99%, he went above and beyond, delivering 120% in support. I became bolder and more proactive after being with them. I am grateful to Yvonne Yim, our graduate program coordinator, for her timely responses and

genuine care. I would also like to express my gratitude to my landlady, Miss Christelle Chieu, for providing a peaceful and comfortable home over the past three years, allowing me to be unbothered by life after work.

I feel lucky to benefit from this remarkable era, with rich resources and AI advancements like YouTube, Google, NPTEL, and especially ChatGPT (although many times it has attempted to fool me in a “smart” way), which have allowed me to explore fundamentals and improve efficiency. I am grateful for every challenge along the way (especially the pandemic, which began just a week after my arrival), each one building my resilience.

Finally, I want to express my heartfelt appreciation to my parents, Huilan Xiong (熊惠兰) and Yuanfu Zhou (周远傅), for their patience in allowing me this time away from them, and special thanks to Jiangtao Wu (吴江涛) for his unconditional love and for taking such good care of my parents in my absence.

I know my acknowledgements have been long, but I am thankful to reach this point—though my appreciation extends far beyond these words. If you hate yourself, do a PhD—it can destroy parts of you that you never imagined. If you love yourself, pursue a PhD, as it can transform the rest of you in ways you never thought possible.

Yating Hu (胡雅婷)

Oct. 1st, 2024

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List of abbreviations

AA	Aluminum alloy
Al	Aluminum
Bo	Bond number
Ca	Capillary number
CA	Contact angle
Fr	Froude number
OD	Trichloro-octadecylsilane
ODE	Ordinary differential equation
Oh	Ohnesorge number
OT	Trichloro-octylsilane
Re	Reynolds number
SAM	Self-assembled monolayer
We	Weber number
We_n	Normal Weber number
We_t	Tangential Weber number

Chapter 1

Introduction

1 Introduction

As the name suggests, droplet impact refers to the interaction between a droplet and a surface. Usually, the droplet is liquid, while the surface can be either liquid or solid. This chapter will briefly recap the fundamentals of droplet impact, including key observations, applications, and impact outcomes, and review various models discussed in the literature, with special attention to droplet spreading – one of the most important phenomena following impact. Additionally, this chapter will note the symmetric spreading in normal impacts and the conditions under which this symmetry is broken. The behaviour of an impacting droplet is a fascinating subject, with many unanswered questions. Finally, this chapter will present the research questions addressed in this thesis and outline its scope.

1.1 Fundamentals of droplet impact

1.1.1 Observations and applications

From the olive oil spilt on the kitchen stove leaving a splash, to the ink printed on paper forming letters, to the rain falling on a pond creating ripples, droplet impact is a phenomenon we encounter every day. The liquid-solid interaction has captured researchers' attention for more than a century¹ due to its vast applications across various industries. These applications span areas such as biochemistry, oil harvesting, electronics, agriculture, energy, and beyond^{2–8}.

Understanding droplet impact in biochemistry is crucial to creating effective drug delivery and diagnostic techniques. It also facilitates better oil extraction from reservoirs in oil harvesting. For electronics manufacturing processes like inkjet printing and microelectronics production, accurate control over droplet deposition is essential. Pesticide applications in agriculture greatly depend on the understanding of how droplets interact with soil and plant leaves. In addition, studying droplet

impact directly influences the energy sector by improving the efficiency of fuel injection systems in engines and reducing heat loss in the piping system.

Droplet impact research is important to both scientific inquiry and real-world applications. It not only broadens our understanding of everyday events, but also drives technological developments that can benefit various industries. This is especially crucial for applications that rely on the diverse outcomes of droplet impact.

1.1.2 Impact outcomes

Major outcomes post-impact are spreading, receding, splashing, rebounding, and fingering, among others^{9,10}. Take the most common impact as an example: a droplet impacts normal to a solid surface. The droplet spreads out quickly upon contact, creating a thin liquid layer called a lamella. Receding occurs after the lamella reaches its maximum expansion and moves back towards its original shape. Splashing takes place if the kinetic energy from the impact is high enough, causing tiny secondary droplets to fly away from the lamella. After receding, the liquid may coalesce, reforming into a droplet that can bounce off the surface, especially on hydrophobic or superhydrophobic surfaces. When the droplet has high kinetic energy and impacts a surface with certain morphology features, finger-like protrusions, known as fingering, can be observed at the boundary of the lamella. Each of these outcomes results from a complex interplay of factors.

The factors that can affect the impact outcome are^{10–13}: droplet properties, surface properties, impact conditions, and the scale of the system. Droplet properties include the droplet shape and liquid characteristics. Normally, the droplet is observed spherically in the lab, but it can also appear elliptical due to oscillations¹³. Liquid can be Newtonian or non-Newtonian¹⁴, and for Newtonian liquids, the properties mainly refer to their density (ρ), surface tension (σ), and dynamic

viscosity (μ). Besides, the number of droplets and their status play important roles. A single droplet, a droplet chain, and compound droplets result in different outcomes^{15–17}.

Surface properties constitute a broad concept, including different phases of the surface (liquid or solid, where liquid can be viscid or inviscid), morphology (curvature, structures, homogeneous or inhomogeneous), wettability, stiffness, and more. Impact conditions are also complex and are associated with factors such as impact velocity (v_i), ambient environment (gas or vacuum, temperature, etc.), inclination (α) of the impact surface, motion of the surface, the impact angle (normal or oblique impact). Furthermore, the scale of the impact system affects the outcome as well. Under the same impact conditions, the droplet with a different diameter (D_0) acts differently, and the size of the surface can result in edge effects and variations in characteristic lengths.

The factors mentioned above influence the forces exerted on the impacting droplet, leading to different impact outcomes. These forces typically include surface tension, inertia, viscosity, and gravitational force (g). To describe the relative effects of these forces and to compare impact outcomes across different scales and conditions, nondimensional numbers are used accordingly^{9,13,18}. For droplet impact, the dynamics can be characterized by the Weber (We) and Reynolds (Re) numbers:

$$We = \frac{\rho D_0 v_i^2}{\sigma} \quad 1-1$$

and

$$Re = \frac{\rho D_0 v_i}{\mu} \quad 1-2$$

Thus, We denotes the balance between inertia and capillary forces, while Re represents the balance between inertia and viscous forces. These two nondimensional numbers are also usually combined to form a new one called the Ohnesorge number (Oh),

$$Oh = \frac{\sqrt{We}}{Re} \quad 1-3$$

which describes the interplay between viscous, inertial, and capillary forces. Additionally, the Bond (Bo) and Froude (Fr) numbers are adopted to consider the effect of gravity against capillary and inertial forces, respectively:

$$Bo = \frac{\rho g D_0^2}{4\sigma} \quad 1-4$$

and

$$Fr = \frac{v_i}{\sqrt{g D_0}} \quad 1-5$$

Furthermore, the capillary length¹⁹ ($\lambda = \sqrt{\frac{\sigma}{\rho g}}$) provides an intuitive understanding of the size scale at which surface tension and gravitational forces are of the same order. In addition to characterizing forces, using nondimensional numbers facilitates the simplification of the complex equations governing droplet impact by reducing the number of independent variables. This simplification is particularly useful when solving problems analytically or numerically²⁰.

1.1.3 Symmetric outcomes of a normal impact

A normal droplet impacting on a flat, stationary, and solid surface results in radially symmetric spreading of the lamella. As the most basic and simplest outcome of the impact, symmetric spreading has been widely investigated due to its relevance in various industrial applications such as inkjet printing, rapid spray cooling, coating, fuel injection, and pesticide application^{13,21}. Upon

impact, the droplet flattens into the lamella, spreading out radially. The maximum spreading diameter (D_{max} , see Fig. 1-1) of the lamella is a critical dimension in the spreading process and has been reported extensively in the literature^{18,21–29}. This maximum spreading occurs because the initial kinetic energy from the impact is dissipated by the viscosity of the liquid and is transformed into surface energy as the surface area of the droplet expands. The determination of D_{max} is essential for understanding and optimizing the performance of various applications where precise control over droplet behavior is crucial.

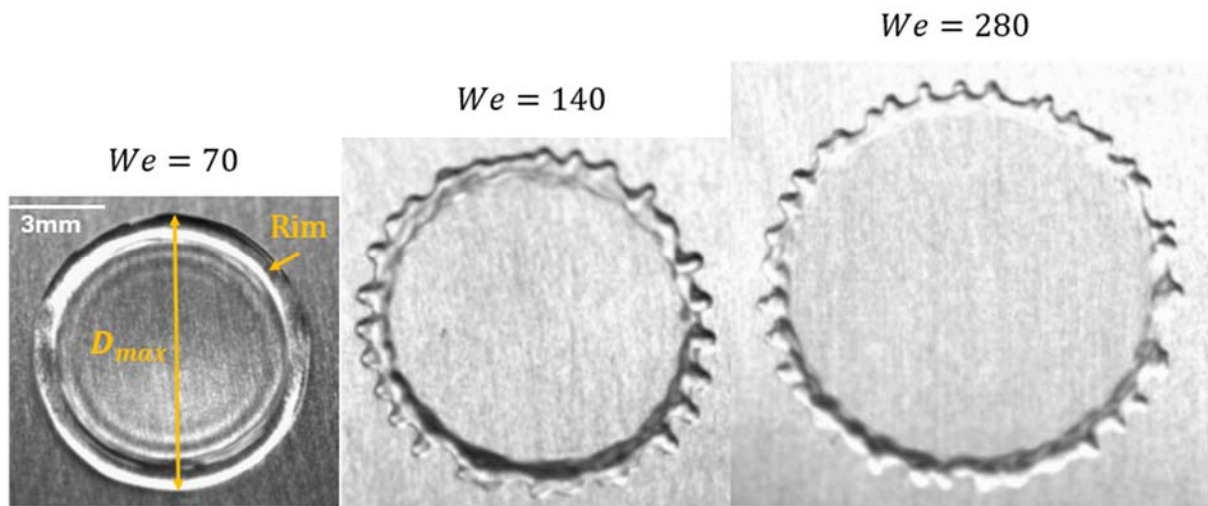


Figure 1-1 Maximum expansion of an impacting water droplet on a flat aluminum surface at different Weber numbers.

The genesis of a rim can have a considerable impact on the maximum spreading diameter. The rim forms as a result of liquid collecting at the edge of the lamella due to the deceleration caused by capillary forces. At low We for a normal impact, the lamella spreads outwards from the center, following the flow from the bulk of the droplet. Liquid accumulates at the lamella edge, creating a thicker and smooth boundary layer known as the rim, see Fig. 1-1. However, in the case of droplet impact with high We , the rim becomes thinner, and this thinning becomes much sharper as the We

increases, as shown in Fig. 1-1. Roughly, from a perspective of mass conservation, the maximum spreading diameter increases as the We increases due to the presence of a thinner rim.

Another parameter of interest in the study of droplet impact is the time taken for the lamella to reach its maximum spreading (t_{max})^{21,26,30–33}. This time parameter is closely associated with the impact velocity and the initial diameter of the droplet before impact. The impact velocity influences the rate at which the liquid spreads, with higher impact velocities leading to faster spreading. Meanwhile, the initial droplet diameter affects the extent of the spreading, as larger droplets have more liquid volume to spread out.

1.1.4 Asymmetric outcomes of an oblique impact

When the impact angle deviates from 90° with respect to the solid surface, known as an oblique impact^{34–36}, the symmetric spreading of the lamella becomes asymmetric due to the tangential momentum resulting from the oblique impact. This causes the spreading shape to elongate, differing significantly from those observed in normal impacts. The impact velocity for an oblique impact can be decomposed into normal velocity component (v_n) and tangential velocity component (v_t), as shown in Fig. 1-2. The normal velocity contributes to radial spreading, while the tangential velocity causes the elongation of the radial spreading.

Therefore, oblique impact leads to an uneven distribution of the impact momentum, and the asymmetric spreading is the result of the competition between the normal and tangential momentum. In some oblique impacts under specific conditions, such as when $We_n/We_t \approx 0.15$ ³⁷, the lamella initially spreads radially post-impact ($0 < t \leq 0.5 \text{ ms}$) since it is dominated by the normal velocity component. As kinetic energy is gradually dissipated over time, the tangential

velocity component becomes more influential, causing the deformation of the radial spreading and resulting in an elongated asymmetric shape.

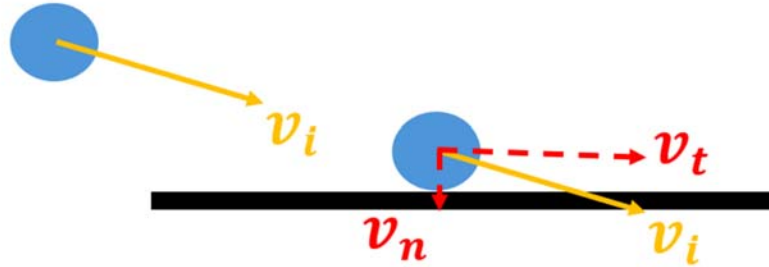


Figure 1-2 Schematic of impact velocity (v_i), tangential velocity (v_t), and normal velocity (v_n).

This distinct outcome, which differs from a normal impact, is often utilized in reconstructing criminal events³⁸. Each impact pattern corresponds to specific impact conditions. Hence, the asymmetric patterns of bloodstains at a crime scene, such as the tails and the elliptical shapes of blood droplets, can reveal the conditions of an oblique impact. These patterns can provide quantitative insights into the impact angle, We and Re associated with the event.

1.2 Models for droplet spreading

In droplet impact studies, significant attention has been given to the spreading phase, as this is a critical phase after impact. The conditions during spreading can lead to various outcomes, such as deposition, or splash, etc., both of which are relevant to applications like printing, coating, and cooling. A key feature of the spreading phase is the maximum spreading, primarily influenced by We and Re , with wettability effects often negligible when these two values are high³⁹. Numerous models in the literature aim to describe maximum spreading in various ways. The most common and simplest way is to equate the energy of the droplet before and after impact based on energy conservation. However, this method merely focuses on two moments: t_0 and t_{max} , and neglects

the process in between. Another widely used way considers the momentum conservation in the rim. This way accounts for both rim and lamella development during spreading, though typically only in the later stages of the spreading. These models often combine experimental, simulated, and/ or theoretical analysis.

1.2.1 Models based on energy conservation

A straightforward way to estimate the maximum spreading width for a normal impact on a solid surface is by applying energy conservation. However, different considerations regarding viscous dissipation and the shape of the droplet at t_{max} result in different scaling laws. Especially, the latter affects the total surface energy of the droplet at t_{max} .

Before impact, the energy possessed by the droplet consists of kinetic energy and surface energy. When the droplet reaches the maximum spreading, the droplet has the increased surface energy, with negligible kinetic energy remaining in the rim. In an extreme case of high We and impact on superhydrophobic surfaces, assuming that the kinetic energy before impact completely converted to the surface energy at t_{max} , the maximum spreading factor $\beta_{max} = \frac{D_{max}}{D_0}$ scales as $We^{1/2}$, as noted by Clanet *et al* ²⁵. Another similar way is to consider volume conservation. In their work, they also derived a scaling law of $We^{1/4}$ by considering the droplet as a disk with a refined thickness at t_{max} , and as a sphere before impact.

However, these two scaling laws are not sufficient to precisely describe the maximum spreading due to the simplifications in their underlying assumptions. The $We^{1/2}$ scaling does not account for viscous dissipation and significantly overestimates spreading for highly viscous liquids and impacts on hydrophilic surfaces²⁷. On the other hand, the $We^{1/4}$ scaling neglects the rim formation and the more complex droplet shape at t_{max} and hence underestimates by approximately 19% for

low We on hydrophilic surfaces⁴⁰. Therefore, researchers^{22,26,30} have attempted to optimize the energy conservation method by considering viscous dissipation.

Viscous dissipation can be estimated as^{28,30,41}

$$W_{vis} = \int_0^{t_{max}} \int_{\Omega} \phi d\omega dt \approx \Phi \Omega t_{max} \quad 1-6$$

where Φ is the averaged viscous dissipation function, and Ω is the volume in which viscous dissipation occurs. Chandra and Avedisian⁴² estimated Φ as

$$\Phi \sim \mu \left(\frac{v_i}{h} \right)^2 \quad 1-7$$

where h is the thickness of the droplet at t_{max} . Pasandideh-Fard *et al.*³⁰ suggested that the boundary layer thickness (δ) near the solid surface, rather than h , is a more appropriate length scale for estimating the magnitude of viscous dissipation. Furthermore, an energy budget analysis^{19,43,44} has been developed to better understand the roles of different forms of energy, including kinetic energy, surface energy, potential energy and viscous energy during the phases post-impact.

According to Roisman⁴⁵, predicting maximum spreading cannot be achieved merely through a universal combination of We and Re based on energy conservation; a more comprehensive physical understanding of the phenomena is required. He categorized the phenomena into two cases: (1) for infinite We , where negligible rim forms and the lamella spreads into a disk shape at maximum spreading; and (2) for finite We , where both rim and lamella are observed.

In the first case, Roisman derived the relation $\beta_{max} \sim Re^{1/5}$, considering both mass and energy conservation, where the kinetic energy is balanced by the viscous dissipation. In the second case,

he noted that the typical length scale associated with the rim scales as $Re^{2/5}We^{-1/2}$, leading to a decrease in maximum spreading with increasing rim length. By combining these two scales, Roisman developed a widely used semiempirical relation⁴⁵ for predicting maximum spreading: $D_{max} \approx 0.87Re^{1/5} - 0.40Re^{2/5}We^{-1/2}$. However, this relation is not applicable for super-viscous or very small droplets, as it does not account for the viscous dissipation that occurs within the rim. This deficiency can be addressed in rim-based momentum conservation models by incorporating either a drag force²¹ or viscous boundary layer^{29,46}.

1.2.2 Models based on momentum conservation

Unlike energy conservation models that focus on specific moments, analytical models based on momentum conservation can capture the dynamics of the lamella and rim throughout the spreading process. These models can be roughly categorized into two types: those that consider the initial phase ($0 < t \leq \frac{R_0}{v_i}$) and those that skip the initial phase, such as the rim-lamella model⁴⁷ and pancake model²⁹.

The rim-lamella model describes the state of the droplet when $t \gg \frac{R_0}{v_i}$, at which point the rim and lamella are clearly seen, and the influence of the droplet bulk becomes negligible, see Fig. 1-3. To capture the time-dependent spreading width, it is typically necessary to solve three ordinary differential equations (ODEs) based on the mass and momentum balances for the rim as well as the rim velocity:

$$\frac{dV}{dt} = 2\pi R(u_0 - U)h_{(R,t)}$$

$$\forall \frac{dU}{dt} = 2\pi R[(u_0 - U)^2 h_{(R,t)} - (1 - \cos\vartheta_{ap}) \sigma/\rho - f_\tau/\rho] + f_g \sin\alpha/\rho \quad 1-8$$

$$\frac{dR}{dt} = U$$

where $\forall$ is the volume of the rim, R is the radius of the lamella, U is the rim velocity, u_0 is the mean velocity of the lamella, h is the lamella thickness, ϑ_{ap} is the apparent contact angle, f_τ is the drag force due to the wall shear stress, f_g is the gravitational force, and α is the inclination of the surface. The form of these ODEs may vary according to the assumptions or scenarios considered^{21,29,46–48}. For example, the drag force can be refined by applying inner and outer flows with a boundary layer being considered. Obviously, with more unknown variables than the number of the equations, these ODEs must be solved together numerically. This requires an initial condition to initiate the calculation. Naturally, the initial condition can be derived from the initial phase post-impact.

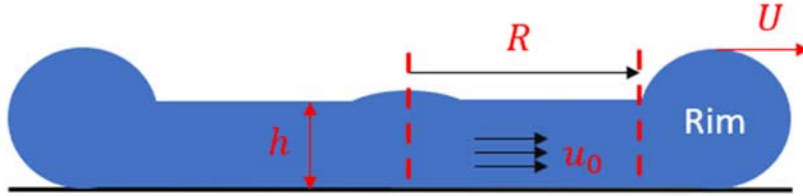


Figure 1-3 Schematic of the rim-lamella model

The dynamics within the droplet during the initial phase are highly complex. At this stage, the droplet bulk is clearly visible, see Fig. 1-4. Following the conventions in the reference⁴⁹, the region within the droplet bulk far from the solid surface is referred to as the far-field region. This region is not yet affected by the solid wall, meaning the flow can be described using a potential function⁵⁰ (and/ or stream function⁴⁹). The region near the solid surface, known as the near-wall region, is

sandwiched between the far-field region and the solid surface. This region is therefore significantly affected by the solid surface, causing a sharp change in the flow velocity direction from vertical to radial. The flow in this region is self-similar^{20,49}, and can be estimated analytically. Overtime, this self-similar region grows until it encompasses the far-field region²⁰. Besides, the jet region, which will further develop into the lamella and rim, is inertial driven and has a free surface, with its tip decelerated by capillary forces. The radial velocity decreases due to the locally high pressure^{20,49} when the flow passes through the narrow opening that connects the near-wall region to the jet region. A great challenge here is determining the height of this narrow opening, although researchers have attempted to estimate it using asymptotic analysis, given the analogy to the water entry problem^{51,52}. Each region has its own dynamics, governed by different boundary conditions that evolve over time.

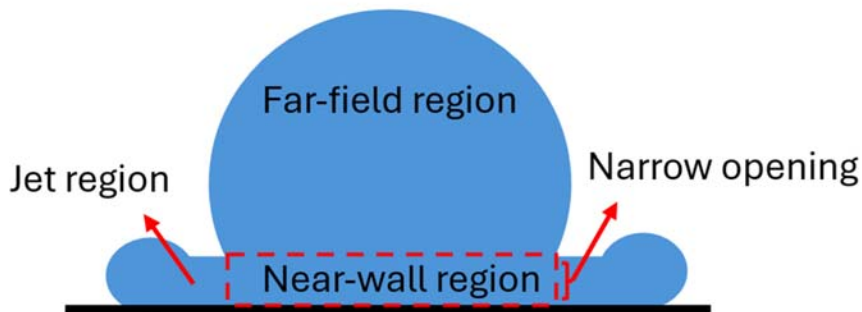


Figure 1-4 Schematic of various regions within the droplet during the initial phase

In order to capture the dynamics of the jet region, which is crucial for spreading, it is essential to understand the dynamics of the near-wall and far-field regions, as they supply the flow that feeds the jet region. Roisman *et al.*²¹ modeled the near-wall region as a viscous creeping flow between two approaching plates, suggesting that the flow in this region is driven by pressure coming from

the far-field region. They provided the averaged thickness of the near-wall region at $t = \frac{D_0}{v_i}$ by applying total axial momentum balance of the droplet and obtained the spreading width at this moment through total mass conservation. Additionally, they deduced the parameters of the flow in the jet region through energy analysis using the velocity profile obtained from the near-wall region. This was done to provide the necessary input for solving the mass and momentum balances on the rim to determine the time evolution of the spreading width, as described in the rim-lamella model.

Riboux and Gordillo⁵¹ established the configuration of the droplet at the moment when the jet region starts to form, which occurs much earlier than the scenario selected by Roisman *et al.* at $t = \frac{D_0}{v_i}$. They defined this moment based on the condition that the jet tip moves faster than the wetted area which results from the downward motion of the droplet bulk. The wetted area was demonstrated to expand with a radius proportional to $\sqrt{3t}$ using Wagner's theory⁵³. In contrast to Roisman *et al.*'s method for determining the thickness of the near-wall region, Riboux and Gordillo found that the thickness is proportional to $t^{3/2}$ by applying an analogy to the water entry problem and using an integral balance of horizontal momentum. The configuration of the droplet at the ejection moment serves as the initial condition for numerically solving the rim-lamella model.

Another commonly used strategy is to skip the complex dynamics of the initial phase and directly solve the rim-lamella model with the initial condition defined through energy-budget analysis or geometric considerations. Fedorchenko and Wang⁵⁴ derived the initial conditions by equating the volumes and kinetic energies of the droplet before and after impact, combined with the consistency of the velocity of the droplet top before and after impact. Eggers *et al.*²⁹ proposed an initial condition at $t = \frac{R_0}{v_i}$, assuming the droplet takes on a pancake shape.

These approaches, whether considering or neglecting the dynamics of the initial stage, aim to determine the initial conditions needed to solve the Eqs. 1-8 numerically. Once these conditions are established, the dynamics of the spreading can be described with the evolution of the rim and lamella.

1.3 Symmetry breaking of a normal impact

Symmetric spreading of the lamella in a radial shape is a key characteristic of a normal droplet impact, and the approaches to capture the spreading dynamics were discussed in Section 1.2. However, this symmetry of the spreading lamella can be easily disrupted by surface fabrication or varying surface conditions.

1.3.1 Surface fabrication-induced asymmetric spreading

Variations in surface fabrication, resulting in various textures and designs, lead to asymmetric spreading during a normal impact. Han *et al.*⁵⁵ applied a photolithography technique to obtain a surface with grate patterns to study anisotropic droplet spreading. Similarly, isosceles trapezoidal cross-sections were machined on substrates by Regulagadda *et al.*⁵⁶ to reduce the liquid-solid contact time through the anisotropic deflection of the lamella. For the same purpose, Bird *et al.*⁵⁷ employed macro-textured ridge silicon surfaces by ablating the surface with a laser to trigger asymmetry in the spreading lamella. In addition, Chantelot *et al.*⁵⁸ attached a glass bead to a silicon wafer to create a singularity that breaks the lamella symmetry, thereby reducing contact time.

Aside from changing the topography of the surface, wettability-engineered surfaces can also lead to asymmetric spreading. Schutzius *et al.*⁵⁹ designed a SiC surface with virus hydrophilic shapes on a superhydrophobic background. This study provides insight into saving liquid by vectoring and morphing droplets for applications like printing. Extreme-wettability-contrast patterns were also

employed by Kim *et al.*⁶⁰ to investigate unusual liquid deposit morphologies for practical processes in rapid printing of functional liquids. Similarly, Lee *et al.*⁶¹ manipulated the spreading shape of the lamella with micro-wetting patterned surfaces, which can be applied to microfluidic applications. For this type of surface design, the hydrophobic areas facilitate the receding of the lamella compared to the hydrophilic areas, leading to asymmetric spreading^{59–62}.

Besides, the combination of varying wetting properties and surface texture is widely explored in the literature, since nano/micro structures and low surface energy coating can enhance superhydrophobicity^{59,60}. This combined strategy allows for precise control over droplet behavior, facilitating advanced functionalities in various industrial processes, including coating, self-cleaning surfaces, and micro-fluidics.

1.3.2 Surface condition-induced asymmetric spreading

Apart from the asymmetry of the spreading brought by surface fabrication, surface condition during droplet impact also plays a role in the symmetry breaking. For example, asymmetric spreading is commonly seen in various practical applications such as coating, inkjet printing etc., where normal impact may encounter rotating surfaces⁶³, flat moving surfaces^{62,64,65} or inclined surfaces^{66–81}. These kinds of surfaces induce an in-plane tangential velocity (v_t) post-impact^{63,65,66}. A rotating surface is different from the other two kinds as its tangential velocity, or linear velocity, is associated with its angular velocity and is tangent to the trajectory of the lamella. However, for flat moving and inclined surfaces, the tangential velocity direction aligns with the trajectory of the lamella. For a moving surface, the tangential velocity is caused by surface motion, while for an inclined surface, it arises mainly from the tangent components of the impact velocity, as shown in Fig. 1-5. Bird *et al.*⁸² speculated that the dynamics of the impact upon these two kinds of surfaces

are similar, but in reference⁶⁶ it was shown that these two scenarios can be considered equivalent only under certain conditions.

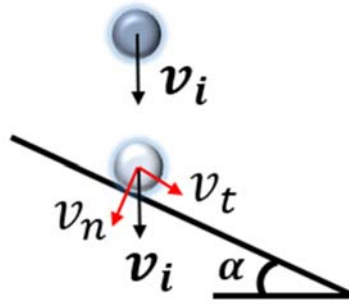


Figure 1-5 Schematic of the velocities involved in the impact on an inclined surface

1.3.3 Symmetry restoration

Spreading symmetry can be easily broken by surface fabrication and conditioning. However, in many applications such as painting, coating, printing and more, maintaining the symmetry is important for precise shape control, high efficiency in coverage, and more importantly, uniform coverage^{83–87}. This is particularly crucial in the electronics industry, where precise printing can significantly affect the performance of electronic devices. In contrast, asymmetric spreading may cause material waste and compromise the coating quality, as it can lead to uneven textures and unwanted patterns. Hence, restoring spreading symmetry is of significant interest.

However, restoring the symmetry is challenging because the causes of asymmetry are complex and arise from intricate dynamics. For example, impacts on moving or inclined surfaces, common scenarios in printing and coating, can introduce considerable asymmetry that complicates the restoration process.

The asymmetric shape of the lamella for impact of a droplet onto a moving or inclined surface is essentially a superposition of the radial spreading and the tangential stretching⁶⁵. These two motions are induced by the velocity normal to the surface (v_n) and the tangential velocity (v_t), respectively. Typically, in the case of an inclined surface, v_n refers to the component of the impact velocity normal to the surface. The tangential velocity stretches the lamella and hence the lamella deforms from the radially symmetric spreading. In Fig. 1-6, the maximum width line (the dashed line) of the lamella splits the lamella into two sides. To be consistent with references^{64,65}, the side that looks blunter is defined as upstream since it is close to the bulk of the droplet that is descending to spread outwards, and the other side is downstream.

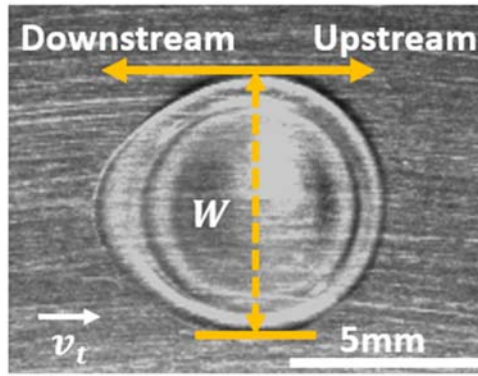


Figure 1-6 Top view of the spreading lamella over an inclined surface. The dashed line is the maximum width line of the lamella, which refers to the lamella width (W). When $t = t_{max}$, $W = W_{max}$.

The width of the lamella depends on the initial kinetic energy⁶². Through the dissipation of the initial kinetic energy in the spreading process, the lamella will reach a maximum spreading width (W_{max})⁶². For the liquid with high surface tension, for instance, water, the upstream will retain a semicircular outline. Given the same v_n , the maximum spreading width is almost the same as for the droplet impact with and without a tangential velocity, i.e., $D_{max} \approx W_{max}$ ⁶².

The downstream of the lamella can be influenced significantly by surface wettability⁶⁵. When the downstream lamella stops spreading, its contact line pins at the impact spot on a hydrophilic surface⁶². However, on a hydrophobic surface, the downstream contact line starts to recede due to typical low hysteresis of hydrophobic surfaces⁶⁵. Meanwhile, the upstream continues spreading on both hydrophilic and hydrophobic surfaces until reaching W_{max} , and the W_{max} on these two kinds of surfaces differs very slightly⁶⁵. As a result, the deformation of the lamella compared to a circular shape is smaller on a hydrophobic surface than that on a hydrophilic surface.

Given the experimental observations that wetting has minimal influence on spreading and hydrophilicity can facilitate receding, it is possible to restore symmetry by manipulating wetting.

1.4 Research gaps

Spreading width, a key phenomenon following a droplet impact on a solid surface, has attracted significant attention due to its applications in various fields, including printing, coating, lap-on-a-chip technology, droplet-guided transport and so on. Significant changes in spreading width take place at various impact velocities with a fixed droplet size. These changes are attributed to the formation of a rim. The rim becomes larger with decreasing impact velocity, leading to a smaller spreading diameter³⁷. Hence, it is of interest to explore the mechanism of rim formation and evolution during spreading.

However, the models discussed in the references^{21,29,47} rely on inappropriate assumptions. Roisman *et al.* estimated the diameter and thickness of the drop at $t \approx \frac{D_0}{v_i}$ as initial conditions for Eqs. 1-8, with the assumption that the droplet bulk acts as a pressure reservoir to drive the flow in the near-wall region. However, experimental results indicate that at this moment the droplet bulk is too weak to serve as the driving force, see Fig. 1-7. This is why their model overestimated the

maximum spreading for low We . This assumption, which does not match the experimental observations, is similar to the one used in the reference⁴⁷ where a consistency condition is applied to the vertical velocity at the top of the droplet bulk. However, this condition does not hold true for $t > \frac{R_0}{v_i}$.

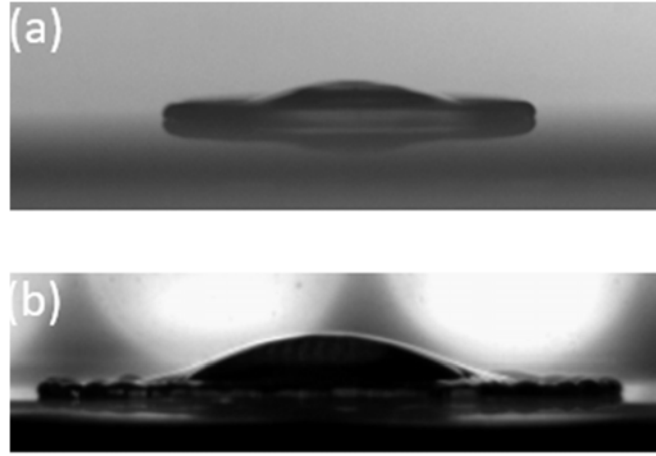


Figure 1-7 Experimental observations of a water droplet impacting on a hydrophilic aluminum surface at $t = \frac{D_0}{v_i}$ for

(a) $We = 70$ and (b) $We = 140$

In the work of Eggers *et al.*²⁹, they set the initial conditions at $t \approx \frac{R_0}{v_i}$ with a pancake shape of the droplet. This assumption lacks clarity of justification for the chosen initial lamella thickness and contradicts experimental observations, which show a prominent droplet bulk at this moment, see Fig. 1-8. Interestingly, their work focuses on very high We ($We > 400$). It should be noted that for $We = 280$ (see Fig. 1-1), the rim is very thin compared to the overall spreading width, indicating that the rim variation is no longer to be a significant factor in the spreading dimension at high We .

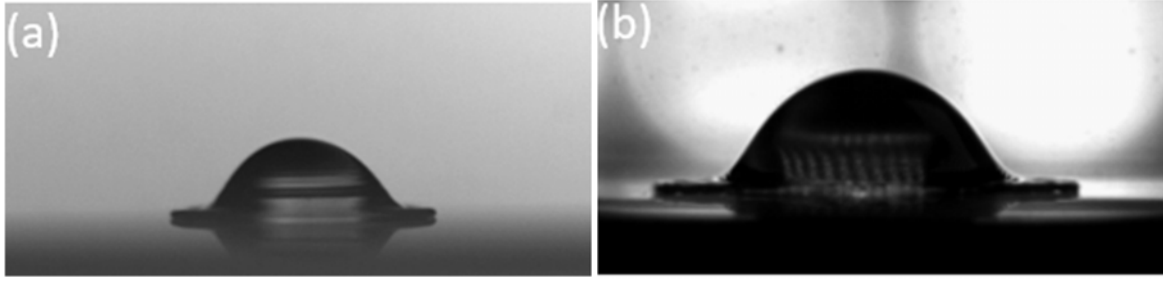


Figure 1-8 Experimental observations of a water droplet impacting on a hydrophilic aluminum surface at $t = \frac{R_0}{v_i}$ for

(a) $We = 70$ and (b) $We = 140$

The models stated in the references^{29,46,50,51} primarily focus on splash phenomena, giving little attention to low We . Besides, the droplet bulk acts as an engine, supplying inertia for lamella expansion. The dynamics within the bulk and lamella differ, complicating the inertial phase scheme. Thus, previous models often begin at a point where the rim and lamella are already established, neglecting the genesis of the rim. However, the rim plays a crucial role in spreading, particularly for low We .

In addition to the variation in spreading width influenced by rim dynamics, controlling the spreading of an impacting droplet is also a crucial topic with practical implications. Most existing studies^{55,57–59,61,63}, however, focuses on breaking the symmetry of the spreading lamella to address concerns such as anti-icing, and self-cleaning by reducing liquid-solid contact time. Only a limited number of studies emphasize symmetry regulation by designing the symmetry of substrate surface with specific chemical and physical structure modifications⁸⁸. These studies characterize substrate symmetry through surface pattern geometry, including mirror and rotational symmetry. Very little research has investigated on restoring spreading symmetry from an initially asymmetric spread, which is essential for applications requiring precise control of the spreading shape, for example, electronic fabrication using inkjet printing. In such processes, surface conditions like movement or

tilt can lead to asymmetric lamella spreading, potentially resulting in undesirable patterns on electronic devices. Therefore, exploring methods to correct asymmetric spreading to ensure symmetric spreading under specific conditions is of significant importance.

1.5 Goals and objectives

Given the significant impact of the rim on spreading width, understanding rim dynamics is crucial. To establish a solid initial condition for capturing rim dynamics and initiating numerical calculation for solving Eqs. 1-8, this thesis addresses the often-overlooked explanation of rim genesis. The focus is on low We , where a thick and smooth rim is observed, as at high We , the rim is typically too thin to significantly influence spreading width, and this area has already been extensively studied in the literature. Specifically, this work addresses the timing and configuration of the droplet shape when the rim is about to form.

Moreover, given that spreading symmetry can easily be disrupted in many practical situations, it is natural to explore the reverse scenario, i.e., restoring symmetry from an inherently asymmetric spreading, especially when precise control is required. This thesis, therefore, also addresses the possibility of converting asymmetric spreading into symmetric spreading. The emphasis is on droplet impact on moving or inclined surfaces, which often intrinsically induces asymmetric spreading and is commonly encountered in applications such as inkjet printing, 3D printing, spraying, and similar processes. Specifically, the question to be answered is how to use wettability changes to manipulate the receding of the contact line in each local on the downstream side to counteract the deformation of the lamella caused by v_t .

Hence, the goals and objectives of this thesis are:

- To develop a comprehensive model that elaborates the rim genesis following a normal impact with $We < 100$, $Re < 4693$.
- To build a theoretical framework and design a surface for restoring the symmetry in spreading on moving/ inclined surfaces after impact. The corrected shape is expected to be circular when the lamella reaches its maximum spreading.
- To fabricate the engineered surface for symmetry restoration.
- To experimentally validate the symmetry restoration model and surface design.

1.6 Scope of the thesis

With these goals and objectives in mind, this thesis is structured as follows: Chapter 2 outlines the methodology, detailing the experimental and numerical procedures; Chapter 3 discusses rim genesis, explaining when and how the rim starts to form during a normal droplet impact at low We ; Chapter 4 presents the solution of manipulating asymmetric spreading to achieve symmetric spreading in droplet impacts on moving or inclined surfaces; Chapter 5 details the fabrication of an engineered surface with wettability contrast designed to correct asymmetric spreading; Chapter 6 provides experimental validation of the symmetry restoration; Finally, Chapter 7 concludes this thesis with a summary of findings and suggestions for future work.

Chapter 2

Method

2 Method

2.1 Introduction

This chapter outlines the materials and impact conditions used in this study, along with the methodologies employed for imaging droplet impacts on flat/inclined surfaces and conducting numerical simulations using OpenFOAM to analyze spreading and rim genesis following impact on flat surfaces.

2.2 Experimentation ¹

2.2.1 Materials and preparation

Aluminum sheets (AA 6061, 25 mm *75 mm *1.5 mm, from McMaster-CARR) were selected for testing as a commonly used material in the industry. The as-received sheets were polished with 400-grit sandpaper, cleaned by immersion in acetone and distilled water baths for 20 min each using a ultrasonic cleaner (Cole-Parmer), dried with nitrogen gas flow, and carefully stored in Petri dishes for later use. The detailed fabrication process for the coated aluminum surfaces will be presented in Chapter 5, which elaborates on a developed methodology that is easy and quick to implement for creating a customized wettability contrast to validate the symmetry restoration model proposed in Chapter 4.

DI water was chosen in this study because it is the most common liquid in nature and has a high surface tension. The latter point is important since higher surface tension results in the semi-circular

¹ This section is based on the work published in the paper “Application of Surface Wettability to Control Spreading of an Impacting droplet”, LANGMUIR 2024, 40,4623-4634.

shape of the upstream lamella^{64,66}, which favors correcting the asymmetric spreading that occurs merely downstream. To ensure spreading rather than splashing after impact, the normal We ($We_n = \rho v_n^2 D_0 / \sigma$, D_0 is the original diameter of the droplet before impact) as well as the tangential We ($We_t = \rho v_t^2 D_0 / \sigma$) should be below 400⁶⁵. The physical properties of water from reference⁶⁴ were used as ρ (998.0 kg/m³), ν (kinematic viscosity, 1.0 cSt), and σ (72.8 mN/m).

2.2.2 Experimental apparatus

To observe droplet impacts under various impact conditions, the experimental setup was developed as shown in Fig. 2-1. This set-up consists of a syringe pump, two high-speed cameras, a light, a rotatable stage, and a computer. The syringe pump was used to dispense the droplet with a diameter of 2.5 ± 0.1 mm. The surface was placed on a rotatable stage below the syringe. The velocity components (v_n and v_t) generated by the impact velocity (v_i) can be adjusted by both the height of the syringe and the inclination of the stage. The top and side views of the lamella spreading post-impact were captured by Phantom V1610 and M310 (manufactured by Vision Research), respectively, with a recording speed of 10,000 fps.

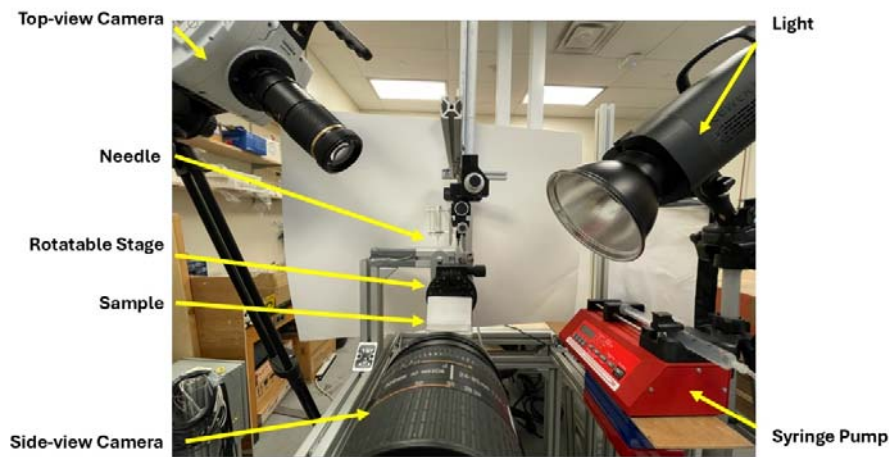


Figure 2-1 Schematic of the experimental set-up

The rotatable stage, a precision manual rotating table from Optics Focus, enables varying the surface inclination for various impact conditions. This stage is connected to a homemade precision machining right-angle bracket composed of Al alloy blocks (see Fig. 2-2). The bracket provides a flat surface to position the sample securely. The sample is affixed to the stage using double-sided tape.

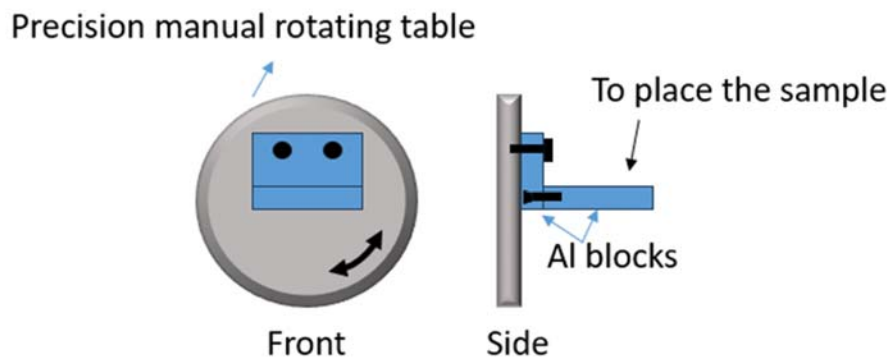


Figure 2-2 Schematic of the rotatable stage

2.2.3 Characterization

Surface wettability was indicated by static contact angle, advancing contact angle, and receding contact angle. The static contact angle was measured using the sessile drop ($10\ \mu\text{L}$) method by a drop shape analyzer (KRÜSS DSA100E). Receding and advancing contact angles are measured using a needle-in method, wherein liquid is steadily injected to or removed from the drop. The advancing/ receding contact angle is measured when the contact line starts to move. The pattern dimension was characterized by a Leica upright microscope (MZ 10 F). The surface morphology was observed using a scanning electron microscope (TESCAN VEGA3) and the surface roughness was obtained with a 3D optical profilometer (Contour GT-K).

2.2.4 Statistical analysis

In this thesis, each impact test was repeated six times. The static contact angle was measured at three different spots. The advancing and receding contact angles were measured twice at different spots. The data for length measurements were presented as the standard deviation based on the experimental recordings, while the static contact angle data were represented as the median, with the deviation calculated from the maximum and minimum values. For advancing and receding contact angles, only the median values were reported.

2.3 Numerical method

The numerical model established in references^{89,90} was employed to simulate the spreading and impact dynamics of a droplet on a flat surface. This simulation utilized a two-phase flow model, solved using OpenFOAM with the interFoam solver. Here, the two-phase flow involved liquid and air within the same domain, separated by an interface, and the interface was defined by the volume of fluid (VOF) method⁹¹. The VOF method employed Eulerian coordinate system to solve the governing equations as follows:

$$\nabla \cdot \vec{U} = 0 \quad 2-1$$

$$\frac{\partial \alpha}{\partial t} + \nabla \cdot (\vec{U} \alpha) + \nabla \cdot (\vec{u}_r \alpha (1 - \alpha)) = 0 \quad 2-2$$

$$\rho \left[\frac{D\vec{U}}{Dt} \right] = -\nabla p + \mu \nabla^2 \vec{U} + \vec{F}_b + \vec{F}_s \quad 2-3$$

The governing equations include the continuity equation for incompressible liquid, the advection of the volume fraction (α), and the Navier-Stokes equation. The volume fraction is defined as the ratio between the volume of the immiscible liquid in a computational cell and the total volume of

that cell within the mesh. The equations describe the following variables: $\vec{U}$ is the velocity vector, $\vec{u}_r$ is the relative velocity of the liquid to the air at the free surface, t is time, ρ is the density, p is the pressure field, μ is the dynamic viscosity, $\vec{F}_b$ is the body force and $\vec{F}_s$ is the surface force. The surface force is particularly important at the free surface. Therefore, to precisely capture the dynamics of free surface, surface tension was incorporated into Eq. 2-4 as

$$\vec{F}_s = \sigma \kappa \nabla \alpha \quad 2-4$$

where σ is the surface tension force, and κ is the mean curvature of the free surface, approximately given by

$$\kappa = \nabla \cdot \left(\frac{\nabla \alpha}{|\nabla \alpha|} \right) \quad 2-5$$

In VOF, the two-phase flow is processed as a single phase within each computational cell by volumetrically averaging the physical properties based on α , as given by

$$\mu = \alpha \mu_1 + (1 - \alpha) \mu_2 \quad 2-6$$

$$\rho = \alpha \rho_1 + (1 - \alpha) \rho_2 \quad 2-7$$

with the subscripts 1 and 2 refer to the liquid and the air phases, respectively. For pressure-velocity coupling, the PIMPLE algorithm was applied, along with adaptive time stepping based on Courant-Friedrichs Lewy condition. For further details, see references^{89,90}.

2.3.1 Simulation domain and boundary conditions

In this thesis, a 2D axisymmetric simulation framework was used to model normal droplet impact, based on the radial symmetry inherent to normal droplet impact on flat, stationary, and solid surfaces. For such cases resulting in a smooth deposition, the droplet's shape, lamella dynamics,

and rim formation are symmetric about the vertical axis passing through the droplet center. This symmetry allows the use of a 2D axisymmetric domain instead of a full 3D simulation, significantly reducing computational cost while preserving the accuracy of key flow features, such as the lamella and rim shapes. While the axisymmetric approach captures the main dynamics of the impact, it has limitations particularly in representing asymmetric phenomena, such as those induced by surface heterogeneities. But these kinds of asymmetric phenomena are beyond the scope of this work.

Therefore, for the impact of a water droplet on a flat static solid surface, axisymmetric spreading was simulated within an air environment. Figure 2-3 displays the schematic of the simulation domain and boundary conditions. The domain sized $3.4D_0 \times 3D_0 \times 0.032D_0$, consists of a droplet and a solid surface at the bottom. The droplet, with an initial radius $R_0 = \frac{D_0}{2}$, was placed on the solid surface and then moved downward with the velocity v_n . Detailed boundary conditions are provided in reference⁸⁹.

At the axis of symmetry, the boundary conditions were $u = 0$, $\partial v / \partial x = 0$, $\partial p / \partial x = 0$, and $\partial \alpha / \partial x = 0$. For the right side and top walls, the Neuman boundary condition was applied to the pressure and volume fraction fields, along with non-slip and impermeable conditions. The bottom wall was treated with a non-slip condition and the Neuman boundary condition for the pressure field.

The contact line dynamics at the bottom wall were modeled using Kistler's model⁹², as implemented in the VOF solver included in the OpenFOAM library. Kistler's model determines the dynamic contact angle based on inputs of the advancing, receding, and static contact angles by solving Hoffman's function as a function of the capillary number ($Ca = \frac{\mu u_{cl}}{\sigma}$, where u_{cl} is the contact line velocity)^{89,90}.

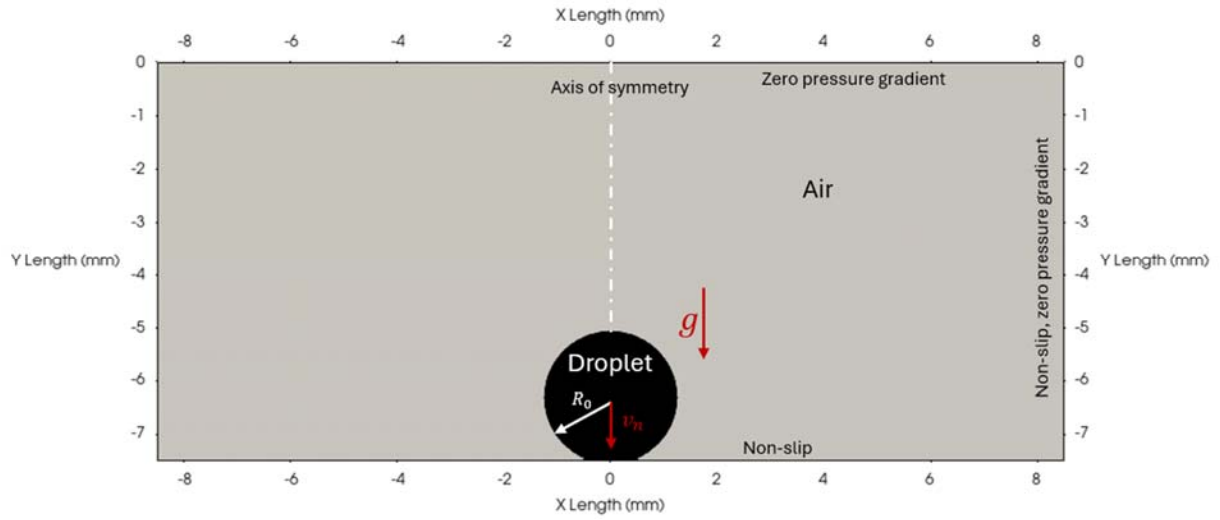


Figure 2-3 Simulation domain and initial and boundary conditions

2.3.2 Mesh sensitivity analysis

The simulation domain was discretized using a structured Cartesian uniform mesh. A water droplet with a diameter of 2.5 mm impacting an aluminium surface at $We = 70$ was simulated using the approach presented in references^{89,90} for various mesh sizes (500×500 , 600×600 , and 700×700 , see Fig. 2-4 as an example). The advancing and receding contact angles of the simulated surface are 98° and 15° , respectively. The spreading radius of the lamella for different mesh sizes was plotted with respect to time in Fig. 2-5 till it reached equilibrium. In general, the time-dependent spreading radius is quite similar for different mesh sizes; however, finer mesh sizes tend to yield more accurate results. The averaged difference in spreading radius between mesh sizes 500×500 and 600×600 is $18\mu\text{m}$, while it is $9\mu\text{m}$ between 600×600 and 700×700 . Given these results and considering computational expenses, the mesh size 600×600 was selected for use in this work.

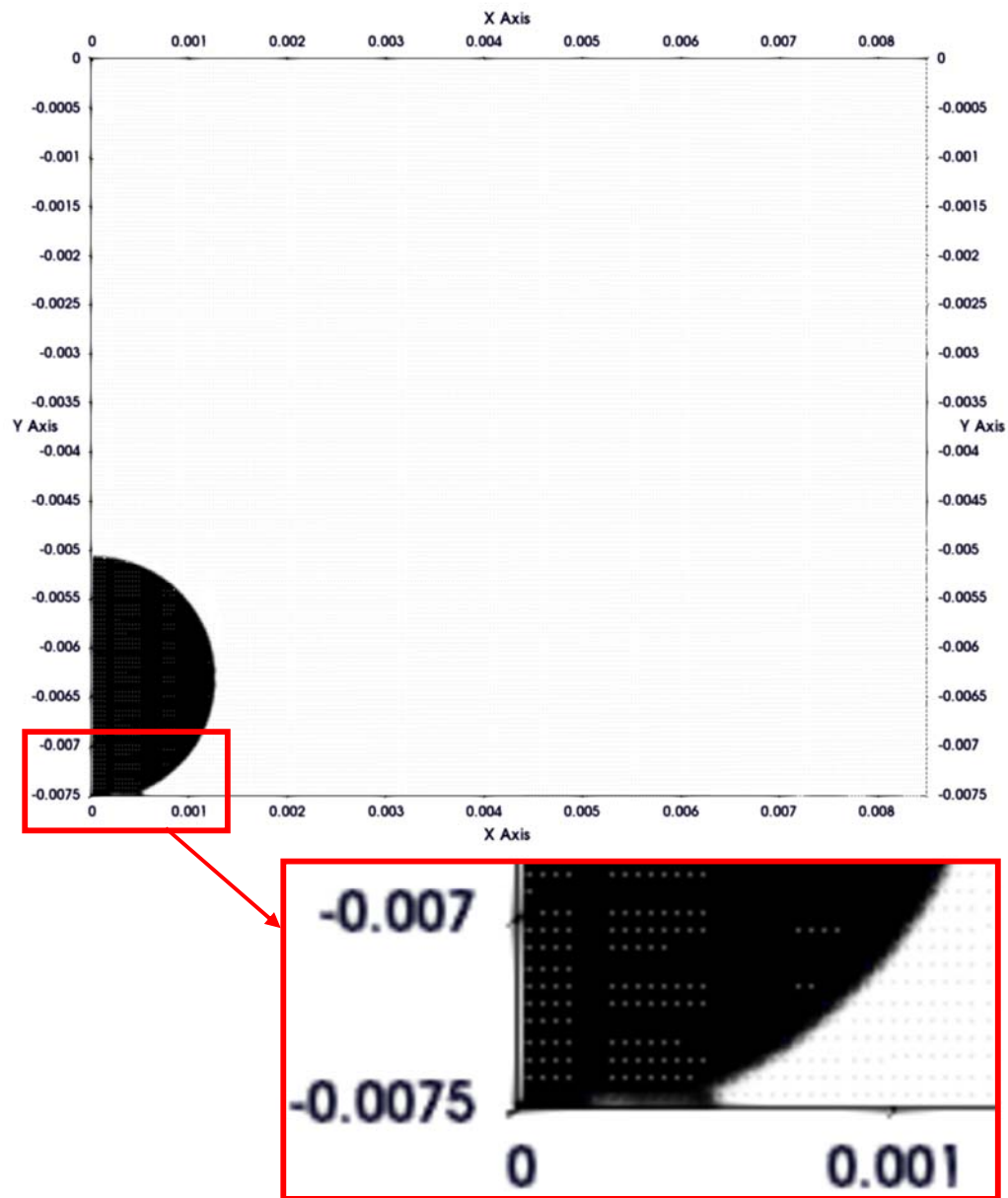


Figure 2-4 Uniform mesh used in this work

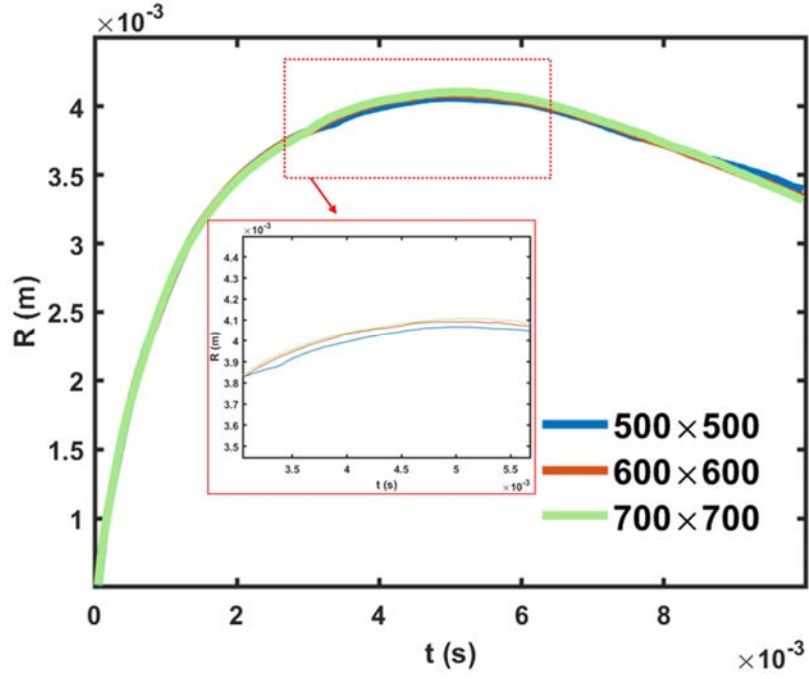


Figure 2-5 Time-dependent spreading radius for various mesh sizes

2.3.3 Validation of OpenFOAM simulation

In Fig. 2-5, the mesh sensitivity analysis shows that the maximum spreading radius is $4.10 \pm 0.01 \text{ mm}$, which matches well with the experimental value of $7.31 \pm 0.04 \text{ mm}$ in diameter shown in Fig. 2-6, an example of maximum spreading for $We = 70$. In addition, Fig. 2-7 presents a comparison of the real and simulated impacts. Overall, the simulation performed using OpenFOAM qualitatively captures the key characteristics of the impact.

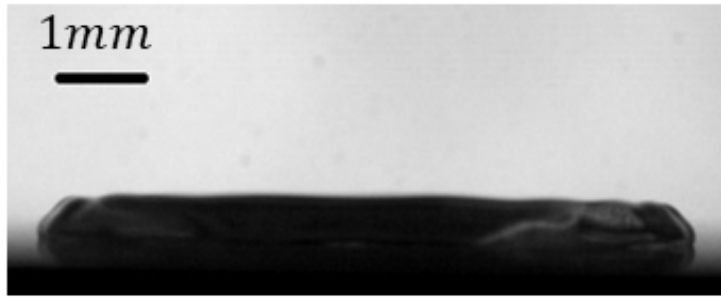


Figure 2-6 Maximum spreading of a droplet after impact at $We = 70$.

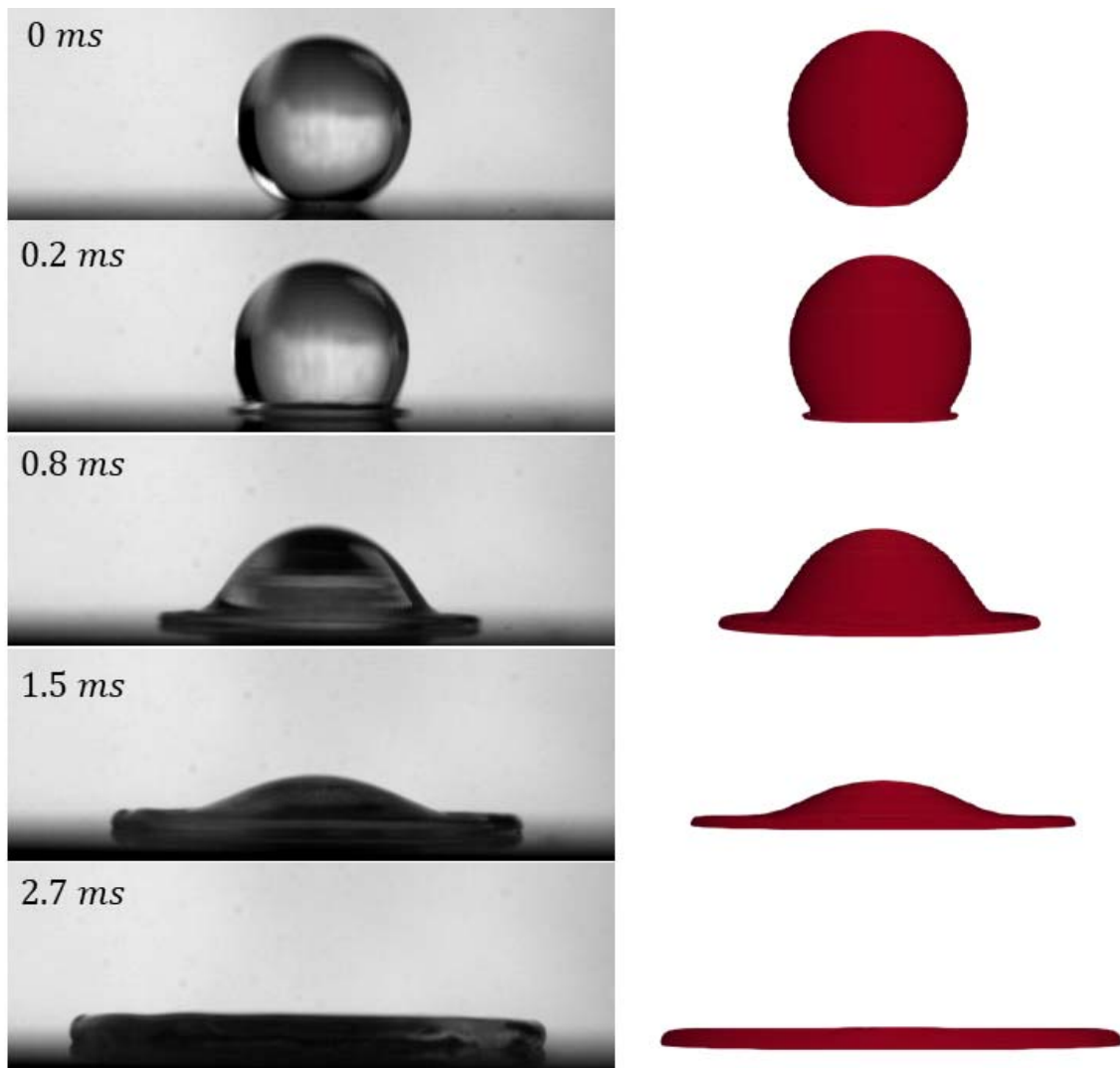


Figure 2-7 Comparison of real and simulated impacts for $We = 70$. The simulation is displayed in an extruded visualization.

2.3.4 Resolution analysis

To observe the impact, the high speed cameras were first calibrated using a grid scale with a length of 0.25 mm for each square. Consequently, the side-view recordings of impacts at $We = 70$ achieved a resolution of 0.02364 mm per pixel. For a droplet with a diameter of 2.5 mm , the height of the droplet and the length of the spreading lamella are on the order of $O(1)\text{ mm}$, while the thickness of the rim is of $O(10^{-1})\text{ mm}$. Therefore, the number of pixels across the droplet is approximately $O(10)\sim O(10^2)$, while the pixel representation for the rim thickness is around $O(1)$. Hence, the droplet's height and lamella's length can be resolved adequately, but the resolution may lead to challenges in accurately capturing the rim height.

In the OpenFOAM simulation, the mesh size was determined to be 600×600 based on a mesh sensitivity analysis as stated earlier. Given the simulation domain size of $3.4D_0 \times 3D_0$, each mesh cell represents a horizontal length of 0.01417 mm and a vertical height of 0.0125 mm . Hence, for the same droplet, the cell numbers representing the droplet height and lamella length reach the order of $O(10)\sim O(10^2)$, while the rim height is on the order of $O(1)$. Therefore similar to the experimental recordings, the droplet height and lamella length can be well resolved. It is also possible to measure the lamella and rim heights, which are of the same order of magnitude, but with a sacrifice in accuracy.

Chapter 3

Rim genesis at spreading phase for a normal impact

3 Rim genesis at spreading phase for a normal impact

This chapter delves into the formation of the rim during a normal droplet impact at low Weber numbers (We), where a smooth, thick rim can be observed. Understanding rim genesis is crucial as it provides the initial conditions for initiating numerical calculations, such as solving systems of ordinary differential equations (ODEs) that account for mass and momentum conservation, rim velocity and other variables like variations in lamella thickness. These calculations are essential for capturing the rim dynamics during droplet spreading post-impact. As previously mentioned, the process of rim evolution in the literature remains ambiguous, with most studies employing either a trivial or unrealistic assumption to define the initial conditions before numerically solving the ODEs. This approach often leads to discrepancies between the models presented in the literature and experimental observations, particularly at low We . Therefore, it is important to explore rim genesis as an accurate initial condition for feeding into the ODEs. To address this issue, it is essential to gain a deeper understanding of the lamella's shape and the underlying mechanisms that contribute to rim genesis.

3.1 Morphological dynamics of droplet impact

3.1.1 Lamella shape

Understanding the mechanisms behind lamella shape is key to understanding both the genesis and the shape of the rim, since the development of the lamella serves as a precursor to rim genesis. In the literature^{46,51,54}, the lamella is described as a slender, thin liquid sheet that is ejected radially and spreads tangentially across the solid surface. This characterization is supported by both experimental observations and simulations. However, the underlying reasons for the lamella's shape in this manner are not explained.

Shortly after droplet impact (Fig. 3-1a), the lamella can potentially take shape in one of the two ways: either as a bulge that grows as more liquid is fed in from the droplet bulk, or as a thin liquid sheet, which is widely accepted as fact, see Fig. 3-1c. Below, I aim to explain why the lamella must form as a thin sheet rather than an increasing bulge.

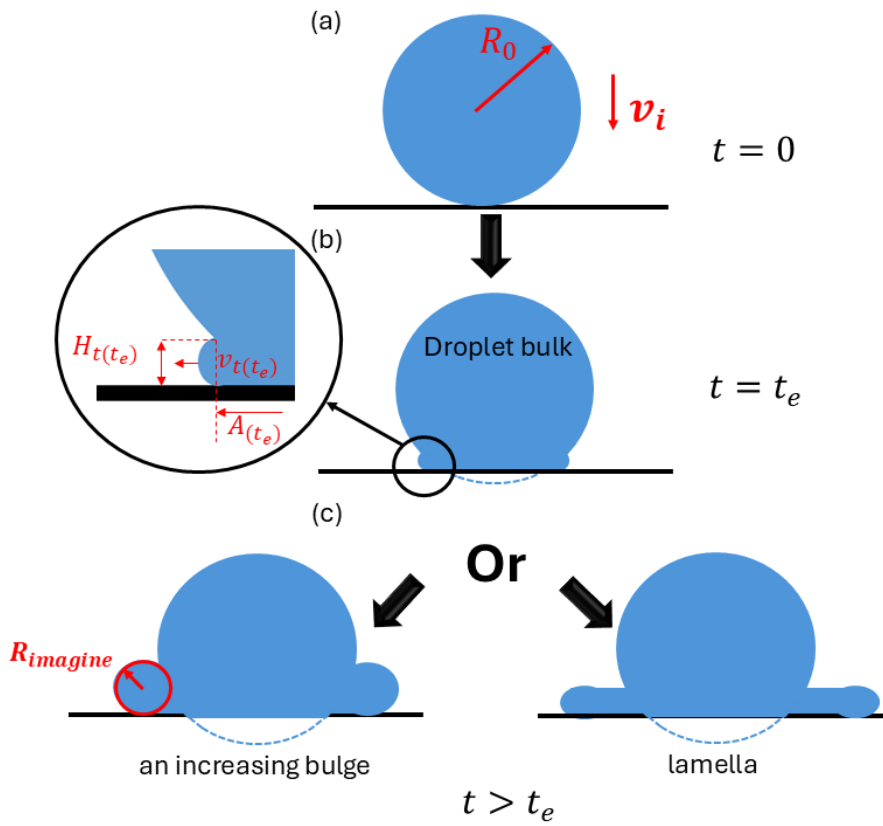


Figure 3-1 Schematic of jet shape after impact

Riboux and his coauthors^{46,51,93} point out that the lamella (or more precisely, the jet) is not visible at the moment the droplet first contacts the solid surface, but rather appears at a specific time called ejection time, $\tilde{t}_e$, which denotes the moment the jet becomes observable from the bottom of the droplet (Fig. 3-1b). They derived $\tilde{t}_e$ through a dimensionless analysis, based on the condition that

the tip of the jet must move faster than the wetted area with the diameter of $A_{(t)}$, which is driven by the descending bulk of the droplet. Therefore, the expression of $\tilde{t}_e$ is given as ⁵¹

$$c_1 Re^{-1} \tilde{t}_e^{-1/2} + Re^{-2} Oh^{-2} = c^2 \tilde{t}_e^{3/2} \quad 3-1$$

where they set $c_1 = \sqrt{3}/2$ and $c = 1.1$, adjusted based on experimental results. The value of $\tilde{t}_e$ can be obtained using MATLAB's *fsolve* toolbox. The wetted area also refers to the distance between the symmetry axis to the root of the lamella once the lamella becomes visible⁹³.

Here, letters with a tilde on top represent dimensionless parameters. Following the convention in the literature⁵¹, R_0 , v_i , and $\frac{R_0}{v_i}$ are selected as characteristic scales of length, velocity and time. The dimensionless form of $A_{(t)}$ is denoted as $\tilde{A}_{(\tilde{t})}$. Up to the characteristic impact time $\tau = \frac{R_0}{v_i}$, the flow inside the droplet can be described by potential flow^{53,94}, as the viscous effects are negligible due to the thin boundary layers near the solid surface, which have not yet grown enough to influence the flow within the droplet bulk. As shown in Fig. 3-2, the height of the droplet bulk decreases uniformly at a linear rate until τ , after which the descent slows, implying a notable effect from the viscous boundary layer in decelerating the downward motion. By applying Wagner's theory⁵³, $\tilde{A}_{(\tilde{t})}$ is deduced as a function of time: $\tilde{A}_{(\tilde{t})} = \sqrt{3\tilde{t}}$ ⁵¹, a result confirmed later by Philippi *et al*⁴⁹.

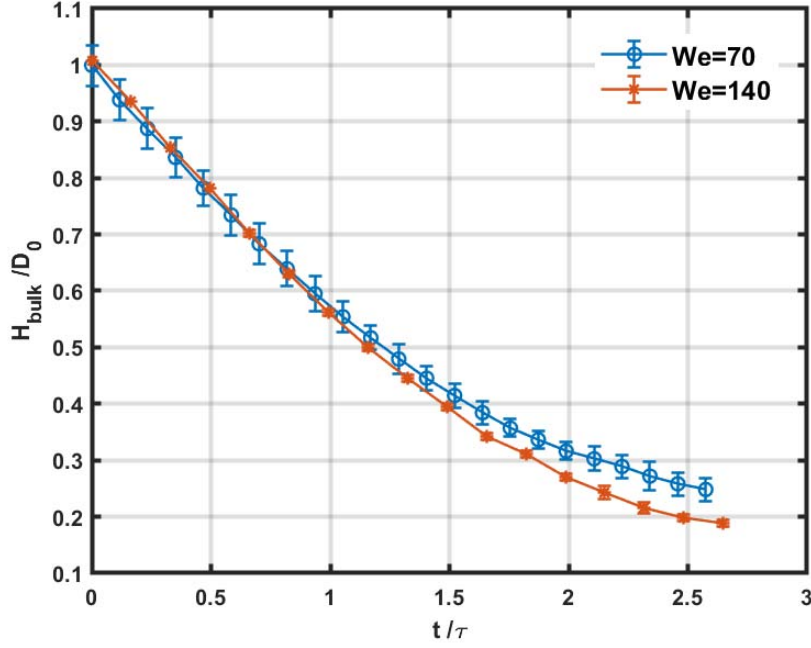


Figure 3-2 Variation of droplet bulk in height over time for droplet impacts at $We = 70$ and $We = 140$. Droplet bulk height (H_{bulk}) and time (t) are scaled by the initial droplet diameter (D_0) before impact and the characteristic

impact time ($\tau = \frac{R_0}{v_i}$), respectively.

Furthermore, Riboux *et al.*^{51,93} determined the configuration of the droplet at $\tilde{t}_e$: $\tilde{A}_{(\tilde{t}_e)} = \sqrt{3\tilde{t}_e}$; the lamella is ejected with a velocity of $\tilde{v}_{t(\tilde{t}_e)} = \frac{1}{2}\sqrt{\frac{3}{\tilde{t}_e}}$; and the thickness of the lamella edge is approximately $\tilde{H}_{t(\tilde{t}_e)} \simeq \frac{\sqrt{12}\tilde{t}_e^{3/2}}{\pi}$. This configuration is thus considered the initial state before the lamella begins to develop. With this foundation established, the next step is to determine the shape of the lamella.

Although experiments observed the lamella as a thin liquid sheet, an initial assumption is made that the lamella forms as an increasing bulge, and then demonstrate why this assumption is incorrect. The cross-section of the bulge is conceptualized as a full circle, representing the maximum

curvature the bulge can achieve, and thus the greatest capability it can have to accommodate the liquid flux from the droplet bulk. In other words, if the full circular cross-section cannot handle the incoming flux, then partial circular cross-sections certainly cannot. To assess whether the bulge with a full circular cross-section can maintain its shape, the Laplace pressure of the bulge is compared to the dynamic pressure of the incoming flux. The dynamic pressure is generated by the outward motion of the jet at the bottom of the droplet because of the impact. This implies that for the bulge shape to persist, the dominant dynamic pressure of the flux must be balanced by the Laplace pressure of the bulge, characterized by an imaginary radius $R_{imagine}$, see Fig. 3-1c. The value of $R_{imagine}$ can be determined using volume conservation, for details see Appendix. Specifically, when the spherical droplet is impacting the solid surface, the portion “eaten” by the surface, as denoted by the dashed curve in Fig. 3-1, is transferred to the jet, which forms the imagined bulge.

Accordingly, the Laplace pressure is given by:

$$P_{lap(t)} = \frac{\sigma}{R_{imagine(t)}} + \frac{\sigma}{R_{imagine(t)} + A(t)} \quad 3-2$$

The dynamic pressure of the jet at the location of $A(t)$ can be described by:

$$P_{dyn(t)} = \frac{1}{2} \rho u_{A(t)}^2 \quad 3-3$$

where $u_{A(t)}$ is the radial velocity at the location of $A(t)$, given by $\frac{dA(t)}{dt}$, in a frame of reference moving at a velocity $\frac{dA(t)}{dt}$ ^{51,93,95}.

Now, the difference between $P_{dyn(t)}$ and $P_{Lap(t)}$ can be obtained. If the result is significantly greater than zero, it implies that the dynamic pressure overpowers the Laplace pressure.

Consequently, such strong dynamic pressure would disrupt the bulge shape, causing the flux to eject abruptly in the radial direction and form the thin, flat lamella.

Another way to determining the jet shape is by comparing the tangential momentum flux at the location of $A_{(t)}$ with the capillary forces. Assuming the jet has a full circular cross-section, the difference between the momentum flux and the capillary forces is expressed as,

$$F_{diff} = \rho u_{A(t)}^2 H_{a(t)} - 2\sigma \quad 3-4$$

where $H_{a(t)}$ is estimated⁹³ by $\frac{\sqrt{12}}{3\pi} R_0 \tilde{t}^{3/2}$. If the tangential momentum flux exceeds the capillary forces, then flux will overcome the constraints imposed by the capillary forces, leading to the formation of a thin, flat lamella.

Earlier, the lamella was initially assumed to develop as an increasing bulge, contrary to experimental observations that indicate its shape as a thin liquid sheet. Although the results disproving this assumption are not presented here, the outlined process provides a framework for understanding why the lamella ultimately takes the form of a thin sheet. Details of the results for $We = 70$ will be presented in section 3.2.3.

3.1.2 Rim genesis

Understanding the form of the lamella shape is crucial, as it establishes the foundation for rim genesis. For droplet impacts at low We , when $t \geq t_e$, the lamella develops into a thin liquid sheet. As time progresses, the deceleration at the edge of the lamella due to capillary forces leads to a smooth thick rim, as seen in Fig. 3-3a. The lamella remains relatively flat, allowing us to model the flow within it as a laminar flow, described by a mean velocity $u_{(t)}$.

The assumption of laminar-like flow is based on several considerations. Under the impact condition $We < 100$, the Re for the lamella is estimated to decrease from $O(10^4)$ to $O(10^3)$, based on the radial velocity at the lamella root (the location of $A_{(t)}$). In comparison, the classic threshold for the transition to turbulence in free flow over a flat surface is $Re \sim O(10^5)$. Since the estimated Re for the lamella remains significantly below this threshold, the assumption of laminar-like flow is justified. Additionally, the unique dynamics of the lamella – being a thin liquid sheet subject to rapid radial expansion due to the impact and deceleration caused by viscous and capillary forces – further stabilize the flow and suppress the development of turbulence.

According to O’Naraigh and Mairal’s simulation⁹⁶, a recirculation flow was observed inside the rim when the droplet approached its maximum spreading. They attributed this recirculation to minor head loss, caused by sharp changes in geometry. This occurs as the lamella flow enters the rim through a very narrow neck, which is restricted by the presence of a growing boundary layer. Wei and Thoraval⁹⁷ also noticed in their simulations that the top and bottom of the rim exhibit opposite velocity directions, implying a circulating motion within the rim. Interestingly, a similar phenomenon was experimentally observed by Clanet *et al.*²⁵. They scaled up the lab environment using a transparent balloon to mimic the droplet. By placing tracers inside the balloon, they visualized a vortical motion at the balloon’s edge when it reached maximum spreading. This vortical motion validates the recirculation shown in O’Naraigh and Mairal’s simulation.

Hence, the laminar flow within the lamella is proposed to gradually transition through the neck region into the rim region, where deceleration takes place, leading to the change at the end of the lamella from laminar flow to a quasi-circular motion. This motion is characterized by a mean linear velocity, $u_{\theta(t)}$. Over time, this motion develops into full recirculation within the rim. During the early stages of spreading, the neck is not prominent, and the flow remains governed by inertial

forces, allowing the flow at the lamella's end to retain its laminar behavior, see Fig. 3-3c. However, as the boundary layer grows and the neck becomes narrower, inertial forces weaken, enhancing the recirculation within the rim.

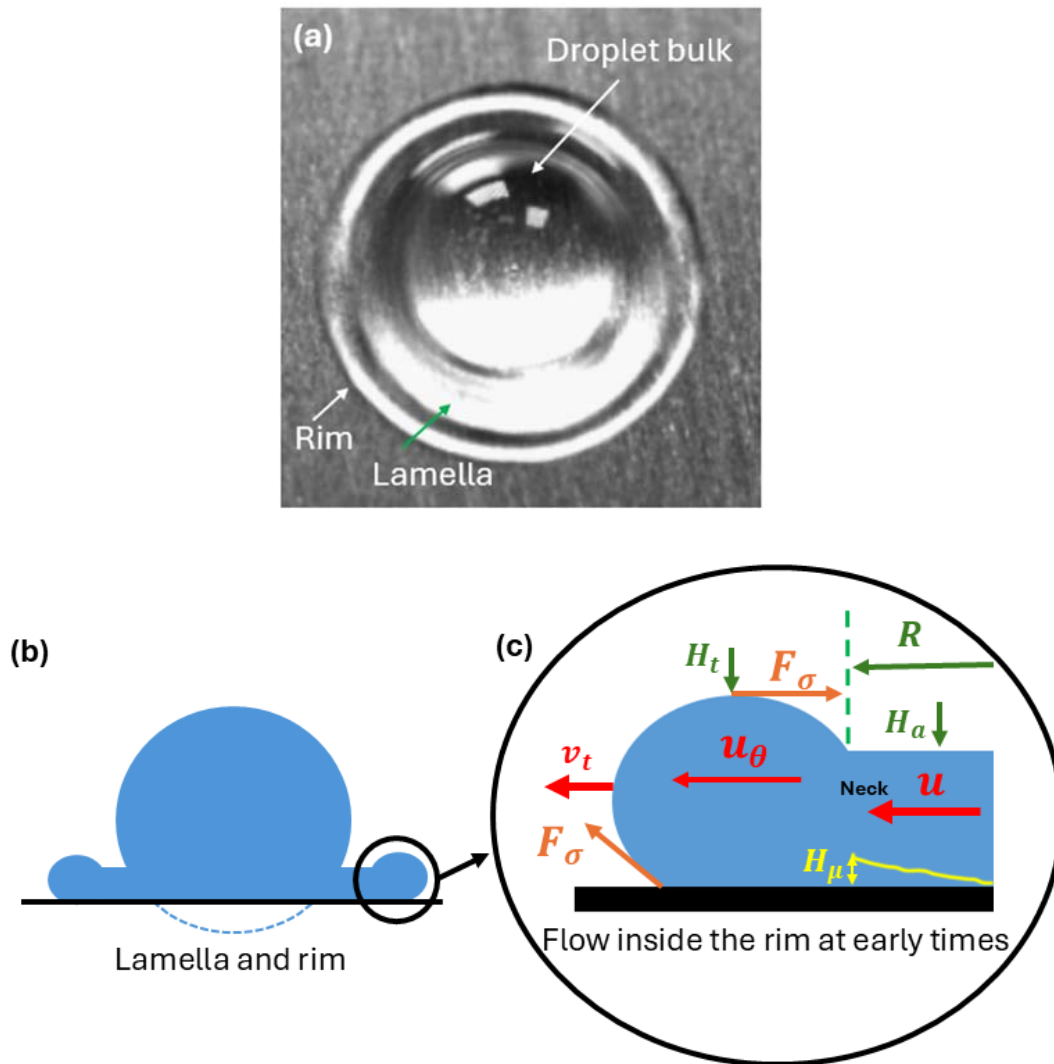


Figure 3-3 Lamella shape (a) experimental view from top for $We = 70$; (b) schematic of an impacting droplet from a side view; (c) zoom-in at lamella edge

With this assumption in mind, the incoming flux from the lamella gradually feeds the end of the lamella due to deceleration and changes in geometry, leading to a smooth bulge, or rim. As more

flux enters the rim, it continues to grow. Essentially, the smooth shape of the rim results from this developing circulating flow at the lamella's end. In other words, the curvature of the rim is driven by this motion. Therefore, the Laplace pressure within the rim is mainly balanced by the dynamic pressure induced by the flow. This gives the “centrifugal” pressure as follows,

$$P_{cen} = \frac{1}{2} \rho u_{\theta(t)}^2 \quad 3-5$$

and the Laplace pressure within the rim is given by

$$P_{Lap_rim} \approx \frac{2\sigma}{H_{t(t)}} \quad 3-6$$

where $H_{t(t)}$ is the rim thickness. The linear velocity u_{θ} can be described in terms of $H_{t(t)}$ by equating the dynamic and Laplace pressures. It should be noted that the term “centrifugal” refers to the evolving circulation, even though at the early stages, the flow appears more like a laminar flow.

To track the growth of the rim, according to mass conservation, the radial mass flux from lamella must equal the mass flux into the lamella's end. The radial mass flux per unit arc length from the lamella is estimated as

$$\Delta m = \rho(u_{t(t)} - v_{t(t)})(H_{a(t)} - H_{\mu(t)}) \quad 3-7$$

where $v_{t(t)}$ is the radial velocity of the rim, the lamella thickness, $H_{a(t)}$, is simplified by assuming the lamella shape to be a uniform flat sheet, $H_{\mu(t)}$ is the boundary layer thickness given by $\sqrt{\nu t}$, and the mass flux into the lamella's end per unit arc length is estimated as

$$\Delta m \approx \rho u_{\theta(t)} H_{t(t)} \quad 3-8$$

Using these relationships, one can estimate the time when the rim catches up with the lamella in thickness by comparing $H_{a(t)}$ and $H_{t(t)}$. This requires knowledge of $v_t = \frac{dR(t)}{dt}$, where $R(t)$ is the spreading radius from the droplet center to the rim, derived from mass conservation by considering that the “eaten” portion of the droplet transfers to the lamella and the rim. The velocity $u_{(t)}$ relative to the ground is estimated using Riboux and Gordillo’s relation⁵¹ as $\frac{2dA(t)}{dt}$. These estimations hold for $t \leq \frac{R_0}{v_i}$, which means the potential flow is still dominant within the droplet bulk. For details see Appendix.

The approach outlined above is to determine the time when the rim starts to appear and the configuration of the droplet at that moment. However, it is important to note that this approach only applies to impact under low We conditions, when one can see a smooth and thick rim. It does not account for rim undulations that occur at high We . For instance, Fig. 3-3a displays the smooth rim at $We = 70$, whereas Gordillo *et al.*’s work⁴⁶ shows that undulations become noticeable when $We \geq 100$. Therefore, for low We impacts, We must be below 100. This approach, while effective for low We , is not sufficient to explain rim genesis at high We .

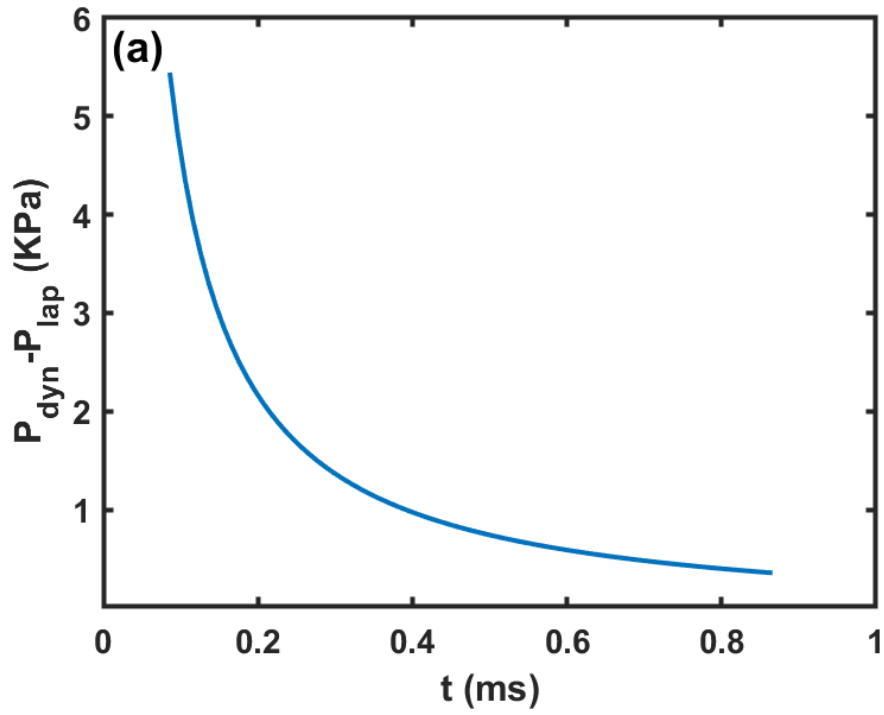
3.2 Results and discussion

3.2.1 Jet shape

As previously mentioned, the jet shape following impact can be determined by comparing the dynamic pressure at the jet root with the Laplace pressure, assuming a circular cross-section of the jet. For the impacts at $We = 70$, the time-dependent pressure difference is shown in Fig. 3-4a. At t_e , the dynamic pressure exceeds the Laplace pressure by 5.5 KPa and remains dominant

throughout the time span $t_e \leq t \leq \frac{R_0}{v_i}$. This dominance indicates that the lamella's bulge shape cannot be maintained due to the higher dynamic pressure.

Besides, Fig. 3-4b displays the variation over time in the difference between the momentum flux and the capillary forces at the location of the jet root. The momentum flux is consistently stronger than the capillary force, with this disparity increasing due to the growing $H_{a(t)}$. As a result, the jet evolves into a thin, flat liquid sheet, consistent with the lamella observed in the experiment.



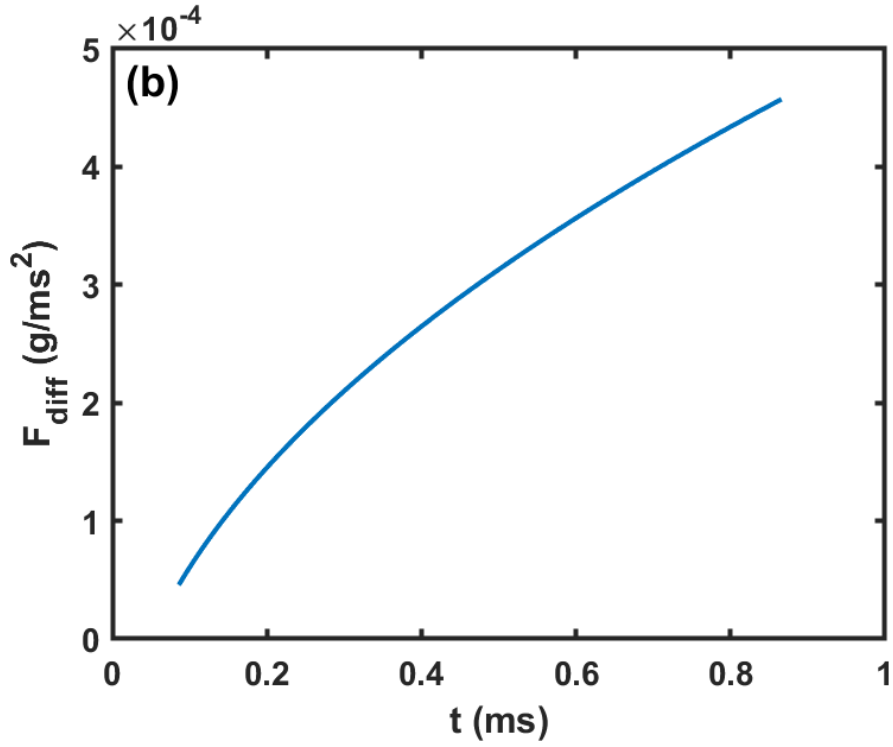
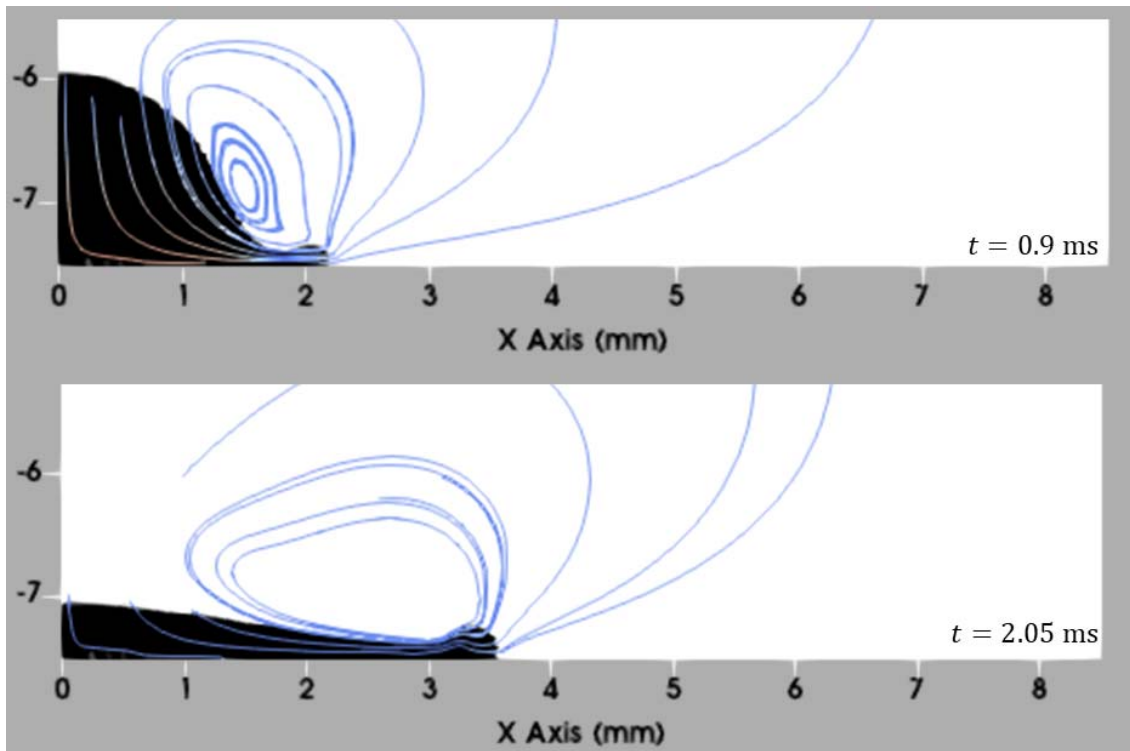


Figure 3-4 Variation of (a) pressure difference and (b) difference between the momentum flux and capillary forces, at the location of $A_{(t)}$ over time.

3.2.2 Evolution of the flow at the lamella's end

The curvature of the rim region is assumed to result from the developing circulating flow at the lamella's end. The streamlines of the flow within the droplet, obtained via OpenFOAM for a droplet impact at $We = 70$, clearly illustrate the evolution of this circulating flow, transitioning from a laminar state to full recirculation at maximum spreading, as shown in Fig. 3-5. This transition is induced by the growing boundary layer and the weakening inertial forces. Although Fig. 3-6 indicates that the boundary layer is much thinner than the lamella based on calculations up to the critical moment $\frac{R_0}{v_i}$, it still affects the flow direction. The outer flow slides along the boundary layer, and when the boundary layer gets thicker, the outer flow is lifted and gradually

begins to circulate in the rim region, driven by the deceleration due to capillary forces, as depicted in the streamlines at the rim region in Fig. 3-5. At the early stage from t_e to $\frac{R_0}{v_i}$, the relatively straight streamlines in the lamella and rim regions indicate a laminar-like flow, and it spans the entire cross-section of the rim region. The mean flow in the lamella region estimated as $\frac{2dA(t)}{dt}$ results in Re values on the order of $10^3 \sim 10^4$, which supports the assumption of predominantly laminar flow, as the Reynolds number threshold for the transition from laminar to turbulent flow in free flow over a flat plate is of $O(10^5)$. Given all these, it is reasonable to estimate the mass flow rate within the rim region as expressed in Eq. 3-8.



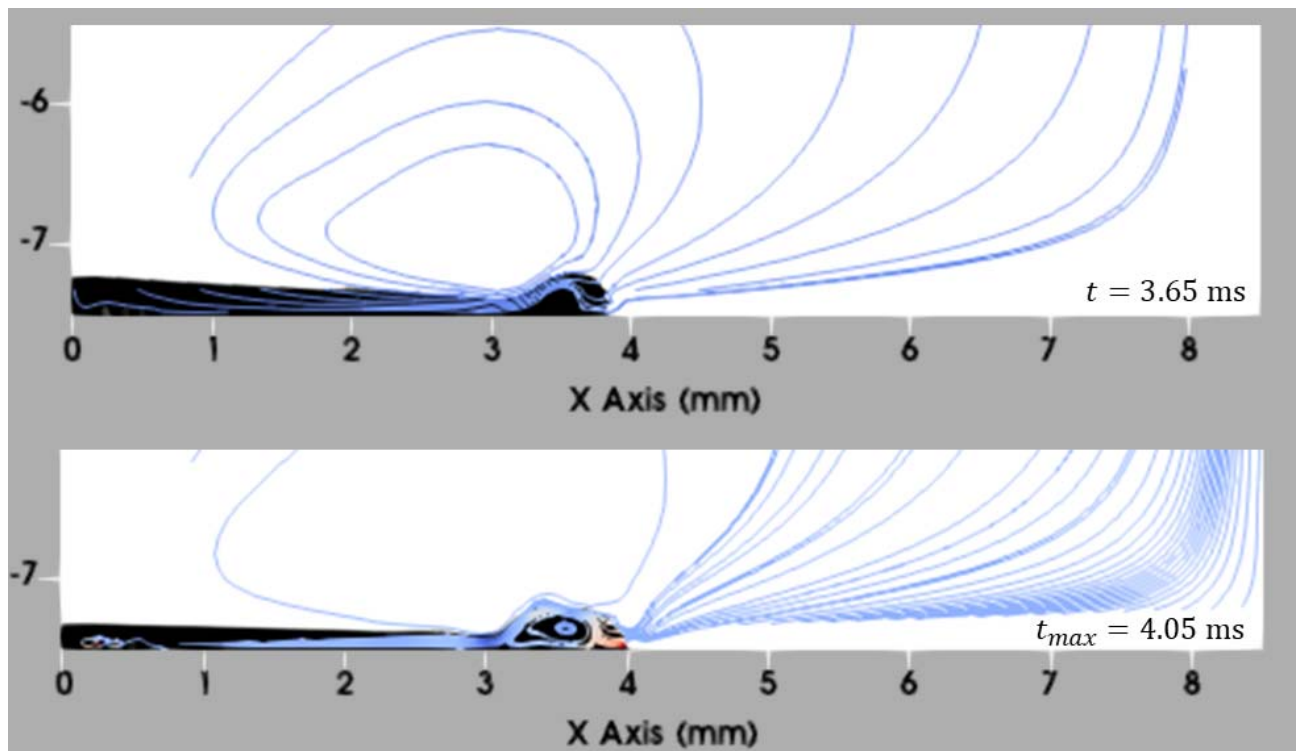


Figure 3-5 Streamlines of the flow within the droplet leading up to maximum spreading, generated using OpenFOAM for an impact at $We = 70$.

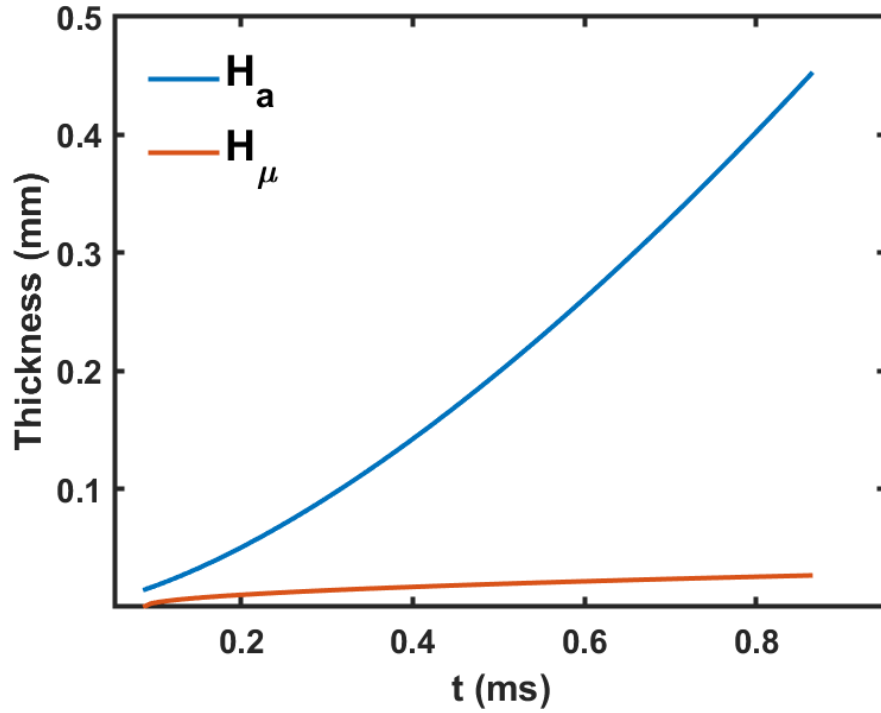


Figure 3-6 Time evolution of lamella thickness (H_a) and boundary layer (H_μ) up to $\frac{R_0}{v_i}$ for the impact at $We = 70$

3.2.3 Time of the rim genesis

The time-dependent lamella thickness and the evolution of the lamella edge have been calculated. The difference between these two thicknesses has been given in Table 3-1. Clearly, at $t = 0.326 \text{ ms}$, the lamella is slightly thicker than its edge by 0.0023 mm . As time progresses to 0.336 ms , the lamella edge thickness surpasses that of the lamella by a small margin of 0.0035 mm . This implies that a rim appears, although this slight difference remains visually indistinct. However, as the lamella edge continues to thicken over time, the rim eventually becomes more pronounced.

Table 3-1 Calculated thickness differences between the lamella (H_a) and the lamella edge (H_t) at different times

t (ms)	0.2	0.3	0.316	0.326	0.336	0.4
$H_a - H_t$ (mm)	0.0364	0.0168	0.0076	0.0023	-0.0035	-0.0501

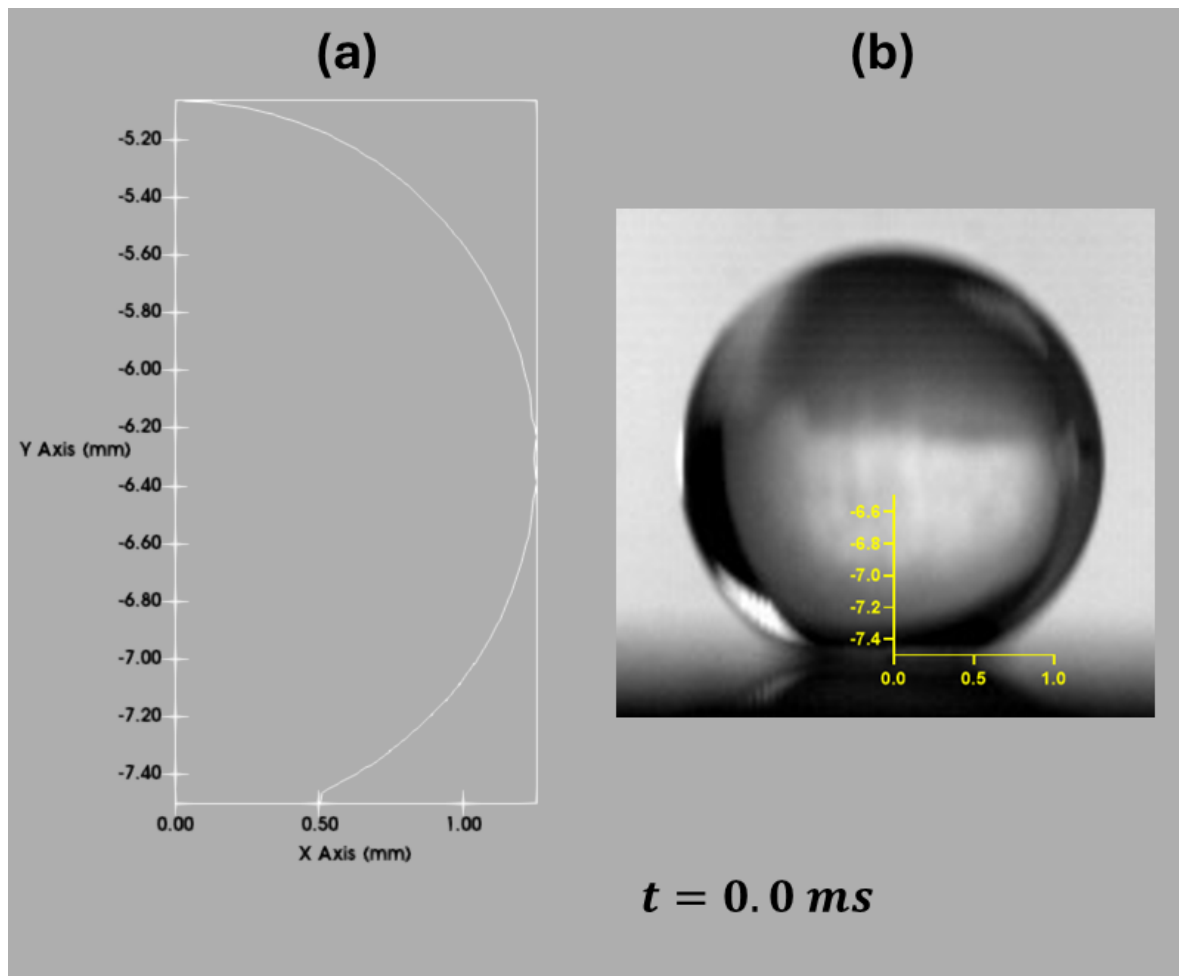
Because of limitations in measurement and observation from experimental recordings, OpenFOAM simulations were conducted to validate the analytical model, particularly for lamella dynamics, which is hidden by the rim in side-view recordings. The analytical work is thus compared with the simulated work from a side view in a 2D form.

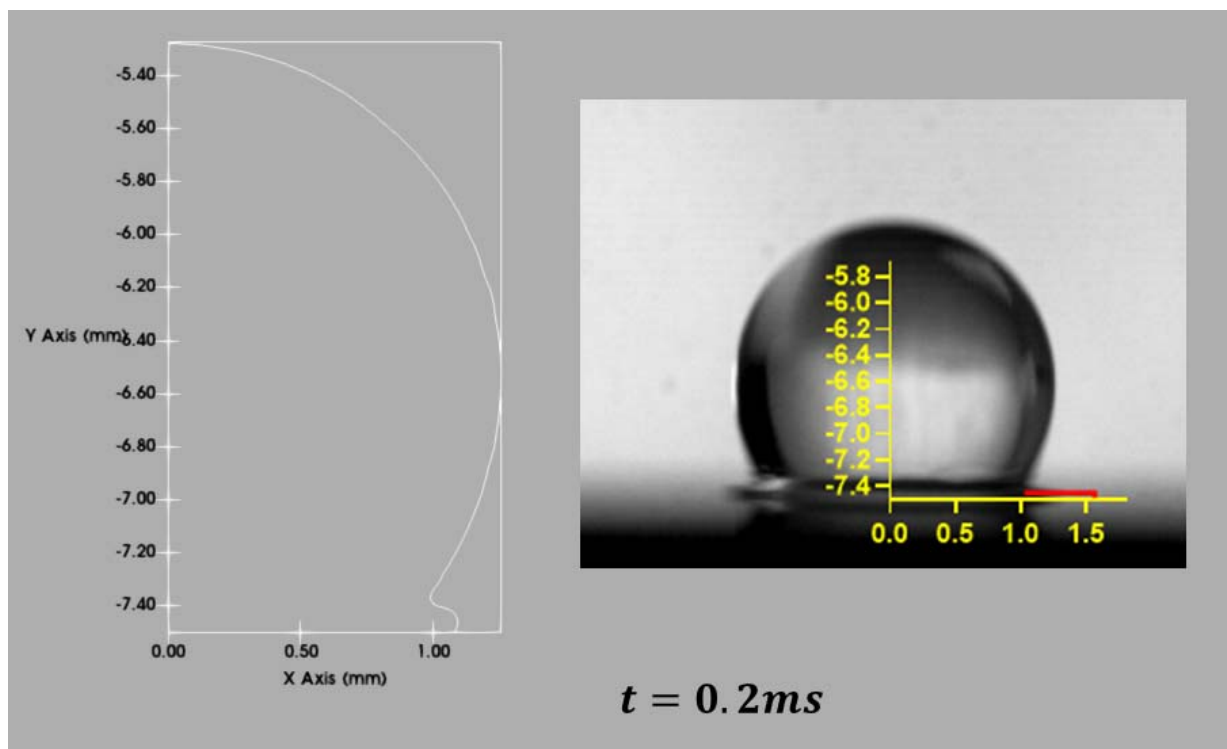
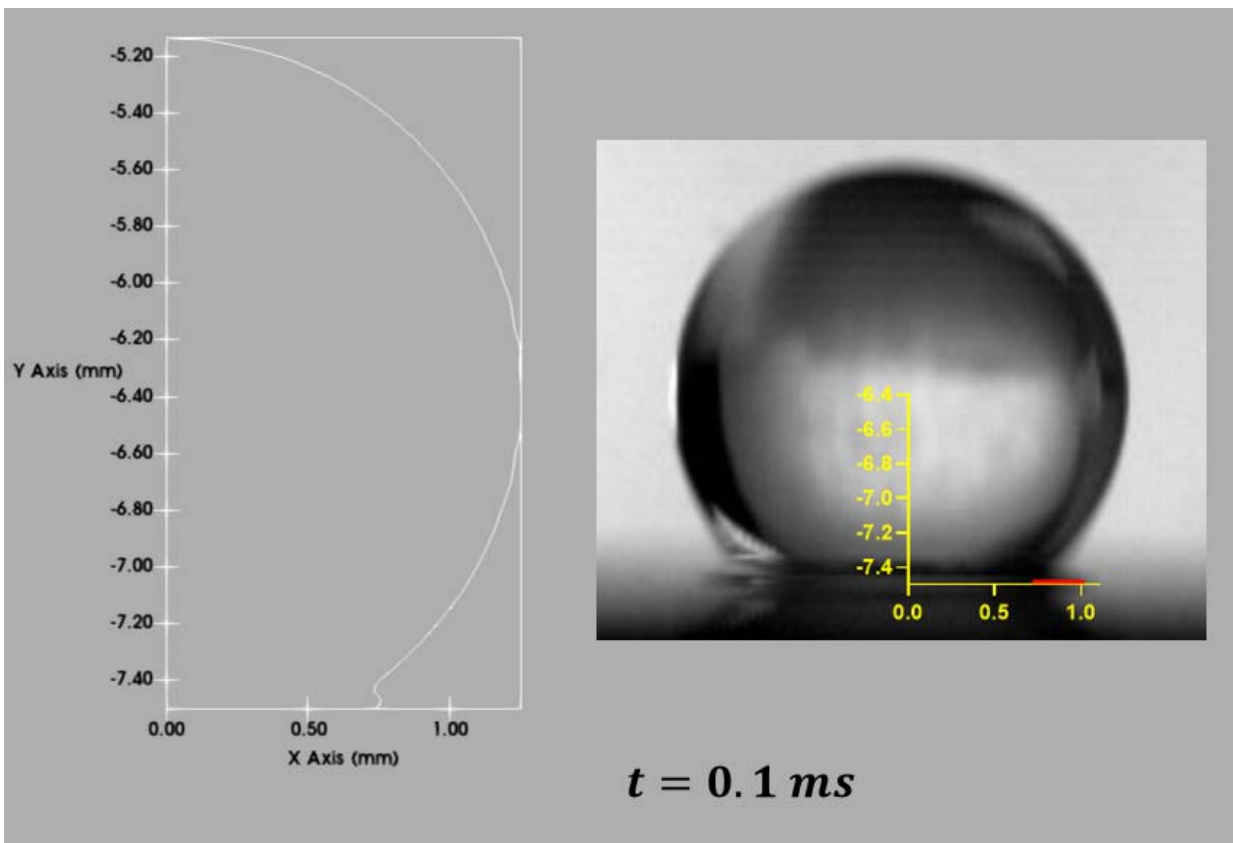
2D analysis is adopted for normal impacts because these impacts can be approximated as axisymmetric events, meaning the key features such as lamella's height and length, as well as rim's height and length, are essentially the same in all radial directions. A 2D simulation is sufficient to describe these key features with a simplified model that neglects the third dimension, significantly reducing computational costs. The results in 2D are more straightforward, making it easier to interpret the key features. In addition, experimental recordings from a side view are also displayed in 2D, allowing for a direct comparison between 2D simulations and analytical results with the experimental 2D images, as shown in Fig. 3-7.

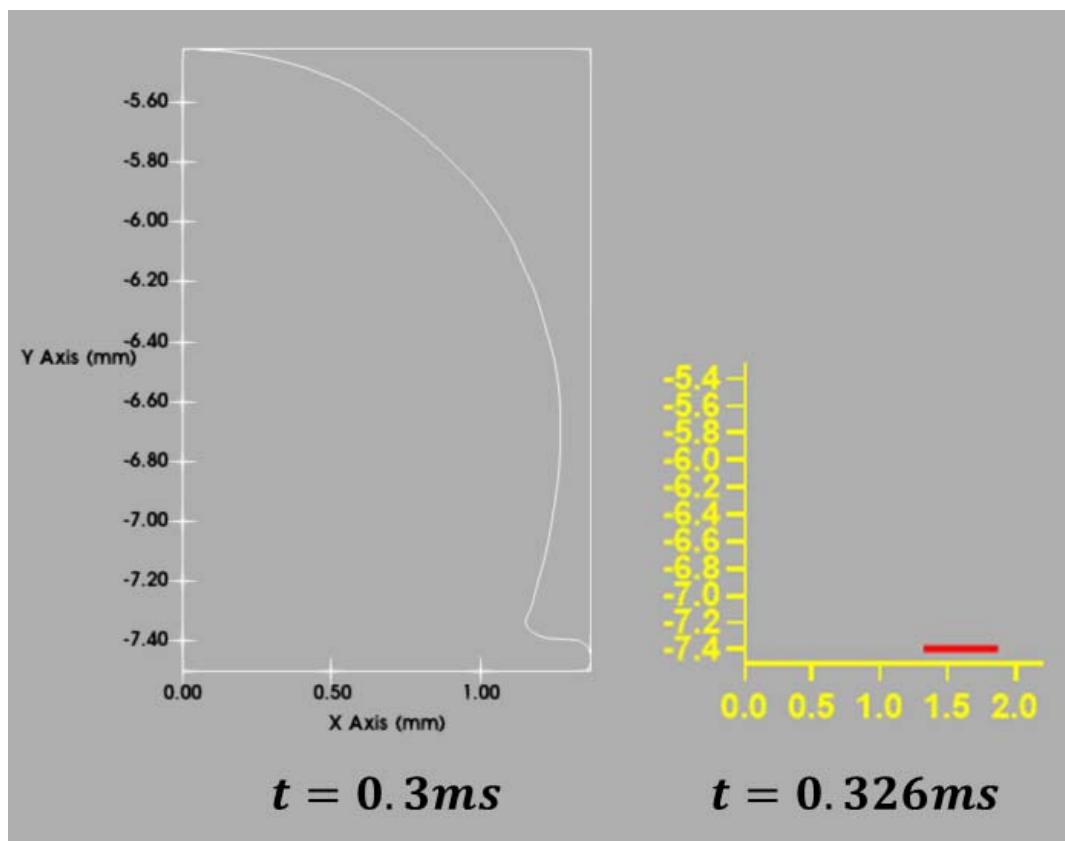
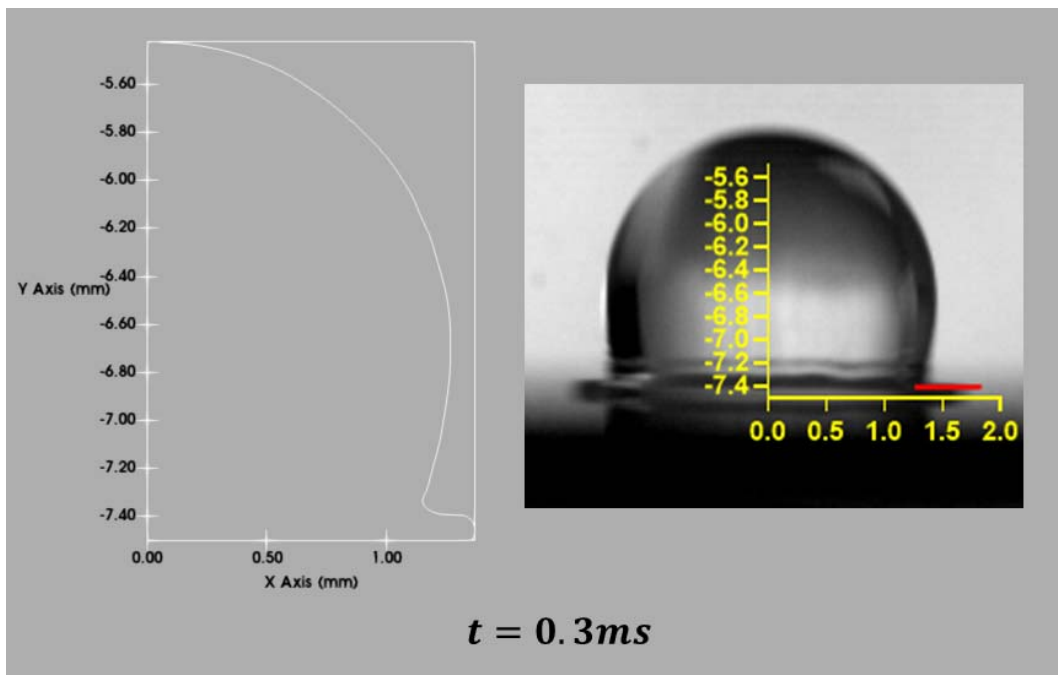
Figure 3-7 presents side-view snapshots of the simulated spreading in OpenFOAM and experimental recordings, with the calculated lamella height indicated by red lines for $We = 70$. The experiments were recorded at 10,000 *fps*, while the calculations were conducted with a time interval of 0.01 *ms*, and the simulation results were saved at a time step of 0.05 *ms*. The red lines start from the lamella root ($A_{(t)}$), where the lamella meets the droplet bulk, and extends to its edge.

Clearly, the lamella root is well predicted using $\tilde{A}(\tilde{t}) = \sqrt{3\tilde{t}}$ ⁵¹ before $t = 0.4 \text{ ms}$. This is because the derivation of $\tilde{A}(\tilde{t})$ is based on a simplified form of the Euler-Bernoulli equation under the condition $t \ll \frac{R_0}{v_i}$, where the local acceleration is the dominant factor⁵¹. The calculated spreading radius, indicated by the end of the red line, is overestimated by approximately 16% before $t = 0.4 \text{ ms}$, compared to the experimental and simulated results. This discrepancy likely arises from the simplifications made in estimating the volume transferred to the lamella portion, the simplifications on the lamella shape as a rectangle, and the underestimation of H_a which results in an overestimation of the spreading width based on the volume conservation. Nevertheless, the calculated results effectively capture the lamella dynamics during the early stage of spreading.

From 0.1 ms to 0.4 ms , the lamella gradually increases in thickness and appears relatively flat after 0.3 ms as indicated by the droplet contours obtained from the simulation. The very tiny line at the end of the red line denotes the height discrepancy between the lamella and its edge. This discrepancy is not obvious approximately on the order of $10^{-2} \sim 10^{-3} \text{ mm}$, as shown in Table 3-1. At $t = 0.2 \text{ ms}$ and $t = 0.3 \text{ ms}$, the lamella is higher than its edge by 0.0364 mm and 0.0168 mm , respectively. This discrepancy decreases to 0.0023 mm at $t = 0.326 \text{ ms}$, and at the next time step, the lamella edge catches up and surpasses the lamella in height by 0.0035 mm , indicating the appearance of the rim.







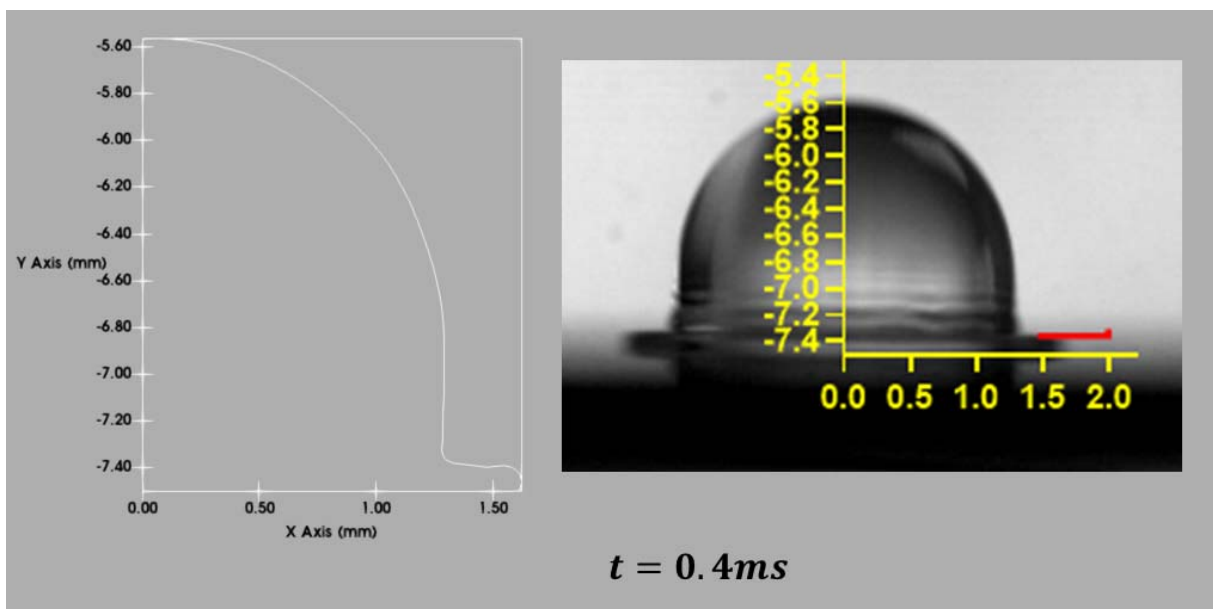
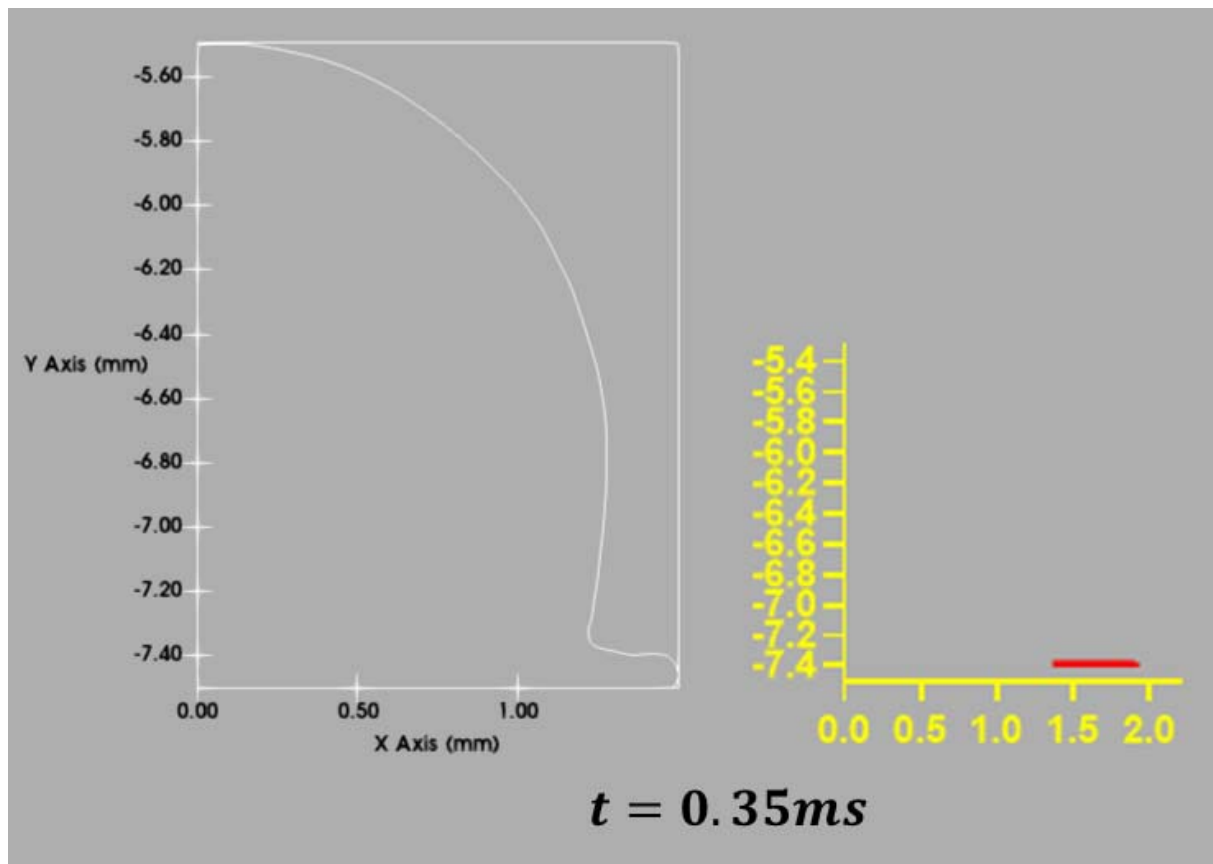


Figure 3-7 Comparison of lamella evolution among OpenFOAM simulation (left), experimental results, and calculations (red line), for an impact at $We = 70$. The red line starts from the location of $A_{(t)}$, which represents the

lamella root, and extends to its edge. The tiny line at the end of the red line indicates the discrepancy between the lamella and its edge: a downward line suggests a lower end, while an upward line indicates the formation of the rim.

A flat red line signifies that the height of the lamella and its edge are equal, indicating the onset of rim genesis.

Based on the calculation, it can be inferred that approximately at $t = 0.326 \text{ ms}$, the rim is starting to form. Next, the configuration of the droplet at this moment should be established to serve as the initial condition for the subsequent rim-lamella model.

3.2.4 Droplet configuration at the onset of rim genesis

For a water droplet impacting a flat hydrophobic Al surface at a low $We = 70$, the jet is about to be seen at $t_e = 0.086 \text{ ms}$ according to Eq. 3-1, and based on previous discussions, at $t = 0.326 \text{ ms}$ (denoted as t_r), the rim is about to form. The configuration of the droplet at this moment, including the radius (R_r) of the spreading lamella as well as the rim thickness (H_r), is illustrated in Fig. 3-8, and summarized in Table 3-2.

Table 3-2 Droplet configuration

	$t_r \text{ (ms)}$	$R_r \text{ (mm)}$	$H_r \text{ (mm)}$
Calculation	0.326	1.768	0.105
Simulation	0.3	1.366	0.104
Experiment	0.3	1.495 ± 0.090	0.095 ± 0.013

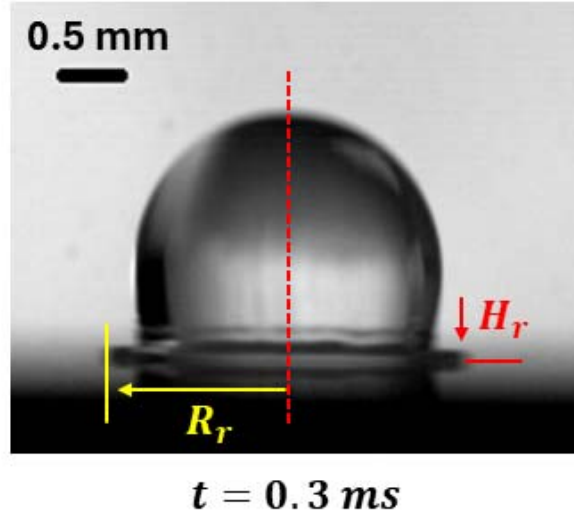


Figure 3-8 Rim thickness and lamella radius

Table 3-2 displays excellent agreement among the calculated values, OpenFOAM simulation and experimental results for the droplet configuration at approximately $t_r = 0.326 \text{ ms}$. The simulation supports the proposed model explaining rim genesis, and the experiment further confirms this model. This calculated configuration can be applied as a reliable foundation to the subsequent rim-lamella model for maximum spreading prediction. However, this will be addressed in future work.

3.3 Conclusion

Rim genesis has been discussed in the context of low We impacts, where a smooth rim can be seen. Before delving into the rim genesis, the jet shape was firstly explained since this is the precursor to subsequent rim development. Following an impact, the jet is tangentially ejected from the droplet bottom, and its shape has to be a flat sheet because capillary forces are insufficient to counteract the incoming flow, which possesses a greater dynamic pressure.

The analytical model elaborates the mechanism of rim genesis for impacts at low We . In this model, laminar-like flow within the lamella at the early stage gradually accumulates at its end, i.e., the rim region, due to deceleration caused by capillary forces. A rim occurs when the mass accumulation results in a thicker rim region compared to the lamella. The Laplace pressure within the rim region is balanced by the dynamic pressure of the decelerating flow, leading to the variations in rim curvature.

This work includes experimental validation of the proposed model, supported by OpenFOAM simulations that provide more details. The model not only identifies the moment the rim begins to form but also characterizes the droplet configuration at that instant. This configuration can be further used as the initial condition to feed the rim-lamella model, enabling a comprehensive understanding of the spreading process and maximum spreading.

Chapter 4

**Spreading control for an oblique impact:
asymmetric spreading to symmetric spreading**

4 Spreading control for an oblique impact: asymmetric spreading to symmetric spreading¹

Drop impact on a flat surface induces a symmetric spreading of the lamella, resulting in a circular spreading shape. In contrast, during impact on an inclined or moving surface, the spreading becomes asymmetric due to a tangential velocity (v_t) along the surface. To address this asymmetry, a model was developed in this chapter based on the Taylor-Culick theory. This model can restore the symmetry of the lamella by considering a wettability contrast. To demonstrate this effect, a surface design was proposed featuring a stripe pattern on aluminium sheets to highlight the wettability contrast. For water droplet, under conditions where both We_n and We_t are below 300, ensuring a deposition outcome, the model predicts effective correction of the deformed lamella shape when $0.51 \leq We_n / We_t \leq 2.04$.

4.1 Method

4.1.1 Shape correction

To make an asymmetric lamella symmetric at t_{max} , the deformation on the downstream lamella due to v_t should be corrected in the spreading process within the period from 0 to t_{max} . The correction is performed by manipulating wettability to facilitate the receding of the downstream contact line to counteract the stretch caused by v_t . On the downstream contact line, see Fig. 4-1a, different points, e.g., P , should recede at different velocities since the amount of stretching for lamella is varied as per local. To have an estimation of the velocity needed for contact line at each

¹ This chapter is published in the paper “Application of Surface Wettability to Control Spreading of an Impacting droplet”, LANGMUIR 2024, 40,4623-4634.

local, one can use the Taylor-Culick theory⁹⁸⁻¹⁰⁰, which correlates the receding velocity (v_r) of contact line with the receding contact angle (θ_{rec}) as:

$$v_r = \sqrt{2\sigma(1 - \cos \theta_{rec})/\rho h} \quad 4-1$$

where h is the liquid sheet thickness. Here, h is estimated as the thickness of the lamella that fully spreads on a flat stationary surface given the same v_n . Hence, the corresponding θ_{rec} can be determined with a specific v_r .

As such, the general idea is to force each point on the downstream contact line (e.g., P in Fig. 4-1a) to recede towards a point (e.g., P') that ultimately results in a circular lamella shape at t_{max} by manipulating the wettability. To achieve this goal, different locations at the downstream contact line, for instance, P_1 and P_2 as shown in Fig. 4-1b, have different distances to recede. Hence, P_1 and P_2 need different velocities to reach the wanted locations (P_1' and P_2') simultaneously at t_{max} ; from Eq. 4-1, this means that points near center line should have higher θ_{rec} as the distance to recede is longer.

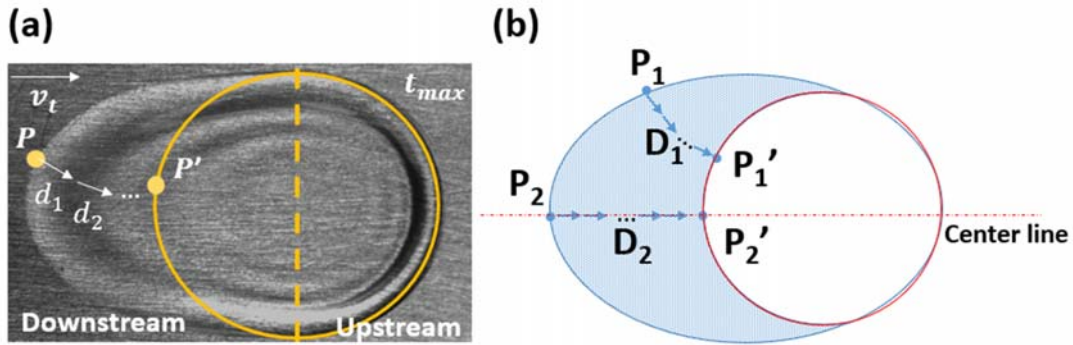


Figure 4-1 Schematic diagrams of restoring the symmetry for the deformed lamella over an inclined surface, (a) the receding route for the outline point to restore the symmetry, d_i ($i=1,2,3,\dots,n$) refers to the receding distance at i_{th} step, and the dashed line is the maximum width line; (b) different distances for different points to recede. The blue

ellipse represents the spreading lamella outline at t_{max} without correction, the red circle denotes the wanted symmetric shape for lamella at t_{max} , the shaded area is the deformed area to be corrected.

To specify the receding distance, one needs to design a receding route for each point (P) on the downstream contact line. Before that, however, one needs to know the positions of the points (P). For this purpose, the model presented in reference⁶⁴, i.e., Eq. 4-2, will be used; in reference⁶⁴ it was shown Eq. 4-2 captures well the transient outline shape of the lamella when a v_t exists,

$$\frac{(x-x_{disp(t)})^2}{p_{(t)}^2} + \frac{y^2}{q_{(t)}^2} = r_{(t)}^2 \quad 4-2$$

where $x_{disp(t)}$ is the shifting factor, $p_{(t)}$ is the stretching factor, $q_{(t)}$ is the width factor, and $r_{(t)}$ is the radius of the lamella spreading in a circular shape over a stationary surface with the same v_n , seen for droplet impact onto a moving or inclined surface. The factors $x_{disp(t)}$, $p_{(t)}$, and $q_{(t)}$ in Eq. 4-2 are functions of t , v_n , v_t , and the factor $r_{(t)}$ is specified by t , σ , Weber and Reynolds numbers; for details see reference⁶⁴. One should note that Eq. 4-1 is commonly used in the inertial regime, and Eq. 4-2 is formulated specifically for liquid viscosity up to 4cSt, and hence this work is tailored to address phenomena in the context of low-viscosity liquids. While viscosity is not the primary focus of this work, we have incorporated viscous effects in estimating the maximum spreading of the droplet to obtain $r_{(t)}$. This is achieved through the expression^{45,101} $\beta_m \approx 0.87Re^{1/5} - 0.4Re^{2/5}We^{-1/2}$.

Given a time increment Δt and a period, using Eq. 4-2 one can generate a series of ellipses. Note Eq. 4-2 is essentially describing a time evolving ellipse. Each ellipse depicts the lamella segment that is formed at the corresponding time step. The lamella's transient shape consists of the current

and previously formed segments (see Fig. 4-2), so at any given time the contact line of the lamella can be captured by the enveloping outline of these ellipses (see the green line in Fig. 4-2).

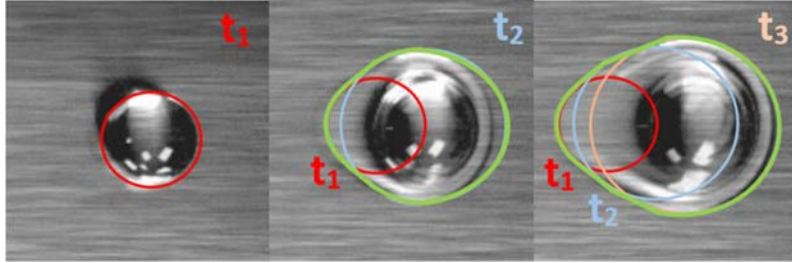


Figure 4-2 Time evolution of the spreading lamella of water, described by the model in the reference ¹⁰², from time step t_1 to t_3 with an increment Δt . Adapted with permission from the reference ¹⁰². Copyright [2023][SPRINGER NATURE].

Hence, one can obtain the position of the lamella contact line with successive ellipses using Eq. 4-2. These ellipses essentially depict how the lamella propagates in steps over time.

To correct the downstream lamella deformation, we consider that the downstream contact line recedes simultaneously when the upstream lamella is propagating. To illustrate the correction at each time step, let's first look at the snapshot of the spreading lamella at t_2 as depicted in Fig. 4-3a. The lamella without any manipulation at t_2 consists of two elliptical segments, represented by the blue and red ellipses, which were obtained by Eq. 4-2 at t_1 and t_2 , respectively. One should note that Eq. 4-2 is used to estimate the transient shape of the lamella, which means there will be minor differences between the contact line depicted by the ellipse and the real contact line.

The two elliptical segments geometrically intersect at points A and B , approximately making up the contact line $\widehat{ACB}$ and $\widehat{AGB}$ at t_2 . The blue ellipse represents the contact line of the lamella at t_1 , and it is split by line AB into two parts. The right part refers to the upstream side and the left

part denotes the downstream side. From t_1 to t_2 , the upstream side of the blue contact line $\widehat{AEB}$ is spreading towards arc $\widehat{AGB}$ that depicts the upstream of the lamella at t_2 . To correct the deformation on the downstream side, the downstream contact line denoted by $\widehat{ACB}$ should be forced to recede (see the arrows) and cross the red ellipse to the location denoted by the red dashed line, i.e., the wanted downstream contact line at t_2 .

To find the location of the red dashed line, the following can be considered: (1). The red dashed line should be tangent to the red ellipse at points A and B in Fig. 4-3a, i.e., a smooth contact line condition; (2) All points on the red dashed line should have the same curvature so that the wanted receding contact line can enhance the tendency of achieving the final radially symmetric lamella, i.e., symmetry condition. Hence, we find an incircle tangent to the red ellipse at A and B as shown in Fig. 4-3a. The arc of the incircle $\widehat{AFB}$ is selected to be the receding contact line at t_2 .

The above operation means that the downstream contact line $\widehat{ACB}$ is forced to recede to $\widehat{AFB}$, while the upstream contact line $\widehat{AEB}$ continues spreading to $\widehat{AGB}$, resulting in the outline of the lamella at t_2 corrected to the new shape consists of $\widehat{AFB}$ and $\widehat{AGB}$ as shown in Fig. 4-3b. Note that this “forcing” as stated earlier shall be facilitated by manipulating the surface wettability as will be shown later.

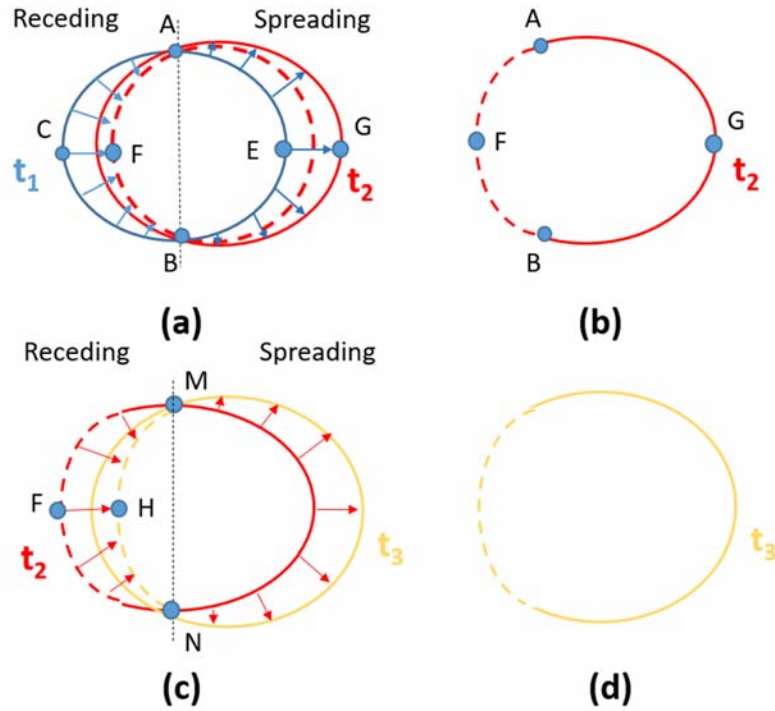


Figure 4-3 The schematic diagram of the correction on the transient lamella shape at each time step. (a) Using an incircle (the dashed circle) to define the wanted receding contact line $\widehat{AFB}$ at t_2 ; Arrows denote the receding on the downstream side (left) and spreading on the upstream side (right). (b) The corrected shape of the lamella at t_2 . (c) The similar correction from t_2 to t_3 . (d) The corrected shape of the lamella at t_3 .

When the time progresses to t_3 , the corrected lamella continuously propagates to form a new lamella segment represented by the yellow ellipse (see Fig. 4-3c), and the corrected outline of the lamella at t_2 intersects geometrically with the yellow lamella segment at M and N . To further correct the shape at this step, the downstream contact line $\widehat{MFN}$ should recede to the wanted one $\widehat{MHN}$ at t_3 . $\widehat{MHN}$ is again considered part of the incircle of the yellow ellipse, in the same way it was done for the shape correction from t_1 to t_2 . As such, the corrected lamella at t_3 shown in Fig.

4-3d is obtained. This process will be repeated for the following time steps except the last step from $t_{max} - \Delta t$ to t_{max} .

To achieve a circular shape at t_{max} , the last step is different from the previous steps for the receding on the downstream side. In Fig. 4-4, one can see that the corrected outline of the lamella at $t_{max} - \Delta t$ is depicted as a brown curve. The purple ellipse denotes the lamella segment formed at t_{max} by Eq. 4-2. The downstream contact line JRK is desired to recede to LFQ to give the final “symmetric” contact line at t_{max} ; LFQ is defined by the circle (see the red dashed circle) fitting the upstream contact line of the purple lamella segment, instead of its incircle. In this way, when time progresses to t_{max} , the segment of the contact line JRK is receding to the wanted receding contact line LFQ , while the rest of the contact line in brown is spreading to JSK . As a result, the final corrected shape of the lamella consists of LFQ and JSK , and closely resembles the symmetric lamella shape we target at t_{max} , see the red dashed circle.

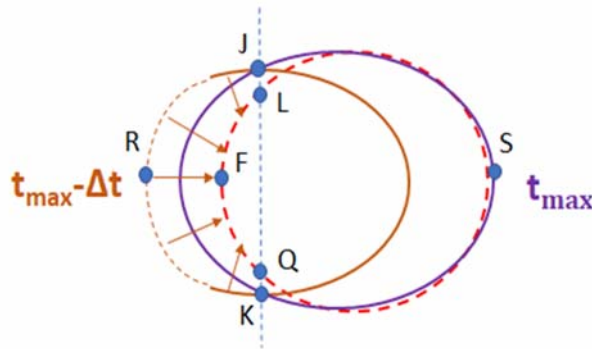


Figure 4-4 The correction at the last spreading step. The red dashed circle denotes the wanted shape of the lamella at t_{max} . The purple ellipse denotes the lamella segment generated at t_{max} . The brown dashed and solid curves represent the corrected lamella at $t_{max} - \Delta t$.

With locations of the wanted receding contact line at different time steps known, the receding distance of each point on the receding contact line for each time step can be calculated. As an example, a snapshot at a certain time step is depicted in Fig. 4-5. Line PO (O is the incircle or circle center) intersects the wanted contact line $\widehat{ANB}$ at N , as such PN is the distance for P to recede. This receding distance is calculated by the positions of P and N geometrically deduced from Eq. 4-2 and the incircle (or circle) equation. Given the time interval Δt , the receding velocity at P is further determined with the consideration of a uniform receding motion. Consequently, one can easily obtain the θ_{rec} to facilitate the receding for point P using Eq. 4-1. Similarly, the respective θ_{rec} can be solved for each point at $\widehat{APB}$ any given time (or position).

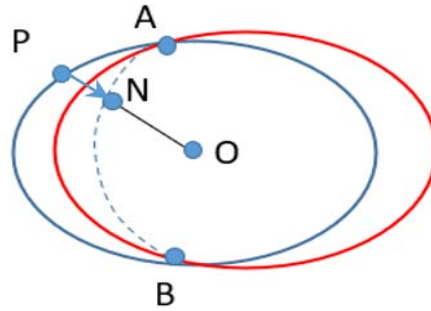


Figure 4-5 Receding distance (e.g., PN) of each point (e.g., P) on the receding contact line.

Due to the sequential movement of the receding contact line with a time increment $\Delta t = 0.01ms$, a surface wetting map for each condition listed in Table 4-1 can be found to yield a symmetric lamella at t_{max} ; such calculations were done using a MATLAB code developed in-house.

4.1.2 Simulated impact conditions

The asymmetric spreading behaviour of the lamella essentially results from the competition between v_n and v_t . The selected impact conditions for modelling aim to investigate the effects of v_n and v_t on the asymmetric lamella shape; see Table 4-1. To hold a wider range of the ratio We_n/We_t , Table 4-1 lists a range of We_n from 20 to 280 with a fixed We_t of 137, based on the data from references^{65,101}.

Table 4-1 shows the test cases, where R_{max}^* refers to the maximum spreading radius of the lamella over a stationary surface post-impact having the same We_n (as predicted by the correlation given in reference¹⁰¹); t_{max}^* is the predicted maximum spreading time found from reference⁶⁵. The conditions shown in Table 4-1 can be considered either for a moving surface or a surface with an inclination angle of α , considering $\tan(\alpha) = v_t / v_n$.

Table 4-1 Impact conditions for a water droplet with various We_n , at the fixed value of $We_t = 137$.

Impact	We_n			
Conditions	20	70	140	280
$R_{max}^*(\text{mm})$	2.652	4.051	4.775	5.455
$t_{max}^*(\text{ms})$	3.750	3.214	2.786	2.464
D_0 (mm)	2.5			

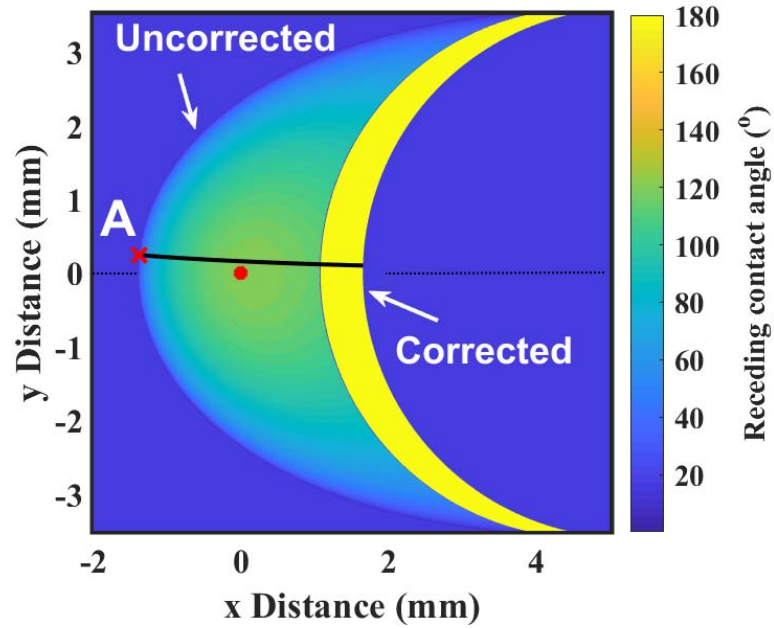
4.2 Results and discussion

4.2.1 Wetting map

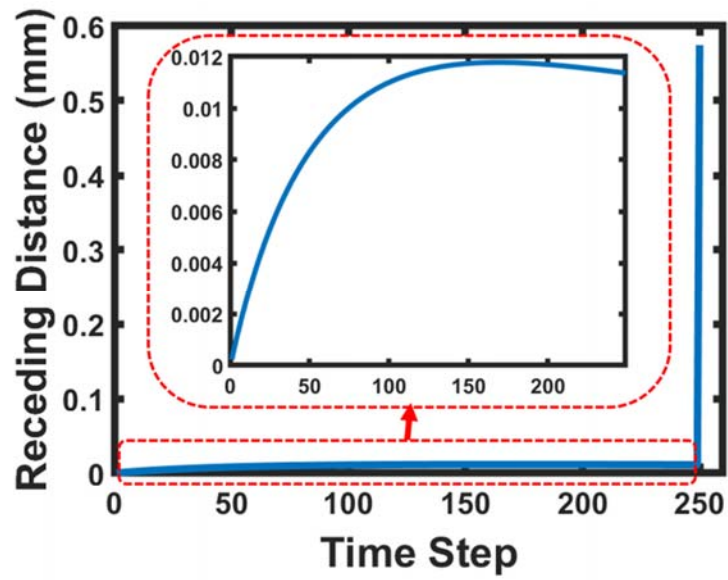
Given a specific impact condition as outlined in Table 4-1, a wetting map can be generated to allow formation of a symmetric lamella at t_{max} . As an example, Fig. 4-6a shows the wetting map for $We_t = 137$ and $We_n = 70$ generated using the procedure developed in the previous section. In this study, we simulate the asymmetric lamella spreading over an aluminium surface with a receding contact angle of 15° . The colours in Fig. 4-6a represent the θ_{rec} value at each local. In general, θ_{rec} becomes larger near the center line as stated earlier. The interpretation of wetting map is as follows: take point A in Fig. 4-6a, which is initially on the uncorrected contact line. To “force” this point to move to the “corrected” contact line, at each time step its distance (Fig. 4-6b) to move is engineered by wetting. As distance traveled at each step determines the contact line velocity and hence θ_{rec} via Eq. 4-1, Fig. 4-6c shows the θ_{rec} for point A at each time step. The receding distance and the θ_{rec} display a similar variation tendency as a result of their positive correlation seen in Eq. 4-1. The change in trend near t_{150} is due to the weaker propagation of the lamella in the later spreading phase. The weaker propagation resulted from the dissipation of the initial kinetic energy, which means contact line is decelerating for $t > t_{150}$. As such, with a shorter distance to recede at each time step, the θ_{rec} decreases accordingly.

The bright yellow area in Fig. 4-6a refers to the area where the last step for receding from $t_{max} - \Delta t$ to t_{max} takes place. This is a special time step as discussed earlier, in this example see Fig. 4-6b at t_{250} that a dramatic rise in the receding distance induces an exceptional high θ_{rec} in this bright yellow area, compared to the previously traversed areas. Furthermore, the distance to recede in the last step exceeds what can be achieved based on Eq. 4-1 due to the wettability limit.

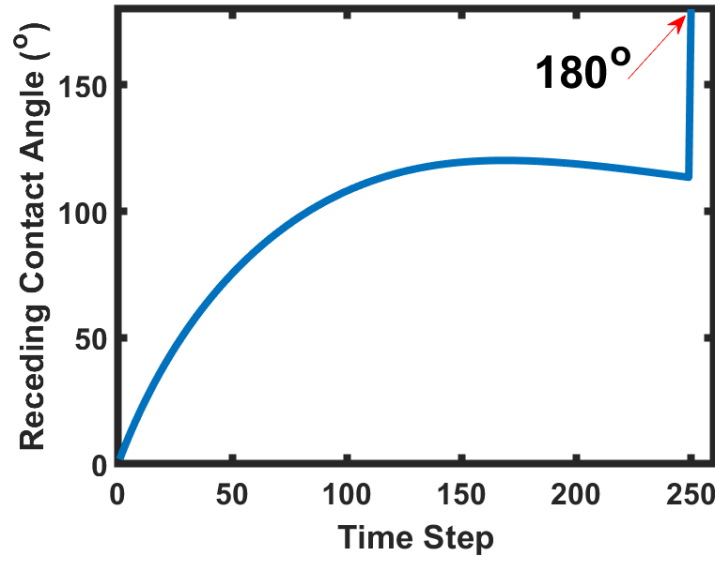
Therefore, the contact angle for the last receding step is manually set to be 180° (the maximum intrinsic θ_{rec} possible), see Fig. 4-6c.



(a)



(b)



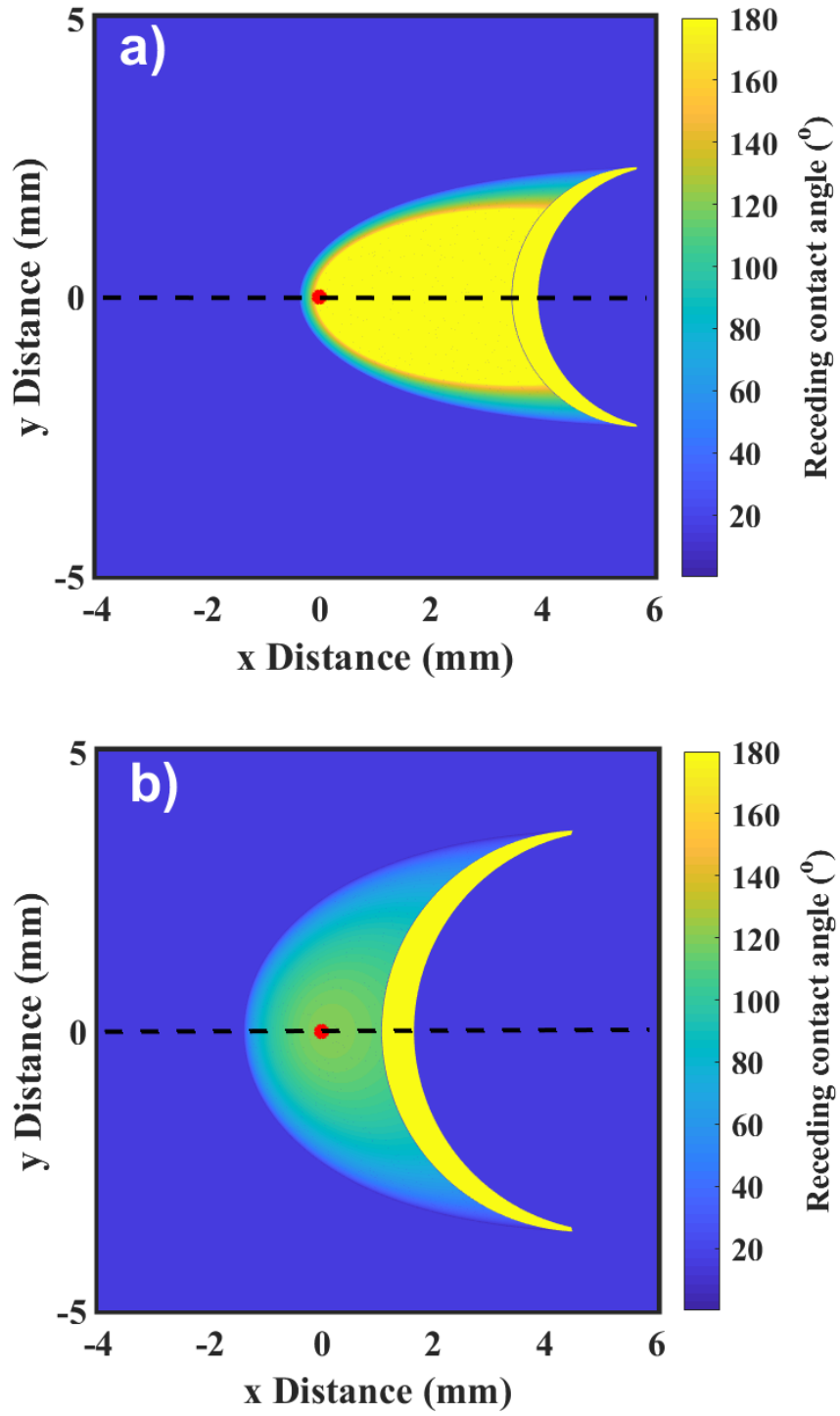
(c)

Figure 4-6 (a) Wetting map for $We_t = 137$, $We_n = 70$. The black line shows the route for point A (red cross) to recede during the spreading process, the red point denotes the impact spot, and the dotted line is the center line. (b) Variation of the receding distance of point A along its travel path for each time step, $\Delta t = 0.01$ ms. (c) Variation of the receding contact angle of point A along its travel path for each time step, $\Delta t = 0.01$ ms.

An increase in We_n results in greater normal momentum, leading to a more radial spreading of the lamella. Meanwhile, the extent of lamella stretching depends on We_t , which means that the ratio of We_n to We_t governs the degree of deformation for the lamella.

Figure 4-7 display the wetting maps for the impact conditions in Table 4-1. Increasing We_n/We_t decreases the lamella deformation along the center line. When $We_n/We_t = 0.15$ (Fig. 4-7a), the lamella is severely stretched due to the relatively high tangential momentum (or v_t). Consequently, it is more difficult to correct the lamella deformation, as implied by the large bright yellow area, i.e. an unattainable θ_{rec} of 180° . However, as We_n increases, the deformation decreases, making

it easier to restore the symmetry of the lamella, especially given $We_n/We_t \geq 0.51$ (Fig. 4-7b, c, d). Therefore, it is possible to correct the asymmetric lamella when $We_n/We_t \geq 0.51$.



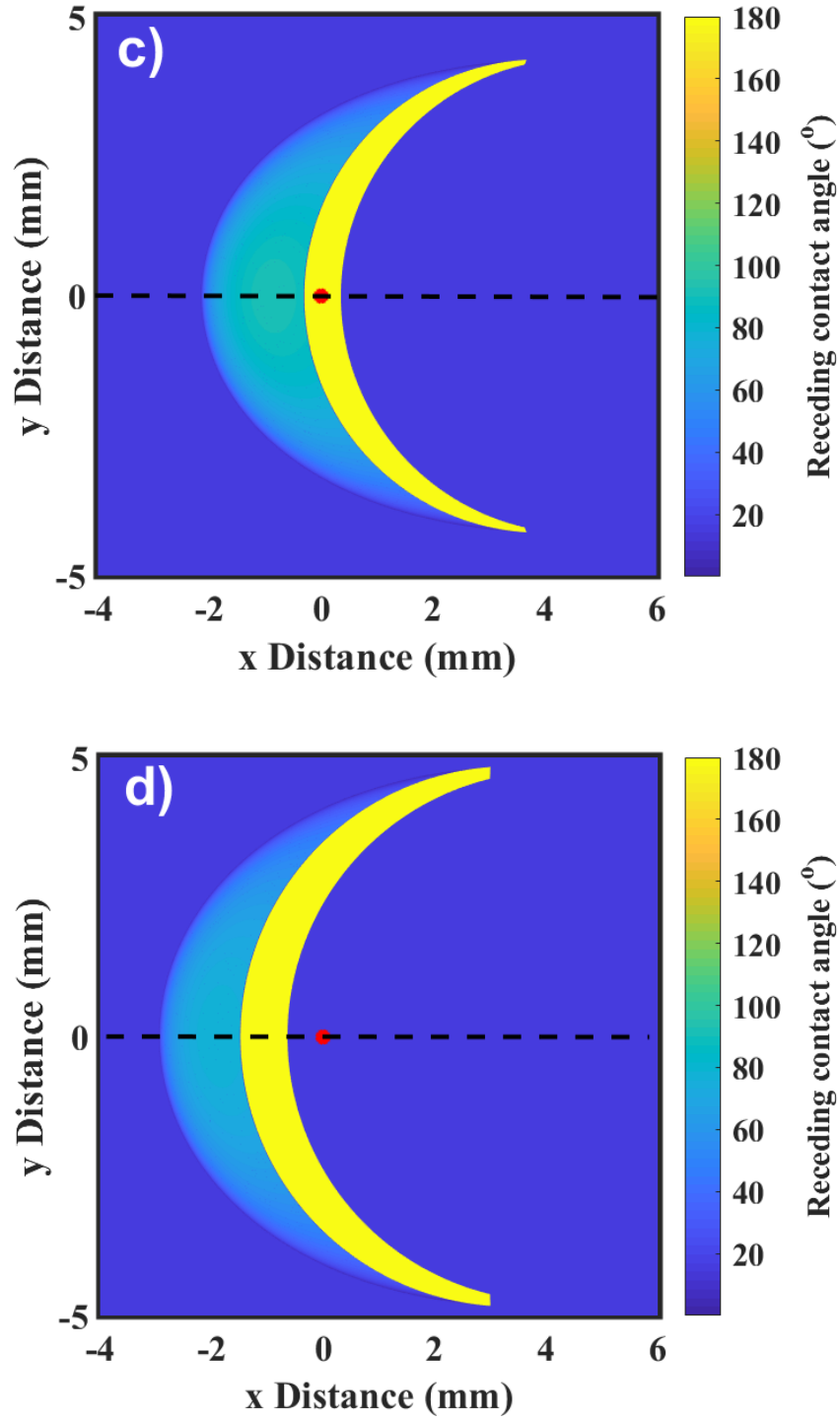


Figure 4-7 Wetting maps for water droplet impact on the condition of $We_t = 137$, (a) $We_n/We_t \approx 0.15$, (b) $We_n/We_t \approx 0.51$, (c) $We_n/We_t \approx 1.03$, (d) $We_n/We_t \approx 2.04$. The red point denotes the impact spot and the dashed line is the center line.

4.2.2 Patch design with a singular wettability contrast

Correcting the lamella deformation is based on the idea of manipulating the wettability. However, it is not practical to fabricate a surface with the complex wettability shown, e.g., in Fig. 4-7. These figures indicate that to correct the lamella deformation a higher receding contact angle is needed for the location closer to the center line. Hence, we propose a practical surface design in the form of a patch with a singular wettability contrast as shown in Fig. 4-8a (dashed rectangle area). In Fig. 4-8a, the blue line refers to the uncorrected shape of the lamella without being manipulated, obtained from Eq. 4-2. The impact spot (blue dot in Fig. 4-8a) as the origin is set. The question now is to determine the wettability contrast for the aluminum surface, considering the original background receding contact angle (θ_2) of 15° . This includes the receding contact angle inside the patch (θ_1), and the width of the patch (Wp).

To answer this question, we will use the wetting map and follow specific procedures for the given drop impact conditions. Firstly, the receding contact angle inside the patch, θ_1 , can be easily read from the wetting map, particularly the center area indicated by the red dashed circle in Fig. 4-8b as an example. Secondly, the patch width (Wp) depends on the dimension of the central area that maintains a consistent colour along the y direction. For our initial attempt, based on the wetting map in Fig. 4-8b, we set θ_1 to 130° , and Wp to 1 mm for the impact condition with $We_t = 137$, $We_n = 70$, and $\theta_2 = 15^\circ$.

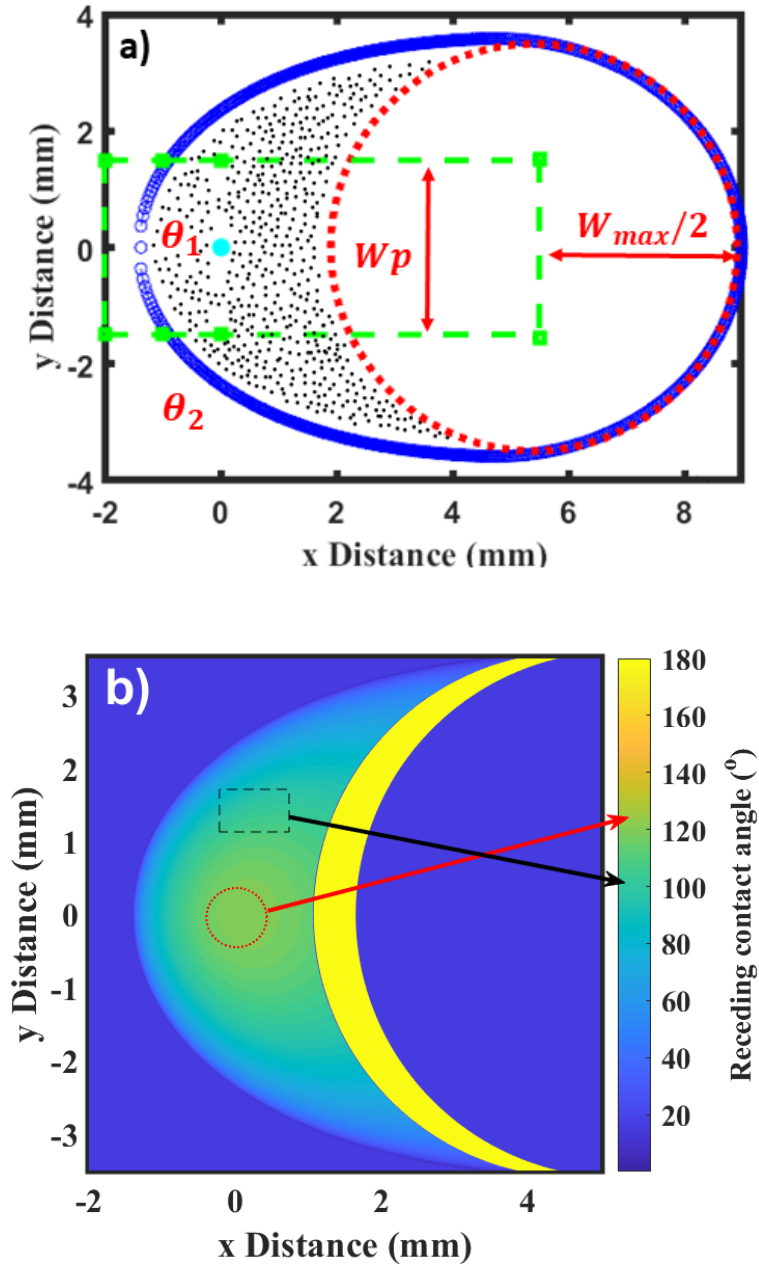
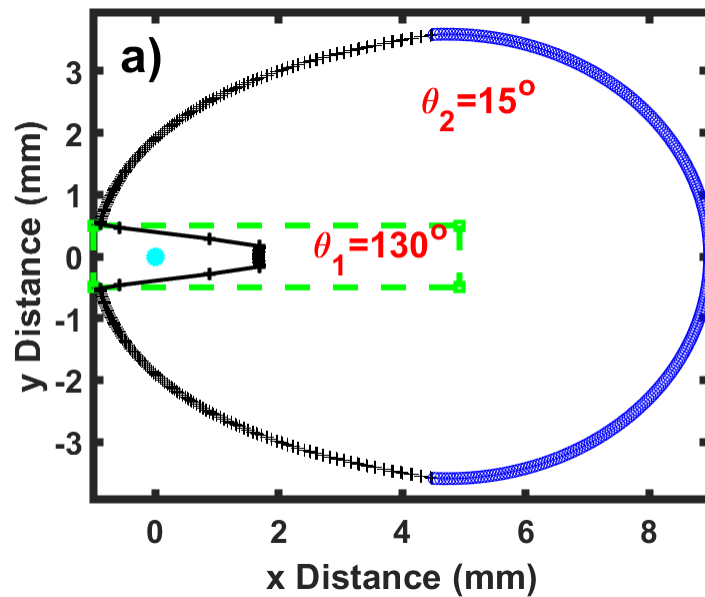


Figure 4-8 (a) Patch design (green dashed rectangle) with a singular wettability contrast (receding contact angle θ_1 inside the patch and θ_2 outside the patch) for $We_t = 137$, $We_n = 70$. The blue line is the outline of the lamella without manipulation. The red dashed circle refers to the wanted final shape of the lamella. The shaded area denotes the deformed area on the downstream.

(b) The wetting map for the deformed area and the selection of the wettability contrast.

With the initial configuration of the patch, we can assess the corrected lamella shape, depicted in Fig. 4-9a, by promoting the receding of the contact line inside the patch at every time step, using the velocity defined by Eq. 4-1 with $\theta_{rec} = \theta_1$. It is evident that even after correction with the patch, the shape remains far from symmetric. This asymmetry is due to the significant difference in the receding velocity of the contact line inside and outside the patch, resulting from the wettability contrast with $\theta_1 = 130^\circ$ and $\theta_2 = 15^\circ$. Importantly, the contact line outside the patch is “frozen” compared to the original configuration without the patch, as θ_2 remains the same. This asymmetry can be reduced by a wider patch with $Wp = 3mm$, as shown in Fig. 4-9b. Although a larger segment of the contact line inside the patch can recede faster with the aid of θ_1 , it is still insufficient to restore the symmetry. Hence, a limit is reached with the correction by merely changing θ_1 and Wp . To achieve a more effective correction, one should also consider changing θ_2 as well.



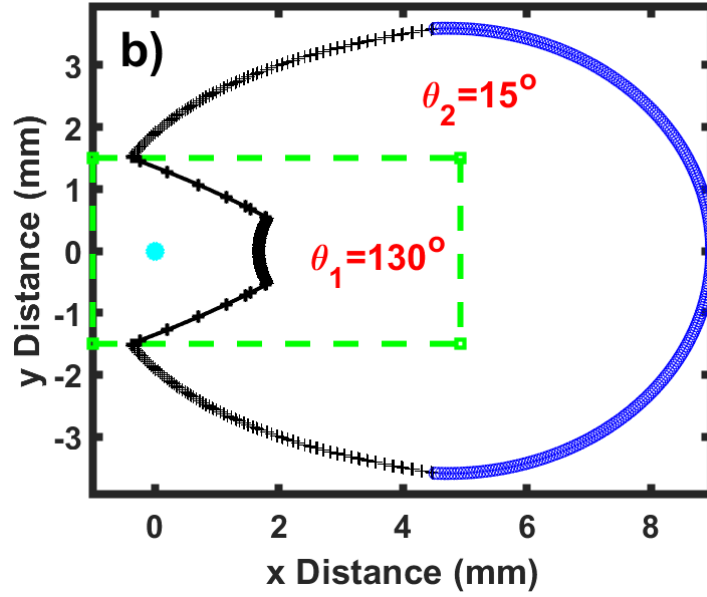


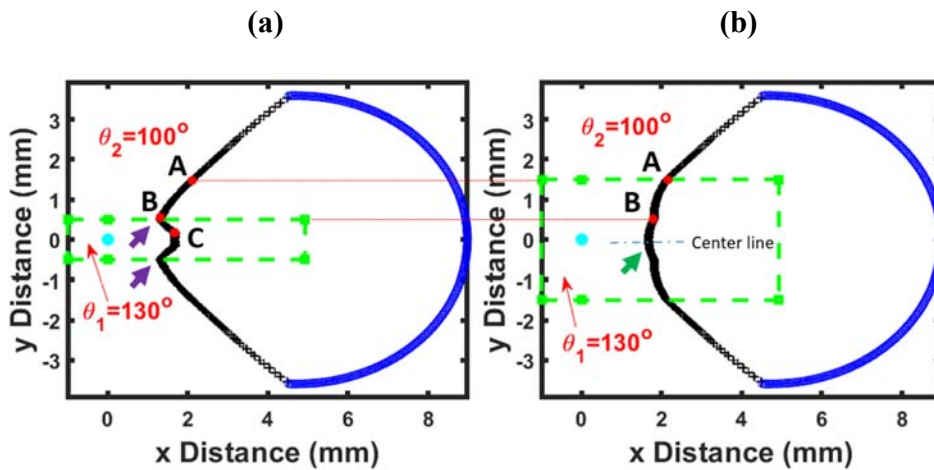
Figure 4-9 The corrected lamella shape at t_{max} , with a patch inside showing a receding contact angle of 130° , under the conditions of $We_t = 137$, $We_n = 70$, and with patch widths of (a) $Wp = 1 \text{ mm}$ and (b) $Wp = 3 \text{ mm}$.

To specify θ_2 , it is essential to refer back to the wetting map in Fig. 4-8b. The purpose of changing θ_2 is to facilitate the contact line outside the patch in catching up with the one inside the patch, ultimately forming a symmetric shape. Therefore, we tentatively consider θ_2 as the value within the area close to the centre area in Fig. 4-8 b, denoted by the black dashed rectangle, i.e., $\theta_2 = 100^\circ$. With this adjustment, new corrected shapes are obtained, as shown in Fig. 4-10a and b, corresponding to $Wp = 1 \text{ mm}$ and $Wp = 3 \text{ mm}$, respectively.

Clearly, under the same wettability contrast, a wider patch can relatively smooth the zigzag (see purple arrows in Fig. 4-10a) of the corrected contact line. The zigzag is caused by the sharp difference in receding velocities due to the sharp patch boundary, compared to the gradual change in wettability seen in wetting map. With a wider patch that covers the segment AB in Fig. 4-10a, a larger part of contact line recedes faster, which helps alleviate the bend in the final corrected shape as shown in Fig. 4-10b with $Wp = 3 \text{ mm}$.

However, one can still see a protrusion in the middle of the corrected contact line (see the green arrow in Fig. 4-10b). This is a result of using the singular wettability contrast instead of the wettability shown in the wetting map, e.g. Fig. 4-8b. The value of θ_1 is selected from the point located at the center line which is stretched the most, so it exceeds the demand of other points along the receding contact line inside the patch. Accordingly, these points will travel farther with this θ_1 value compared to the anticipation in the wetting map, resulting in a relative ‘lag’ at the center line.

With the same patch width, reducing the wettability contrast can soothe the zigzag of the receding contact line as well, see Fig. 4-10c, d and e. This is so as the segment of the receding contact line outside the patch catches up with the segment inside the patch, facilitated by an increasing θ_2 during the receding. Therefore, a smaller wettability contrast can contribute to smoothing the downstream contact line. However, the overall symmetry, i.e., comparing the length in the x -direction to the width in the y -direction, of the corrected shapes in Fig. 4-10 remains roughly consistent.



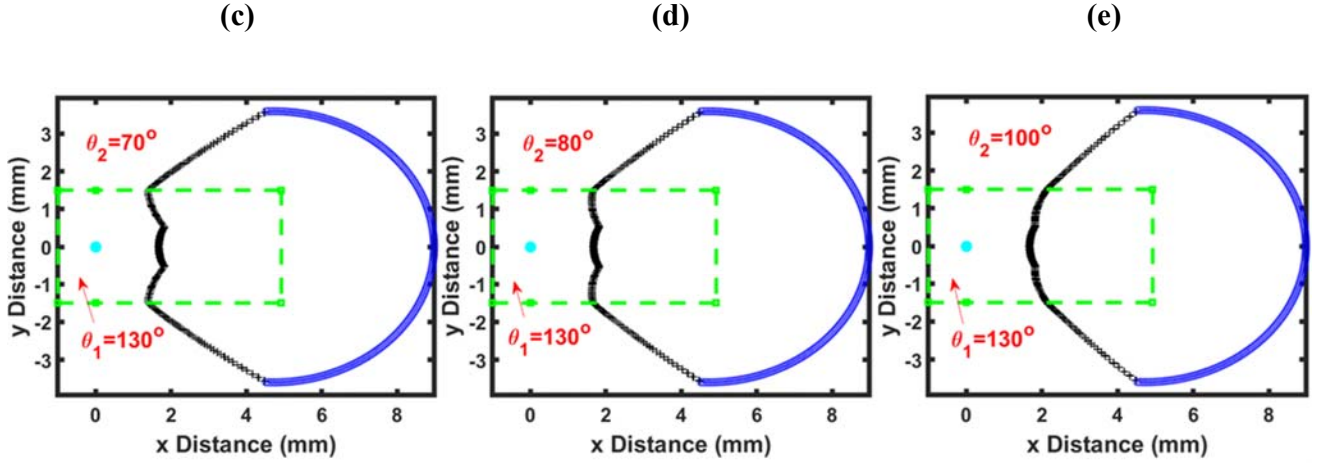


Figure 4-10 The corrected lamella shape at t_{max} on the condition of $We_t = 137$, $We_n = 70$. Red dotted lines are a guide to the eye. (a) and (b): The effect of the patch width on the wanted receding contact line. (c) to (e): The evolution of the wanted receding contact line with an increasing θ_2 .

To achieve a better corrected lamella shape, e.g. in Fig. 4-10b, one may need to adjust Wp and θ_2 together based on the initial setting from the wetting map and compare the resulting shapes. It should be noted that the corrected lamella shape at t_{max} in Fig. 4-10 is an outcome of a 2-D mathematical calculations, without considering the flow effects caused by the impact force and viscous force. These simulated shapes reflect the quasi-static of the lamella contact line in the spreading with the perturbation of the patch.

4.2.3 Correction of the deformed lamella with a patch design

Following the procedure of optimizing the patch design, the corrected downstream contact line resulting from the patch is shown in Fig. 4-11, for the impacts given the conditions in Table 4-1.

In Fig. 4-11, the downstream contact line is corrected at t_{max} to the position of the black line by introducing the patch. Considering the wetting maps shown in Fig. 4-7, addressing the less deformed lamella caused by a lower We_t will be more feasible, particularly when $We_n/We_t \geq 0.51$.

Consequently in Fig. 4-11b, c, and d, the corrected lamella is closer to a circular shape compared to its original one, and one can also see the θ_1 for $We_n = 280$ is 90° (Fig. 4-11d), which is much lower than 130° for $We_n = 70$ (Fig. 4-11b). However, when $We_n/We_t < 0.51$ as shown in Fig. 4-11a, the significant deformation of the lamella caused by high We_t will exceed the capability of the wettability to correct since the maximum θ_{rec} is 180° . Hence, the corrected lamella is still far from a symmetric shape even given $\theta_1 = 180^\circ$.

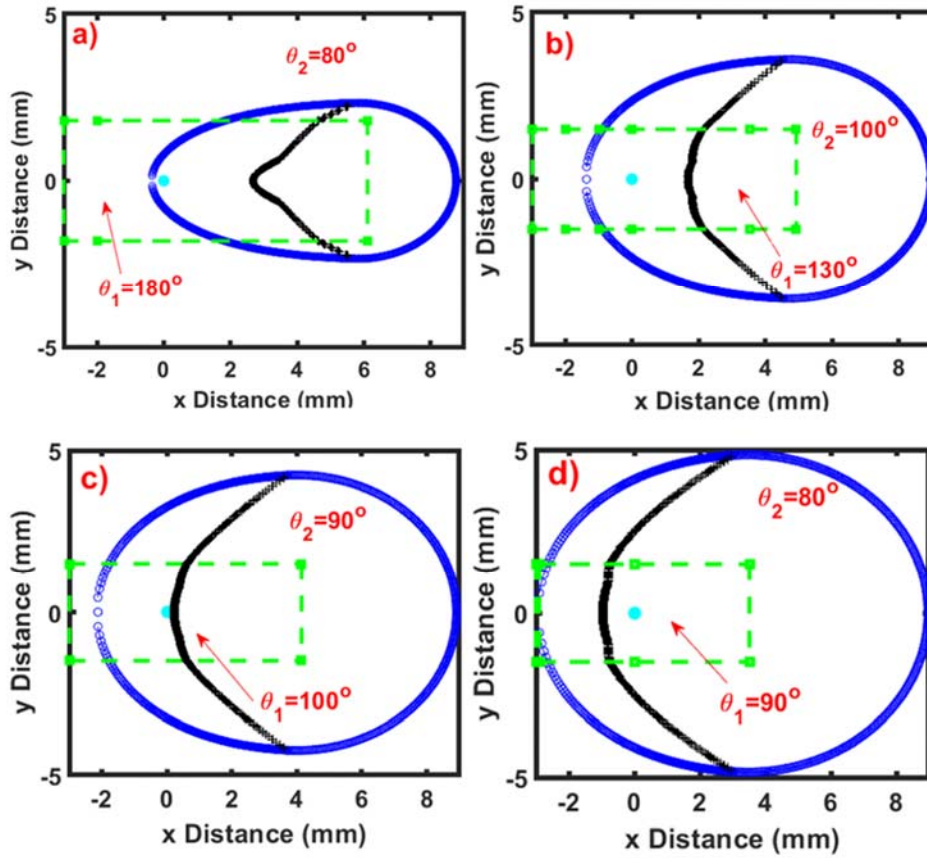


Figure 4-11 Patch design with a singular wettability contrast for the impact with $We_t = 137$ and (a) $We_n/We_t \approx 0.15$, (b)

$We_n/We_t \approx 0.51$, (c) $We_n/We_t \approx 1.03$, (d) $We_n/We_t \approx 2.04$. The black line is the corrected receding contact line manipulated by the patch at t_{max} . The blue outline is the original lamella shape without manipulation. The blue point refers to the impact spot.

The above prediction indicates that the model can be valid for the impact condition when $We_n/We_t \geq 0.51$. Given the restriction to avoid splash, three experimental conditions, i.e., $We_n/We_t \approx 0.51$, 1.03, and 2.04, were accordingly selected to examine our model, as presented in Chapter 6. These three conditions are the representative cases when We_n is less than, equal to, or greater than We_t , respectively.

Besides, this work also explored the possibility of correcting deformations caused by low-surface tension liquids such as ethanol, given $We_n/We_t \approx 0.47$. The wetting map and corrected shape can be found in Fig. 4-12. As stated earlier, the low surface tension is insufficient to maintain the lamella's semi-circular shape on the upstream side, and wettability adjustments do not effectively address this issue. Moreover, according to Eq. 4-1, lower surface tension will decrease the receding velocity, requiring a higher receding contact angle to compensate, thereby posing a greater challenge for correction. Hence, under the impact condition of $We_n/We_t \approx 0.47$ for the ethanol droplet, correcting the downstream deformation needs an extreme receding contact angle of 180° , yet full symmetry is not achievable. Therefore, while this method effectively reduces downstream deformation for low-surface tension liquids, its ability to restore symmetry is very limited.

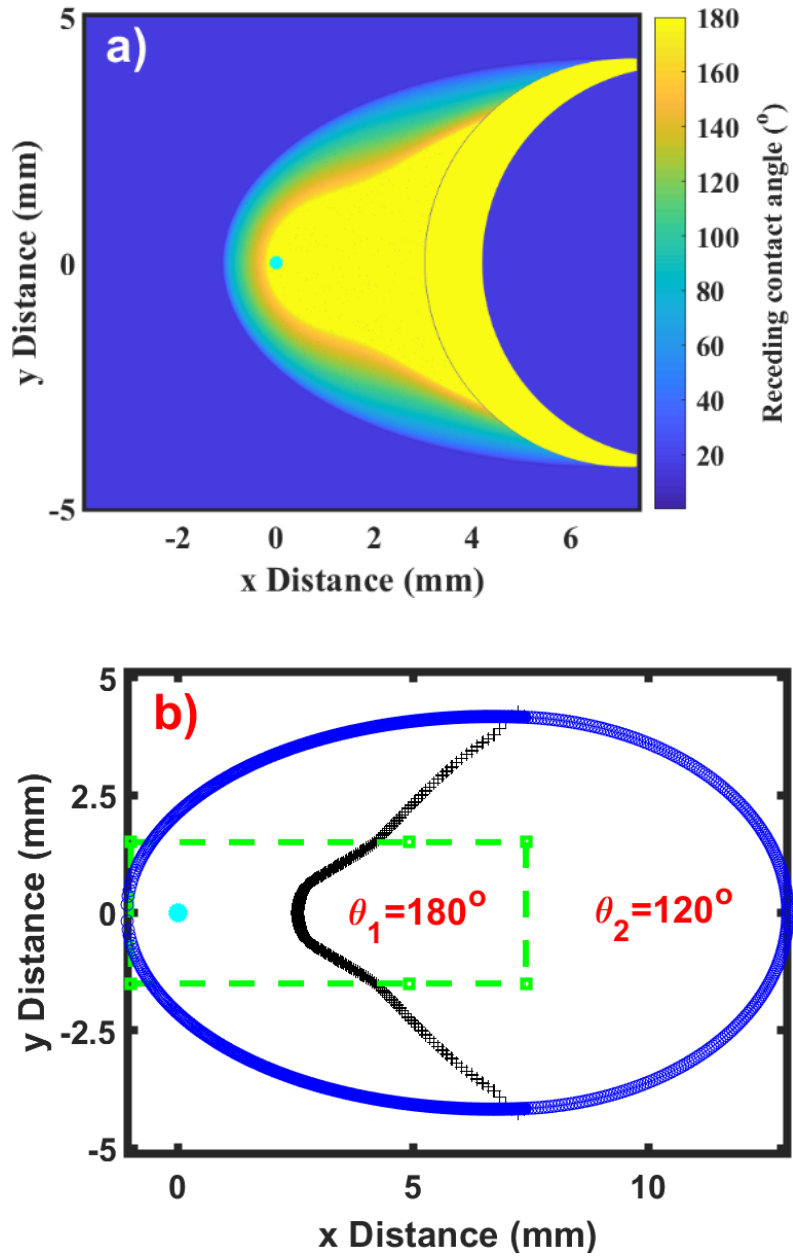


Figure 4-12 a) Wetting map and b) simulated corrected shape for the impact of an ethanol droplet with $D_0 = 2.7mm$, $We_n = 206$ ($v_n = 1.5m/s$), $We_t = 442$ ($v_t = 2.2m/s$) (data sourced from the reference⁶⁴). The blue outline is the original lamella shape without manipulation. Black line denotes the corrected contact line.

The concept of this study is also promising for high-viscosity liquids on an inclined surface, where higher viscosity can dampen the inertial effects, resulting in a smaller deformation. However, on a moving surface, it becomes challenging since higher viscosity can balance the inertia induced by the surface motion, potentially leading to larger deformations. To extend this concept to high-viscosity liquids, modification of Eqs. 4-1 and 4-2 is necessary to incorporate viscous effects, which is beyond the current scope of this study.

Similar to high-viscosity liquids, micrometer-scale droplets under the same impact conditions also present non-negligible viscous effects in addition to surface tension forces during receding, given that $Re \ll 1$ and $Oh \sim 0.067$. Consequently, the Taylor-Culick theory is not strictly valid for micrometer-scale droplets but can be adapted by integrating viscous forces with capillary forces in the momentum balance acting on the rim. Besides, the stronger influence of surface tension and viscous forces in the case of micrometer-scale droplets may lead to reduced deformation during spreading, which favors symmetry restoration.

4.3 Conclusions

This study explores the simultaneous upstream spreading and downstream receding of an asymmetric lamella, aiming to restore a symmetric shape. The investigation is particularly focused on high-surface tension and low-viscosity liquids. The downstream receding can be manipulated by wettability based on the Taylor-Culick theory. A patch with a singular wettability contrast was accordingly proposed to design the surface. The difficulty of restoring the lamella symmetry depends on the competition between We_n and We_t . If $We_n/We_t \leq 0.15$, the lamella will experience significant stretching, and this method may not be applicable. The Taylor-Culick theory, which relates the receding velocity to the receding contact angle, indicates that an upper

limit on the receding contact angle constrains the receding velocity. Consequently, this velocity limit will set a boundary for the validity of this method. This work also discussed the effects of the patch width as well as the wettability contrast on the correction of the lamella shape. One can alleviate the zigzag of the corrected receding contact line by widening the patch or decreasing the wettability contrast. According to calculations based on this model, the deformed spreading shape can be effectively corrected under the conditions $0.51 \leq We_n/We_t \leq 2.04$, with $We_n \leq 300$ and $We_t \leq 300$, for high surface tension liquids like water.

Chapter 5

Fabrication of patterned AA6061 surface with controllable wettability contrast

5 Fabrication of patterned AA6061 surface with controllable wettability contrast¹

Surfaces with a wettability contrast have received much interest for a long time due to their wide applications, such as condensation, water harvesting, printing and so on. This chapter provides a simple low-cost method to fabricate a stripe pattern with a wettability contrast on an aluminium substrate. The pattern is shaped by pencil-drawn masks. The wettability contrast is developed by self-assembled monolayers (SAMs) of trichloro-octadecylsilane (OD) and trichloro-octylsilane (OT), respectively, using a dipping method before and after removing the pencil marks. The wettability indicated as static water contact angle (CA), can be varied by changing the immersion time. The immersion time can be accordingly applied to vary the wettability contrast. The flexibility of this method makes it available for patterns in various shapes and with diverse wettability contrasts.

5.1 Introduction

Wettability-patterned surfaces have attracted increasing attention due to their broad application in electronic devices, water harvesting, condensation, printing, etc.^{103–116}. Many researchers input effort into the pattern with a high wettability contrast to precisely manipulate the motion of water-based materials^{60,103,104,106,114,116}. The pattern with a finer wettability contrast also has been investigated to capture the dynamics of an impinging liquid drop^{59,61,117}. However, most of the studies focused on the pattern with a fixed wettability contrast that is either large or small. Hence, fabricating a tunable wettability contrast is of interest, especially for droplet manipulation

¹ This chapter is based on the work published in the paper “Application of Surface Wettability to Control Spreading of an Impinging droplet”, LANGMUIR 2024, 40,4623–4634.

concerning various shapes and dimensions. Chen *et al.*¹¹¹ drew patterns on the coating surface by laser radiation to obtain a tunable wettability contrast, but the method they proposed is time-consuming since this tunability requires a long ageing period of the coating from several days to nearly a month.

In addition to laser radiation, various methods like lithography¹¹⁰, microcontact printing^{118–121}, inkjet printing¹²², and ink pen¹¹² are utilized to shape patterns on the desired substrate. Especially, an ink pen is a very good option to pattern the substrate by drawing masks without the restraints of the surface curvature. In this work, I independently proposed a similar idea which is using a pencil instead of an ink pen, since pencil marks, unlike ink, are chemically resistant to both aqueous and organic solvents. This makes the pencil a versatile tool for modifying surface wettability.

Modifying surface wettability is commonly implemented by coating combined with or without nano-/micro- structures on the surface. The nano-/micro- structures can enhance or weaken the wettability by increasing the roughness due to the Cassie model^{123–126}. This strategy is adopted to pattern the surface typically with a large wettability contrast using laser¹⁰⁶ and hydrothermal-based method¹⁰³, but these two methods require either a special device or a very high temperature to perform the fabrication, which increases difficulty and complexity in the experiment. Another more feasible way is to coat the surface with self-assembled monolayers (SAMs)^{127–131} of organic molecules. SAM forms when the organic molecules anchor to the substrate covalently by their headgroups and the molecule chains orderly present so that a single layer of molecules attaches to the substrate¹³². Arianpour *et al.*¹³³ investigated the SAMs coatings on AA6061 for hydrophobic and ice-phobic properties. They found that SAMs coatings of trichloro-octylsilane (OT) and trichloro-octadecylsilane (OD) can vary the wettability by changing the immersion times. In addition, OT and OD have the same chemical groups and the only difference is the alkyl chain

length, which implies that these two chemicals will not chemically react but will hydrophobize the surface differently. Hence, OT and OD are promising to be applied to the pattern with a tunable wettability contrast by controlling the immersion time. Besides, coating the surface with SAMs can effectively avoid the roughness difference between wetting and dewetting areas on a micro-scale. Therefore, the disturbance to the drop spreading post-impact introduced by the roughness difference can be neglected. This is important for the applications like printing with a demand for shape precision of the spreading liquid. Hence, a flat surface engineered by SAMs is highly preferred.

Taken together, this work aims to fabricate a pattern with a tunable wettability contrast on AA6061 utilizing SAMs of OT and OD. Instead of an ink pen, a drawing pencil was selected to draw masks on the substrate to shape the pattern since the graphite is chemically stable and resistant to both water-based and organic solutions. The method we proposed is easy, fast and low-cost. It also shows great potential and flexibility in the fabrication of the pattern in various shapes with various wettability contrasts.

5.2 Method

5.2.1 Materials

AA6061 sheets cut into sizes (25mm *75mm *1.5mm) were purchased from McMaster-CARR. Trichloro-octylsilane (OT, $\text{CH}_3(\text{CH}_2)_7\text{SiCl}_3$, 97%, Sigma-Aldrich), trichloro-octadecylsilane (OD, $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$, 85%, Fisher Scientific) and a graphite pencil (12B) were used in this work. It should be noted that the pencil with a softer degree can make it easier to draw on the AA6061 substrate without damaging the surface by scratching.

5.2.2 Sample preparation

The primary steps to fabricate the patch pattern with tunable singular wettability contrast on AA6061 samples are illustrated in Fig. 5-1. The general procedure is as follows:

The as-received aluminum sheets were first polished with 400-grit sandpaper and then cleaned by immersing them in acetone and distilled water baths for 20 min each, using a sonicator. Once dried with nitrogen gas flow, the samples were stored in clean Petri dishes at room temperature. A graphite pencil (12B) was used to cover the background of each sample, creating an exposed T-shaped area. Trichloro-octadecylsilane (OD) and trichloro-octylsilane (OT) solutions were prepared by dissolving the respective chemicals in toluene. Each sample with the exposed area was immersed in the OD solution, pattern side facing upward, for a specific duration. Afterward, the sample was removed from the solution, rinsed with toluene, and then heated in an oven at 60°C for 2 hrs. Subsequently, the sample cooled down to room temperature, and the background was carefully removed using an eraser. Consequently, the T-shaped area was coated with the OD solution, resulting in a hydrophobicity θ_1 . Next, the sample was immersed in the OT solution to fill in the background, followed by a toluene rinse. After repeating the previously mentioned heat treatment, the background was coated with another hydrophobicity θ_2 . Consequently, the sample exhibited a singular wettability contrast between the T-shaped area and the background.

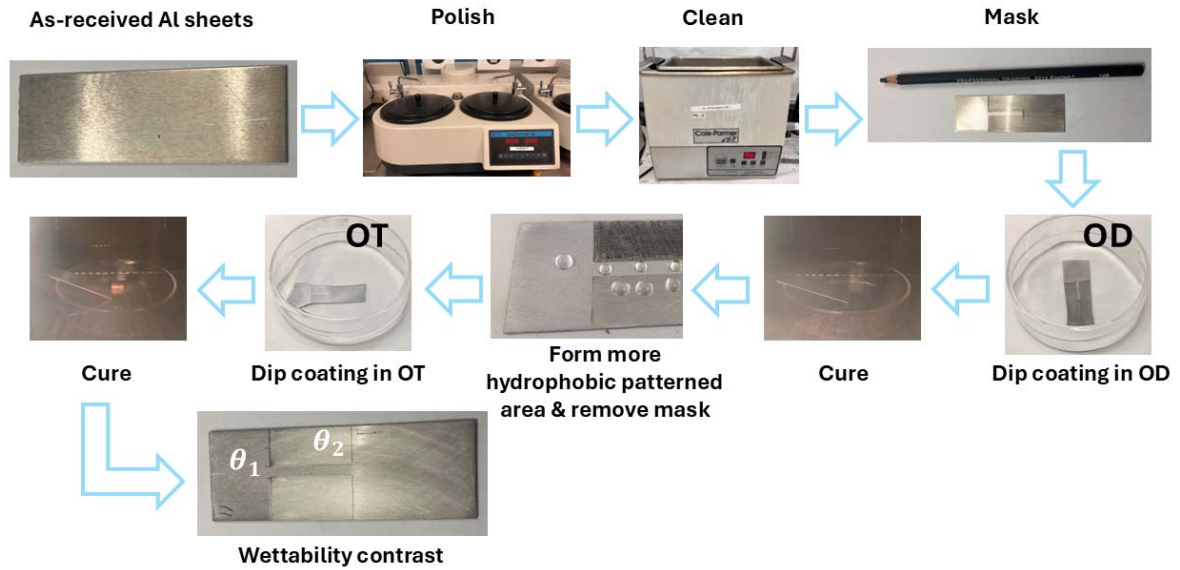


Figure 5-1 Main steps of surface fabrication. The as-received AA 6061 sheet was first polished and then added masks by a pencil after it was cleaned via a sonicator. Coating in the exposed area was made by immersing the sample in OD solution, followed by a heat treatment at 60°C for 2 h. The pencil-drawn masks were carefully removed by an eraser and the dust was blown with an air blaster. To backfill the background, the cleaned sample was placed in the OT solution. The pattern with a wettability contrast was obtained when the sample was taken out of the solution and completed the same heat treatment for the coating with OD solution.

The wettability contrast is tunable by varying the immersion time¹³³. The fabrication details for different wettability contrasts are summarized in Table 5-1.

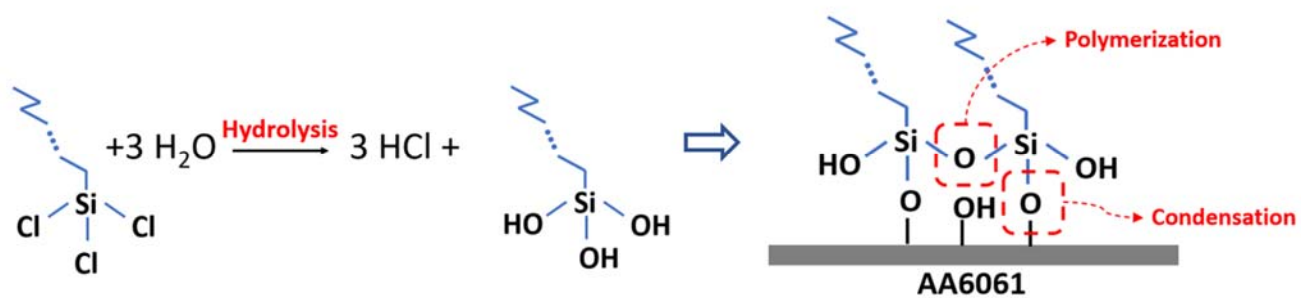
Table 5-1 Sample fabrication information

Sample	OD (mM)	Immersion time in OD	OT (mM)	Immersion time in OT	Patch width
1		6 h		55 min	
2	2.8	20 min	1	10 min	3 mm
3		5 min		2 min	

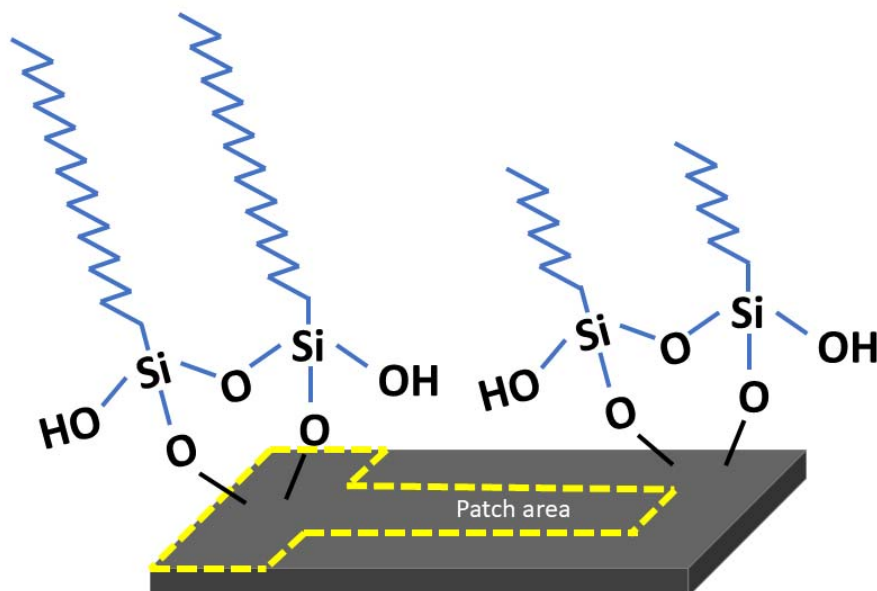
5.3 Results and discussion

5.3.1 SAM formation

The corresponding self-assembled monolayer (SAM) is fabricated using an immersion method. During the immersion of the samples in a silane solution, hydrolysis first takes place that the chloride ions from the silane molecule form hydrochloric acid (HCl) with the hydrogen ions from water, resulting in the formation of silanols (Si-OH) as the head group of the silane molecule. The SAM of the silane molecules can be further formed on the sample surface by the condensation reaction between the silanols and hydroxyl groups on the surface, and the silane molecules will be polymerized between the silanols by the -Si-O-Si- net work, as shown in Fig. 5-2a. With a cover by the pencil marks, an OD SAM can be obtained inside the T-type area. Once the cover is carefully removed, ideally the background will be filled with an OT SAM since the T-type area has been occupied by the OD SAM, as seen in Fig. 5-2b. The patterned sample, e.g. shown in Fig. 5-3, presents a wettability contrast due to the different SAMs inside and outside the T-type area.



(a)



(b)

Figure 5-2 A sketch of forming the SAMs. (a) Hydrolysis of a silane molecule, the mounting of the silane molecule to the surface by condensation and the polymerization of the mounted silane molecules; (b) The T-type area with the SAM of OD molecules and the background with the SAM of OT molecules.

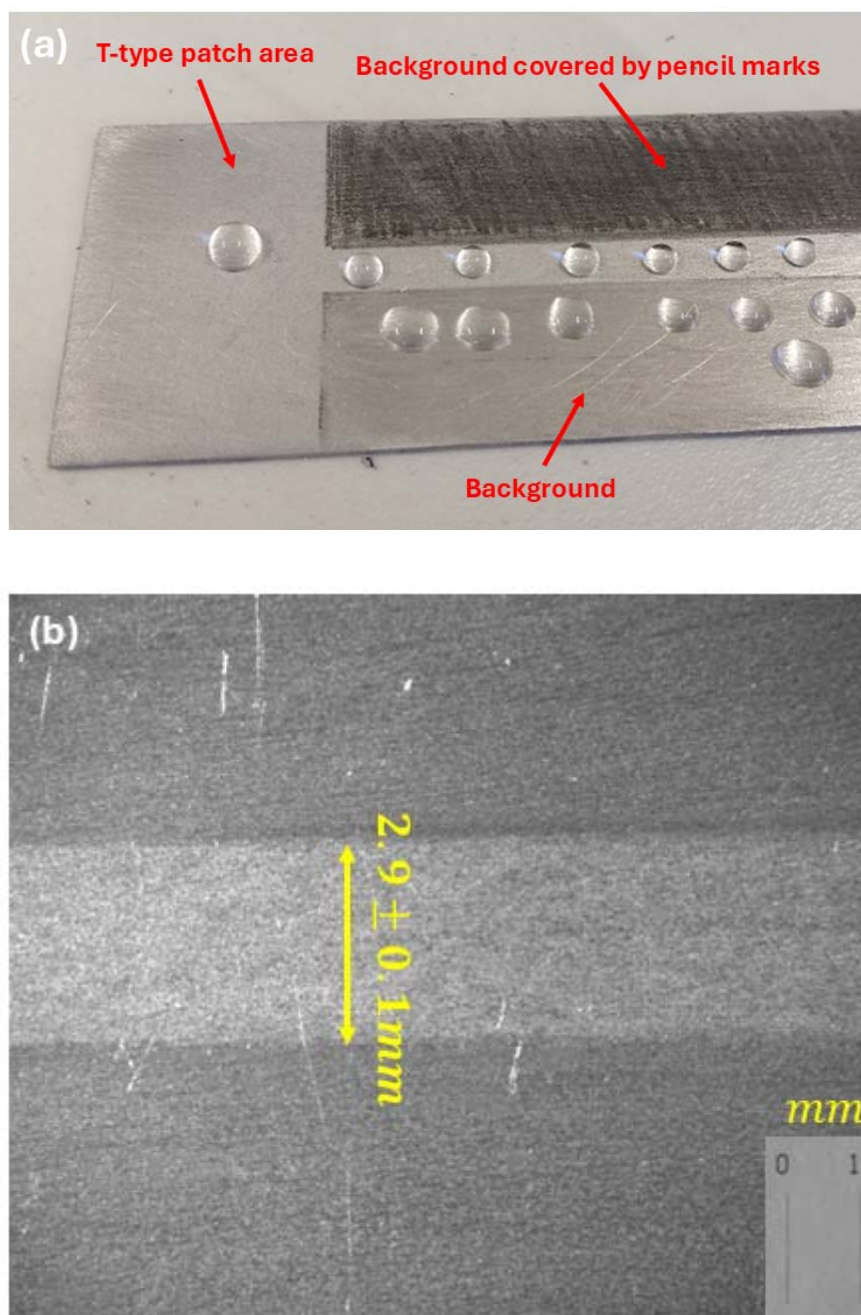


Figure 5-3 Patterned samples: (a) wettability contrast of the pattern, indicated by the shapes of sessile droplets; (b) patch width measured using a LEICA microscope.

5.3.2 Wettability

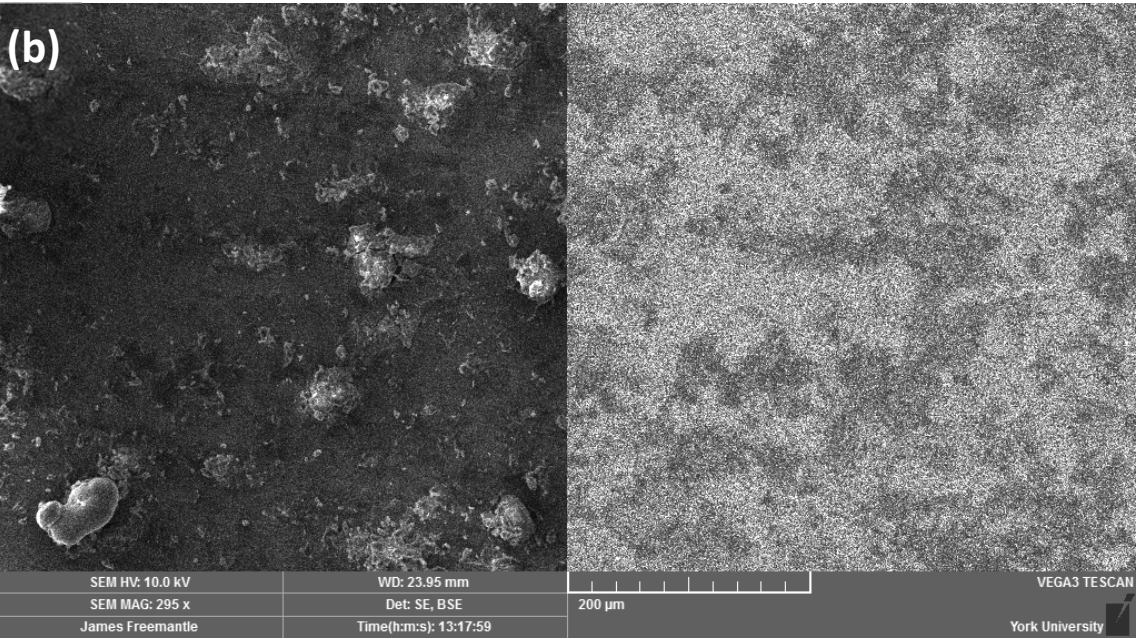
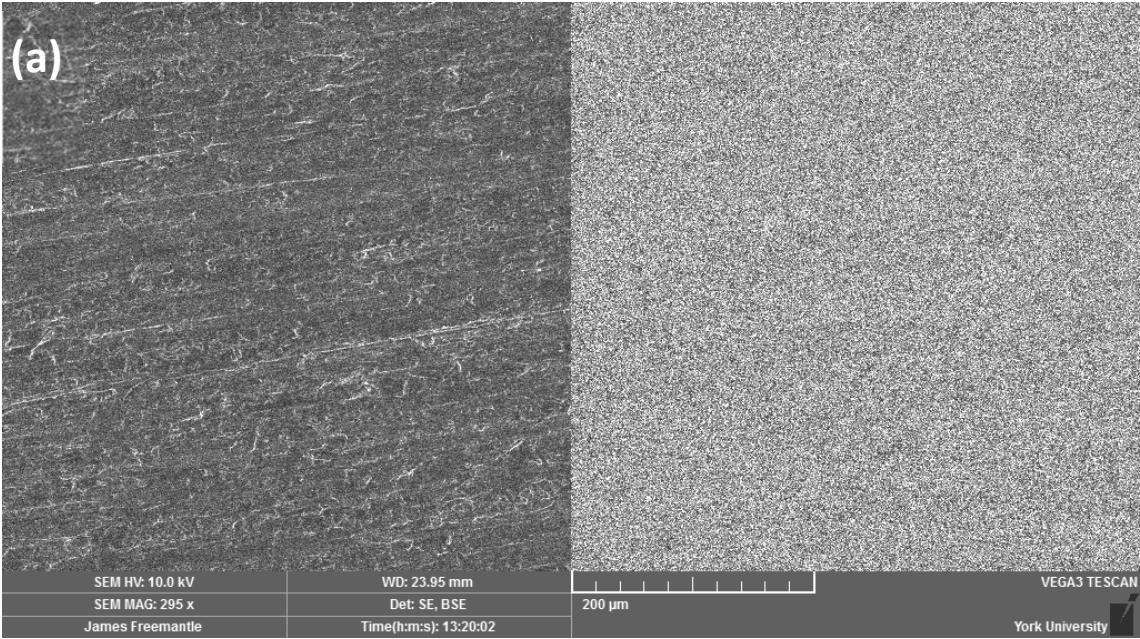
The surface wettability for all samples, including static, advancing, and receding contact angles, is listed in Table 5-2. After coating, Samples No. 1, 2 and 3 became more hydrophobic, along with the advancing contact angle showing a general increase and the receding contact angle improving significantly, compared to the uncoated surface. Notably, Sample No.1 displays the highest static, advancing, and receding contact angles among all four samples, in both the patch area and the background. Sample No. 2 is slightly more hydrophobic than Sample No.3, based on the static contact angle values inside and outside the patch area. However, the advancing and receding contact angles of these two samples showed little change. For each sample, it is clear that all three types of contact angles are higher in the patch area than in the background, indicating a strong wettability contrast across the patterns on each sample.

Table 5-2 Sample contact angle (CA) information

Sample No.	Patch area			Background		
	Static CA	Receding CA	Advancing CA	Static CA	Receding CA	Advancing CA
1	$145^{\circ} \pm 9^{\circ}$	143°	153°	$120^{\circ} \pm 4^{\circ}$	90°	135°
2	$113^{\circ} \pm 2^{\circ}$	73°	120°	$100^{\circ} \pm 4^{\circ}$	68°	104°
3	$101^{\circ} \pm 2^{\circ}$	75°	117°	$86^{\circ} \pm 2^{\circ}$	58°	99°
No coating	Static CA: $73^{\circ} \pm 2^{\circ}$		Receding CA: 15°		Advancing CA: 98°	

5.3.3 Surface morphology and roughness

The morphology of the samples was scanned to gain a better understanding of the different wetting behaviours under different coatings. The SEM images in Fig. 5-4 display the surface structure of both uncoated sample and Sample No.1 from Table 5-1. Notably, after coating, clusters are clearly visible on the surface. These nano-/micro- structures enhance the hydrophobicity of the surface. Backscattered electron (BE) image provides the information of the elemental composition, with heavier elements appearing brighter. The backscattered electron images shown in Fig. 5-4 also indicate that new atoms, specifically carbon (C) and silicon (Si) from the alkylsilane groups, were introduced to the surface structure after coating. Besides, with longer immersion times and longer alkyl chains in OD, larger clusters formed in the patterned area of Sample No.1 (see Fig. 5-4b), implying an increased density of alkylsilane groups on the surface. This is also supported by the increased dark area observed in the BE image of Fig. 5-4b compared to Fig. 5-4c. Since alkylsilane groups efficiently reduce surface energy, the surface becomes more hydrophobic as the concentration of alkylsilane groups increases. Hence, Sample No.1 presents a wettability contrast between the patch area and the background.



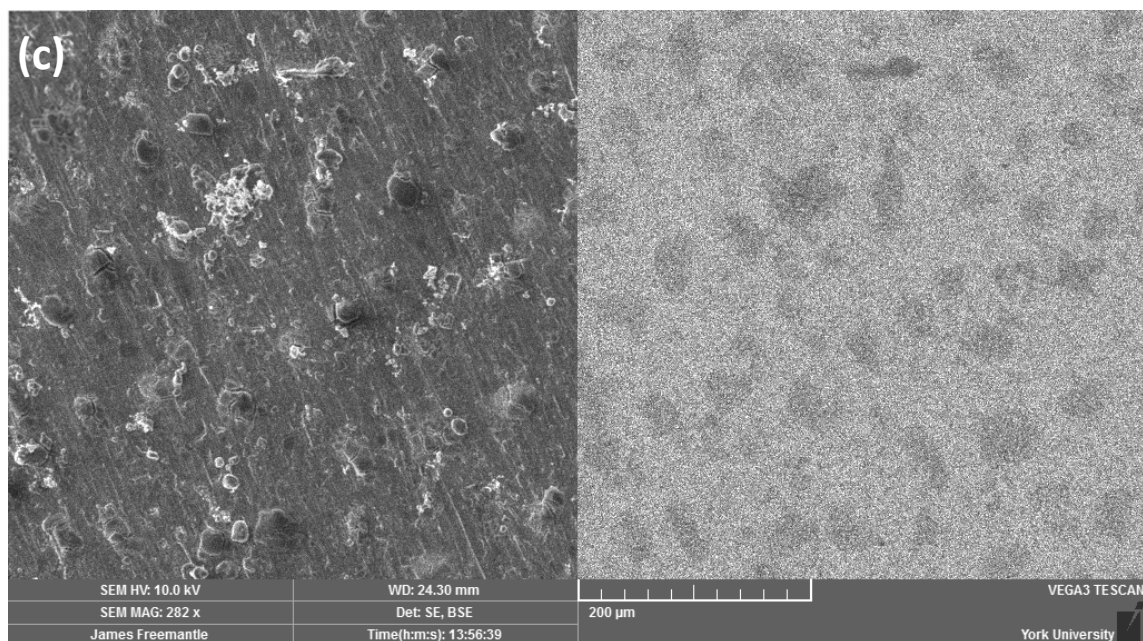


Figure 5-4 SEM (left) and BE images (right) of (a) uncoated Al sample and sample 1 from Table 5-1: (b) pattern area coated with OD (6 h) and (c) background coated with OT (55 min)

The comparison of surface structures between Samples No. 1 and 2 is shown in Fig. 5-5. Figure 5-5a displays the patch area of Sample No. 1 coated with OD for 6 h, Fig. 5-5c shows its background coated with OT for 55 min, Fig. 5-5b shows the patch area of Sample No. 2 coated with OD for 20 min, while Fig. 5-5d shows its background coated with OT for 10 min. Longer immersion times result in more and larger clusters forming on the surface for both OD and OT solutions, as seen in Fig. 5-5a and b for OD coatings and Fig. 5-5c and d for OT coatings. This explains why Sample No. 1 exhibits overall more hydrophobic behavior compared to Sample No. 2. Additionally, within each sample, either Sample No. 1 or 2, it is clear that with longer immersion times and the OD solution, which has a longer alkyl chain, the patch areas (Fig. 5-5a and b) are more hydrophobic than its corresponding backgrounds (Fig. 5-5c and d), as evidenced by the more prominent clusters created on the surface.

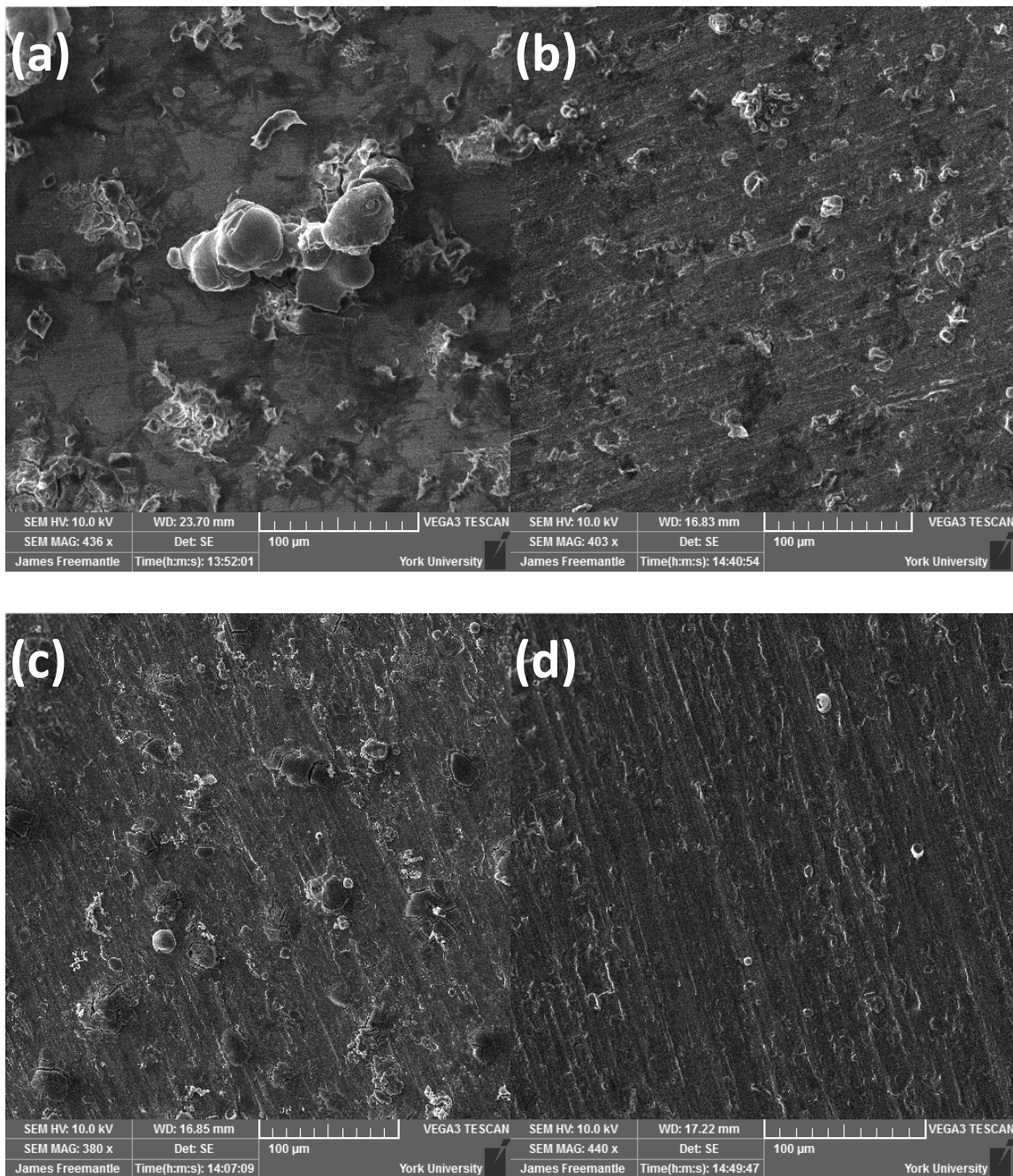


Figure 5-5 SEM images of samples from Table 5-1: Sample No.1 with (a) patch area coated with OD (6 h) and (c) background coated with OT (55min); Sample No.2 with (b) patch area coated with OD (20 min) and (d) background coated with OT (10 min).

Surface roughness has been measured for all the samples with a 3D Optical Profilometer (Contour GT-K, Bruker). The values given in Table 5-3 are indicated by R_z , which is the average absolute value of the five highest peaks and the five lowest valleys over the evaluation length¹³⁴, as provided by this profiling system. Clearly, except for the θ_1 (patch) area on Sample No.1, which exhibits a dramatic increase in roughness, the roughness of other areas after the coating process remains within the same order of magnitude ($\sim 10^3$ nm). Therefore, the exceptional increase in θ_1 for Sample No.1 can be attributed not only to the presence of alkylsilane groups but also to the higher surface roughness. Figure 5-6 displays the topography of both the patch and the background areas for Sample No.1, obtained through stitching data acquisition, where the rough structures are noticeably denser in the patch area.

Table 5-3 Sample roughness (R_z)

Sample No.	Roughness of the θ_1 area (nm)	Roughness of the θ_2 area (nm)
1	16075	8449
2	7055	3841
3	4817	3602
Original surface without coating for comparison	7161	

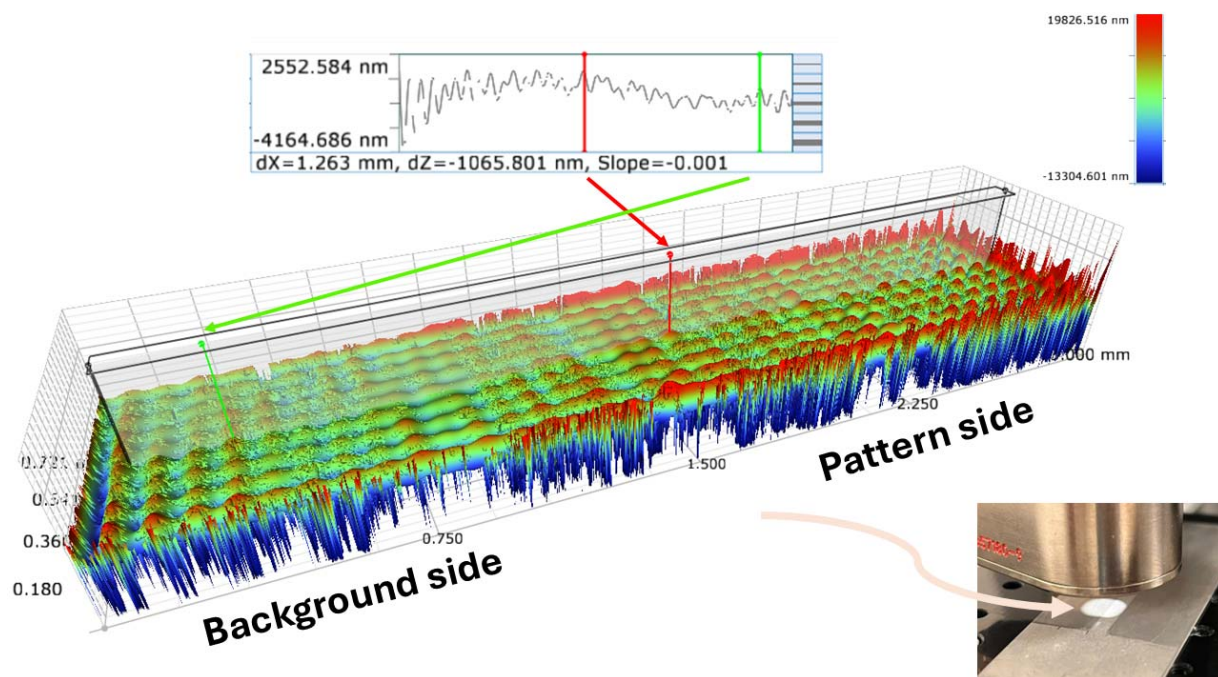


Figure 5-6 Topography of the patch and background for Sample No.1, obtained by stitching and displayed using a Fourier filter. The plot above shows the variation in roughness along the cross-section depicted in the figure. Two locations in this cross-section, randomly selected to present the roughness of the pattern and background, are marked by red and green pillars, respectively. The location marked by red is 1065 nm higher than the one marked by green, as given by dz .

5.4 Conclusion

A dipping method using trichloro-octylsilane and trichloro-octadecylsilane solutions was proposed to create different self-assembled monolayers for fabricating a pattern with a wettability contrast on an AA6061 surface. The wettability contrast is tunable by adjusting the immersion time, with hydrophobicity increasing as immersion time increases, resulting in static contact angles ranging from 85° to 154° . The pattern can be easily shaped using a pencil, providing a mask which is stable in various solutions. This method is flexible and feasible for creating diverse shapes and achieving various wettability contrasts.

Chapter 6

Validation of the symmetry restoration

6 Validation of the symmetry restoration¹

With the surface fabrication method developed in Chapter 5, this chapter focuses on validating the symmetry restoration model for droplet spreading, as elaborated in Chapter 4. This correction model is evaluated through a series of experimental tests, comparing the predicted and observed lamella shapes under varying impact conditions. The influence of wettability contrasts on shape manipulation is also discussed. The results demonstrate the model's accuracy in restoring symmetry, providing a solid foundation for its application in scenarios requiring shape control and involving tangential velocity.

6.1 Experimental impact conditions

According to Fig. 4-11, the deformed spreading shape can restore its symmetry when $We_n/We_t \geq 0.51$. To ensure a successful deposition outcome which means no splash, impact conditions of $We_n/We_t \approx 0.51, 1.03$, and 2.04 were deliberately chosen for experimental validation, along with various pattern states of the samples, as summarized in Table 6-1. As mentioned earlier, the deformation of the spreading shape results from the interplay between We_n and We_t , and the selected impact conditions represent three scenarios: where We_n is less than, equal to, or greater than We_t . Surface inclination for each impact condition is listed in Table 6-2.

¹ This chapter is published in the paper “Application of Surface Wettability to Control Spreading of an Impacting droplet”, LANGMUIR 2024, 40,4623-4634.

Table 6-1 Variations in wettability contrast indicated by receding contact angles (θ_1 and θ_2) and patch width (Wp) of the samples for each impact condition.

Sample No.	We_n/We_t	θ_1	θ_2	Wp (mm)
1	0.51	143°	90°	3
2	1.03	73°	68°	
3	2.04	75°	58°	
4	Original surface for comparison		15°	

Table 6-2 Surface inclination for each impact condition

Sample No.	We_n/We_t	α
1	0.51	55°
2	1.03	44°
3	2.04	35°

One may observe significant differences in receding contact angles measured on samples No. 2 and 3 compared to the corresponding settings shown in Fig. 4-11c and d. The simulated shapes, which account for the actual wettability contrasts measured on these samples, are provided in Fig. 6-1. Despite differences in wettability, there is no significant impact on the symmetry of the resulting shapes. This is also evident in the correction for impact conditions of $We_n/We_t \approx 0.51$,

1.03, and 2.04 with the same wettability contrast (e.g., $\theta_1 = 100^\circ$, $\theta_2 = 90^\circ$), as shown in Fig. 6-2. This suggests that the tailored wettability contrasts shown in Fig. 4-11 for different impact conditions represent optimized cases for their respective scenarios. The deformation obtained under these three impact conditions can also be effectively corrected using the same wettability contrast, making this method applicable in various applications.

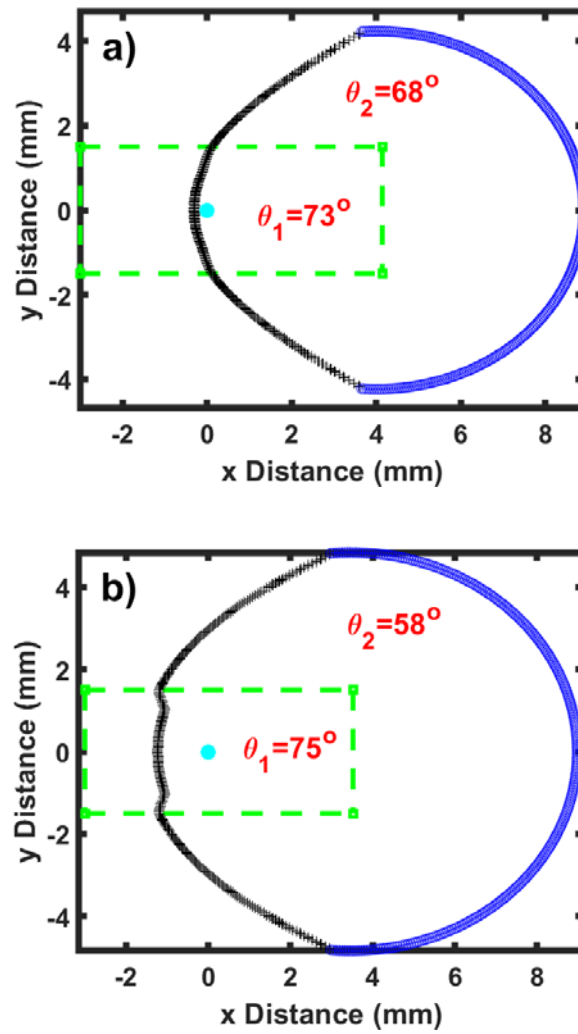


Figure 6-1 Patch design with a singular wettability contrast for the impact with $We_t = 137$ and (a) $We_n/We_t \approx 1.03$, (b) $We_n/We_t \approx 2.04$. The black line is the corrected receding contact line manipulated by the patch at t_{max} . The blue point refers to the impact spot. The wettability contrast aligns with the measured on the corresponding

sample.

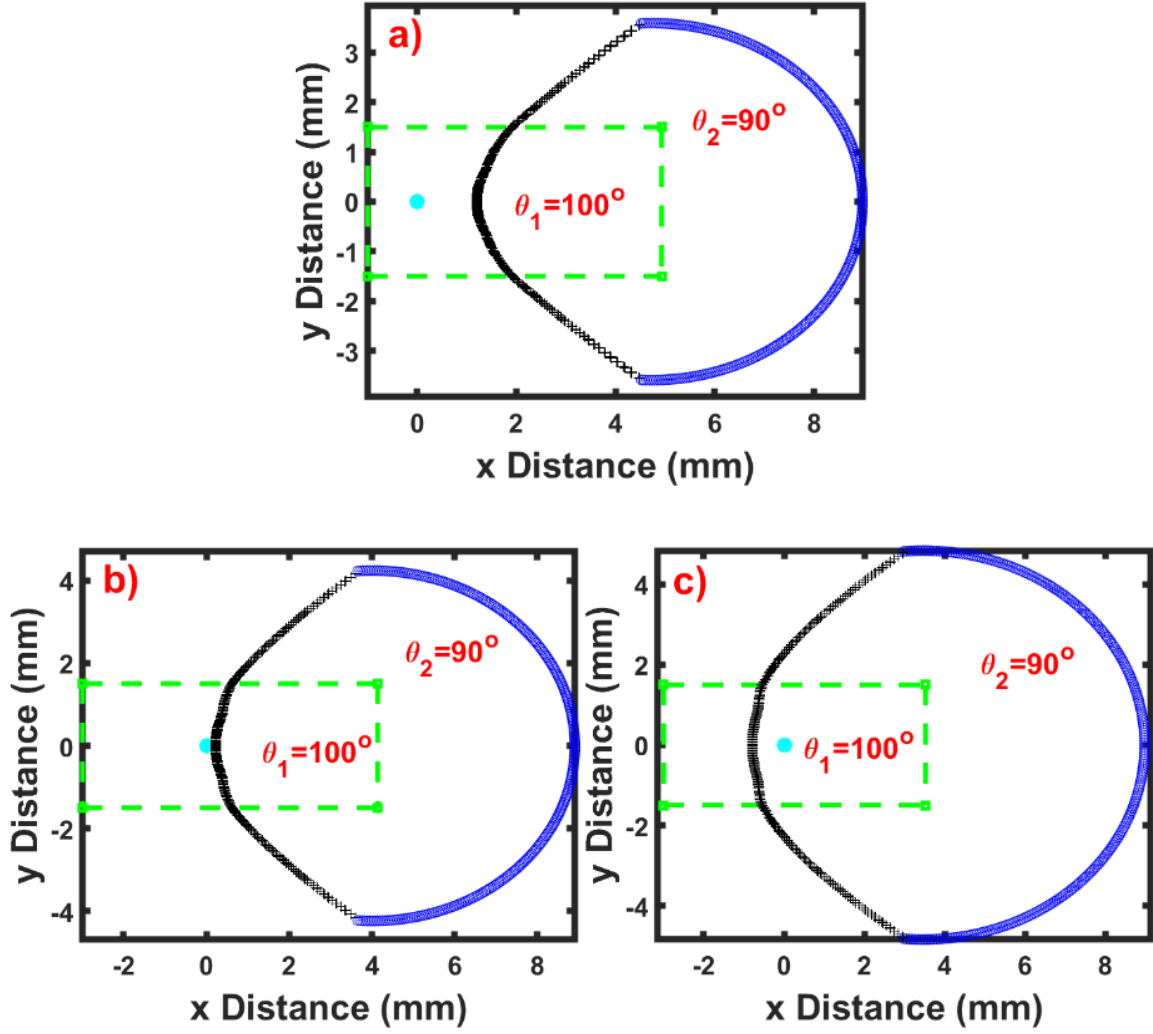


Figure 6-2 Correction with the same wettability contrast for the impact with $We_t = 137$ and (a) $We_n/We_t \approx 0.51$, (b) $We_n/We_t \approx 1.03$, (c) $We_n/We_t \approx 2.04$. The black line is the corrected receding contact line manipulated by the patch at t_{max} . The blue point refers to the impact spot.

6.2 Effect of wettability on upstream spreading

A prerequisite for applying the developed model presented in Chapter 4 to restore the symmetry of the deformed lamella is that the upstream spreading is minimally affected by wettability, meaning that the maximum spreading width will not change significantly. This condition is essential since the model is based on the original lamella shape that only experiences deformation on its

downstream side. The underlying assumption is that the variation of the wettability due to the patch design will not affect the upstream spreading in shape.

For each experimental condition, two types of lamella shape were presented: corrected and uncorrected. The maximum spreading width for each type and condition is shown in Fig. 6-3. The experimental maximum spreading factor ($\beta_m = W_{max}/D_0$) for the original surface in this study is well fitted by the expression^{45,101} $\beta_m \approx aRe_n^{1/5} - bRe_n^{2/5}We_n^{-1/2}$ with $a = 0.8779$ and $b = 0.5975$. For model results, we applied the original expression with $a = 0.87$ and $b = 0.40$ in reference^{45,101} to predict the maximum spreading width and obtain the uncorrected lamella outline (see the blue line in Fig. 4-11). Therefore, this expression is working well in this study.

Besides, one can see that in Fig. 6-3 the maximum spreading width of the corrected lamella closely matches that of the uncorrected one. This observation supports the prerequisite that wettability has little effect on upstream spreading, making it possible to use our model to correct the deformed lamella.

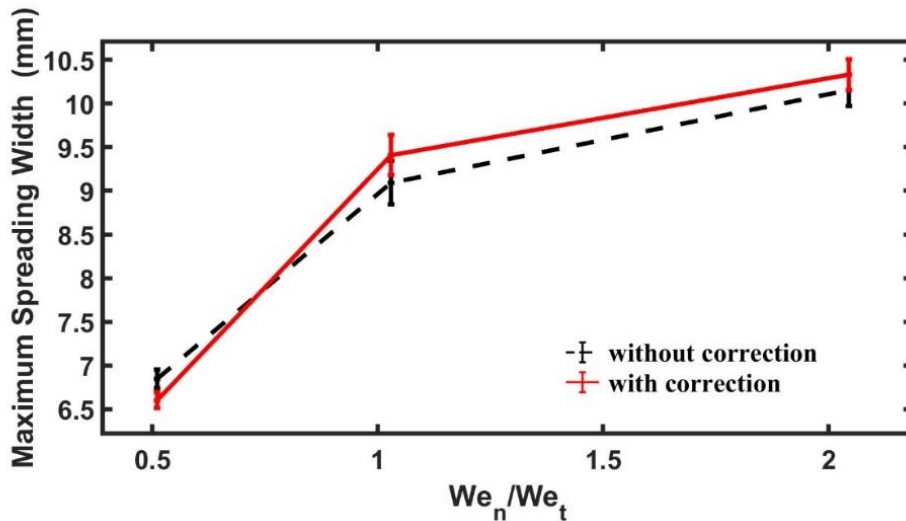


Figure 6-3 The comparison of the maximum spreading width between the lamella with and without correction given various We_n/We_t . Lines are to guide the eye.

6.3 Lamella shape correction under varied impact conditions

The experimental comparison between the corrected and uncorrected lamella shapes at t_{max} is shown in Fig. 6-4. Compare to the uncorrected lamella, it is clear to see the lamella manipulated by the patch has a more symmetric shape, which confirms the effectiveness of this model. Additionally, notable undulations on the lamella rim are observed when $We_n=280$. To reduce the potential risk of splash, the scope of this study for correction is further restricted to $We_n \leq 300$ and $We_t \leq 300$.

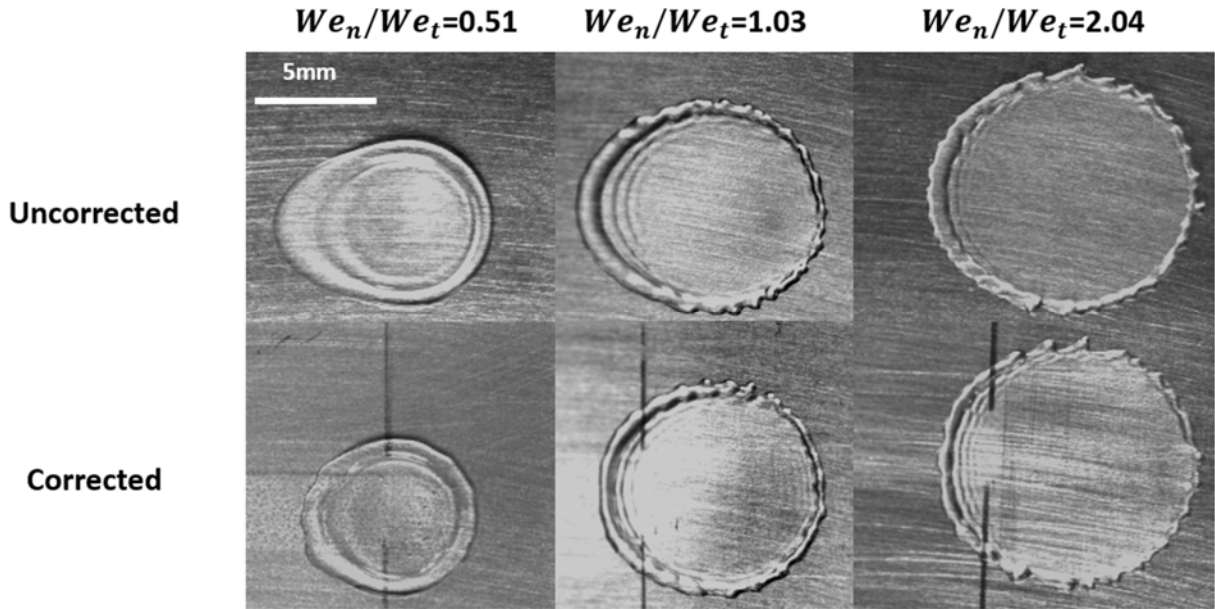


Figure 6-4 The lamella shape before (top row) and after (bottom row) correction at t_{max} given $We_n/We_t \approx 0.51$, 1.03, and 2.04 from left to right. The impact conditions and substrate information are given in Table 6-1. Black lines are pencil marks to indicate the end of the patch for impact tests.

One should notice that the surface roughness can contribute to the pinning effect of the downstream contact line. If the surface is rough, it may result in contact angle hysteresis, introducing a delay in the motion. Additionally, the micro/macroscopic features on a rough surface can enhance the

pinning of the contact line. In this work, the roughness of the samples is provided in Table 5-3. One can see that the roughness of the surface maintains the same order of magnitude ($\sim 10^3$ nm) before and after the coating process, except in the patch area of Sample No.1, where the roughness is approximately doubled. Observing Fig. 6-4, it is evident that the roughness of the samples after the coating process did not hinder the contact line motion. This can be attributed to the improved hydrophobicity, resulting in a reduced contact angle hysteresis—from 83° before coating to $10^\circ \sim 47^\circ$ after coating (see Table 5-2).

A correction indicator (I) was defined as the ratio of the lamella length (L) to width (W) to characterize the correction. Length is defined as the dimension of the lamella spreading in the direction of v_t . For a more symmetric lamella shape, I is closer to 1. In Fig. 6-5, one can see that I is approaching 1 for all the selected impact conditions after the lamella was corrected. The gap between the blue dashed line and the orange line in Fig. 6-5 implies the extent of the lamella deformation to be corrected. This deformation extent decreases with the increase of We_n/We_t .

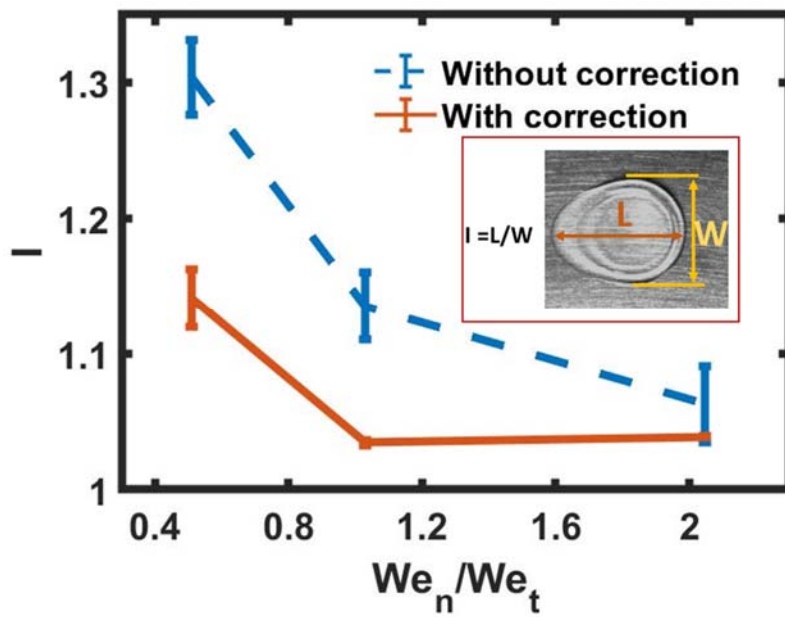


Figure 6-5 Variation of the correction indicator I with $We_n/We_t = 0.51, 1.03$, and 2.04 . Lines are to guide the eye.

6.4 Lamella evolution and correction

Among the three impact conditions, the smallest We_n/We_t , which is 0.51, indicates the weakest normal momentum, and results in the most substantial deformation in the lamella post-impact. Therefore, the impact under this condition is intentionally taken as an example to compare the experimental and simulated lamella shapes at different time steps in Fig. 6-6. It is evident that our prediction exhibits a remarkable alignment with the experimental data. The lamella's evolution, both with and without correction, is further displayed in Fig. 6-7. An expected correction can be observed at each time step starting from 1 ms post-impact, before which the spreading is dominated by inertia forces and hence there is no considerable difference in the shape with and without correction. Overall, the experimental results as expected reinforces the robustness of our method and contributes to a deeper understanding of how wettability can be used to adjust the spreading shape by manipulating the contact line.

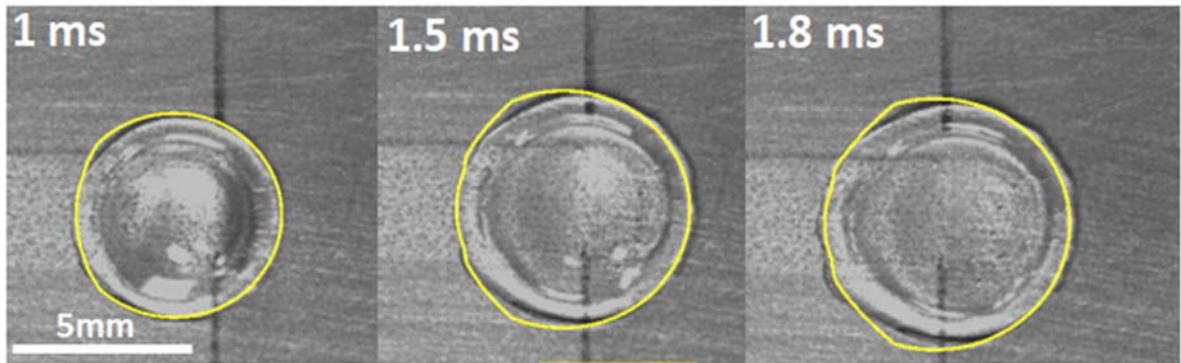


Figure 6-6 The comparison of the corrected lamella spreading between experimental and simulated data (yellow line) at different time steps given $We_n/We_t \approx 0.51$. Black lines are pencil marks to indicate the end of the patch for impact tests.

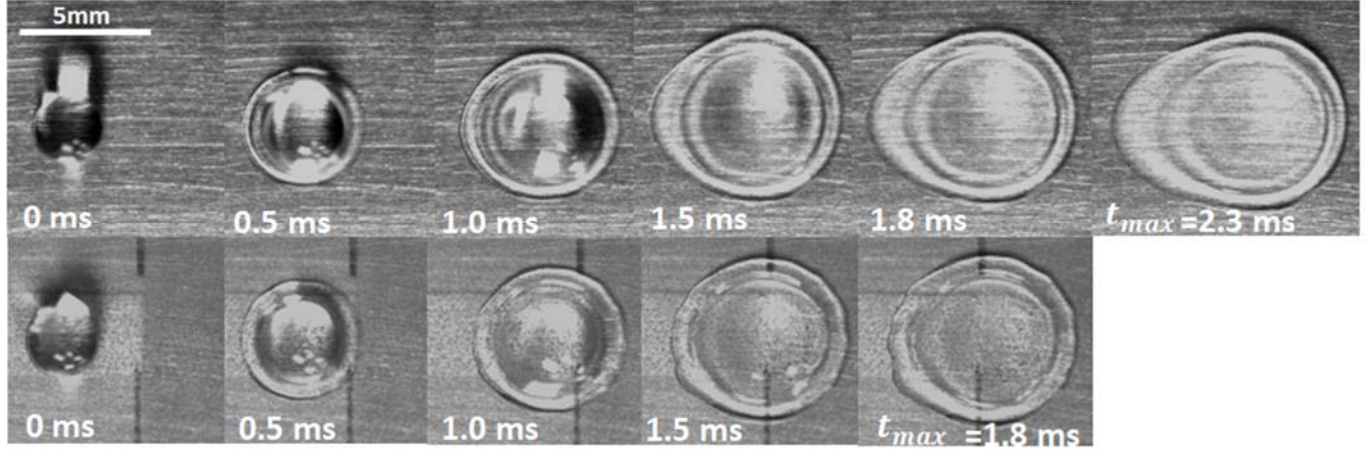


Figure 6-7 The spreading process of the lamella before (top row) and after (bottom row) correction on the condition of $We_n/We_t \approx 0.51$. The sample information is given in Table 6-1. Black lines are pencil marks to indicate the end of the patch for impact tests.

6.5 Conclusions

The symmetry of the corrected shape is not highly sensitive to variations in wettability contrast. The correction model has been successfully validated on inclined surfaces under various impact conditions, and it is also applicable to moving surfaces under the same impact conditions discussed for the inclined surfaces. The experimental results closely matches the predicted results, confirming the validity of this method in promoting more symmetric spreading of water droplets when a tangential velocity is present, given the conditions when $We_n \leq 300$, $We_t \leq 300$, and $0.51 \leq We_n/We_t \leq 2.04$.

Chapter 7

Conclusions and future work

7 Conclusions and future work

This chapter presents the conclusion of this thesis and discusses potential work that could enhance or extend the understanding of the phenomena observed in an impacting droplet.

7.1 Conclusions

The first objective of this thesis, as introduced in Chapter 3, explains the genesis of the rim during the spreading process of an impacting droplet, particularly at low We , where a thick and smooth rim is clearly visible. The rim's formation is closely linked to the behavior of the lamella, a thin sheet that is tangentially ejected from the droplet bottom soon after impact. The ejection is driven by the substantial inertial force, manifested as dynamic pressure, which dominates over the Laplace pressure, preventing the formation of a bulge and leading to a flat sheet instead.

The lamella's internal flow can be described as laminar due to its smooth nature. As capillary forces decelerate the flow, the flow begins to bend at lamella edge, forming a quasi-circular motion. Over time, this motion develops as more fluid from the lamella accumulates at its edge, leading to the formation of the rim. Eventually, a recirculating flow is established within the rim. This developing circulating flow is the essential mechanism behind the rim's formation, and the dynamic pressure generated by this motion must be balanced by the Laplace pressure within the rim, determining its transient curvature.

The proposed theory not only explains the physical genesis of the rim but also provides a precise prediction of the time when the rim starts to form and describes the droplet's configuration at this critical moment. These theoretical predictions align well with independent simulations conducted using OpenFOAM, as well as experimental observations.

Importantly, this work offers more than just an explanation for rim genesis. It provides a refined initial condition for numerical calculations, particularly for solving key equations (Eqs. 1-8) that are crucial for capturing the rim's dynamics over subsequent time steps. This refined understanding is essential for accurately predicting the maximum spreading behavior of an impacting droplet, a key aspect in the broader study of droplet dynamics.

Objective 2, stated in Chapter 4, presents a model developed to control the spreading shape of an impacting droplet with the presence of a tangential velocity, particularly aiming to restore symmetric spreading at t_{max} via wettability. Building on previous work that used time-dependent ellipses to capture lamella propagation, this model leverages geometry to design the receding path of the elongated downstream contact line. By linking the receding velocity to the receding contact angle in a positive relationship as described by the Taylor-Culick theory, a wetting map was developed to outline the wetting conditions required for symmetry restoration.

Based on this wetting map, and acknowledging that receding distance of each local on the downstream contact line decreases with increasing distance from the lamella centerline, a patch design with a singular wettability contrast — higher receding contact angle inside the patch and lower at the background — was proposed for feasible surface fabrication. Calculations show that while wettability does not significantly affect the upstream spreading, the patch design effectively improves the lamella symmetry at t_{max} under condition of $0.51 \leq We_n / We_t \leq 2.04$ for a water droplet.

To experimentally validate the patch design for shape correction, a surface fabrication method was developed to create a patch with tunable wettability contrast on AA6061 sheets, as described in Chapter 5. This method applies two types of self-assembled monolayers formed by dipping the surfaces in trichloro-octylsilane and trichloro-octadecylsilane solutions. The wettability is

controlled by varying the immersion time, with longer immersion resulting in a more hydrophobic surface. The pattern is shaped using pencil marks, which are easily applied and removed from metal surfaces of varying curvature. Additionally, they are chemically stable and do not interact with organic solutions. This method is fast, simple, and requires no special equipment, making it feasible for creating different patterns with diverse wetting requirements.

In this study, three samples with varying wettability contrasts were prepared to validate the shape correction model under three different impact conditions. The experimental observations confirmed a critical prerequisite for applying this model: wettability has only a limited effect on upstream spreading. When compared to the ideal wettability contrasts predicted by the model for each impact condition, the experiments also showed that the corrected shape's symmetry is not highly sensitive to variations in wettability contrasts. This finding aligns well with the model's calculations, which used the same wettability contrast across all three conditions. This makes the approach not only applicable but also feasible for shape corrections across a range of different impact scenarios, demonstrating the robustness of the model in practical applications. The experimental results closely match the model's predictions, supporting the validity of the shape correction model in restoring the spreading symmetry of water droplets with tangential velocity present under the condition of $We_n \leq 300$, $We_t \leq 300$, and $0.51 \leq We_n/We_t \leq 2.04$.

7.2 Future work

Since spreading is a very important phase after impact, this thesis has focused on two key aspects: the genesis of the rim for low We and the control of spreading in the presence of a tangential velocity. Some potential avenues emerge for further research building upon the findings and insights gained from this work.

First, investigating the mechanism behind the formation of undulations on the rim at high We and understanding its genesis is an important avenue for future work. At higher We , the rim becomes thinner and less smooth, making the undulations more prominent. Although the rim plays a less significant role in determining the maximum spreading for impacts at high We , due to its relatively small size compared to the overall spreading width, studying the undulation formation is crucial because it is closely linked to other key phenomena, such as fingering and splashing. The mechanism behind the undulated rim is still unclear — whether it results from the superposition of rim development, similar to low We impacts, plus a shock wave (an assumption not widely accepted due to it diminishes very rapidly), or from the interplay between dominant inertial forces and relatively weaker capillary forces. Additionally, a deeper understanding of rim genesis at high We could provide more accurate initial conditions for numerical simulations, leading to better predictions of maximum droplet spreading.

Future work can expand the 2D simulation into 3D to study rim genesis for high We . In such cases, the lamella and rim become less smooth, and a 2D representation may not adequately capture their key features. The additional dimension is necessary to account for shape variations in phenomena such as waves on the lamella and fingers at the rim.

Second, with the initial condition set for low We impacts as discussed in Chapter 3, the next step involves solving Eqs. 1-8 to capture the rim dynamics during the later phase and to predict the maximum spreading. However, the initial condition obtained in Chapter 3 did not yield a converged solution for the mass and momentum equations when considering viscous dissipation, and it significantly overestimated the maximum spreading in cases where viscous dissipation was neglected. This indicates that for a more precise initial condition, the settings for inner and outer flow inside the lamella, as well as the lamella thickness, are highly sensitive and need to be self-

consistent. It may be necessary to introduce an additional ODE to account for the variation in lamella thickness, rather than relying on existing expressions, which are mostly asymptotic solutions only applicable to specific moments in the spreading process.

Furthermore, the rim genesis model can be extended to impact scenarios on an inclined/ moving surface. With tangential velocity, the droplet bulk, as the source of the flow, moves along the direction of this velocity, causing different behaviors in the upstream and downstream regions. Besides, surface tension also plays an important role in shaping the upstream region. Lower surface tension leads to a sharper upstream shape, while higher surface tension produces a rounder one. This distinct feature may also affect the flow within the lamella in both upstream and downstream regions, and hence affect the rim dynamics, such as variations in the local width of the rim.

Lastly, the fabrication method using SAMs, developed in Chapter 5 for creating the pattern with a controllable wettability contrast on AA6061, can also be applied to other metals with oxide layers, such as copper, titanium, iron/steel and so on. This fast, easy, and low-cost method has versatile applications, extending to various patterns, surface curvatures, and materials.

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Appendix A: $R_{imagine}$ and the correction factor $\mathcal{V}_{diff}$

In Chapter 3, $R_{imagine}$ is determined based on volume conservation. The impacting droplet is depicted in blue, as shown in Fig. A-1a. For simplicity, the dashed blue line represents the ‘eaten’ part of the droplet, which forms the jet due to the impact on the wall. This jet is modeled as an increasing bulge with a radius of $R_{imagine}$, rather than the thin lamella depicted by the red dashed line. The volume of this eaten part is given by:

$$\mathcal{V}_{eaten} = \frac{\pi}{3} (3R_0 - v_i t) (v_i t)^2 \quad A-1$$

Considering the jet portion as a torus with a full circular cross-section, its volume is expressed as,

$$\mathcal{V}_{torus} = 2\pi^2 R_{imagine}^2 (A + R_{imagine}) \quad A-2$$

The value of $R_{imagine}$ can be estimated by equating Eqs A-1 and A-2.

The spreading radius, $R_{(t)}$, is also derived based on volume conservation. In Fig. A-1b, the dashed blue line represents the ‘eaten’ part of the droplet, which contributes to the formation of the lamella.

The lamella, denoted by the red dashed line, has a volume in 3D roughly given by,

$$\mathcal{V}_{lamella} \approx \pi H_a (R^2 - A^2) + \pi H_a (A^2 - d^2) / 2 \quad A-3$$

where $d = \sqrt{R_0^2 - (R_0 - v_i t)^2}$, based on the geometry. The only unknown, R_0 , can be solved by equating Eqs A-1 and A-3.

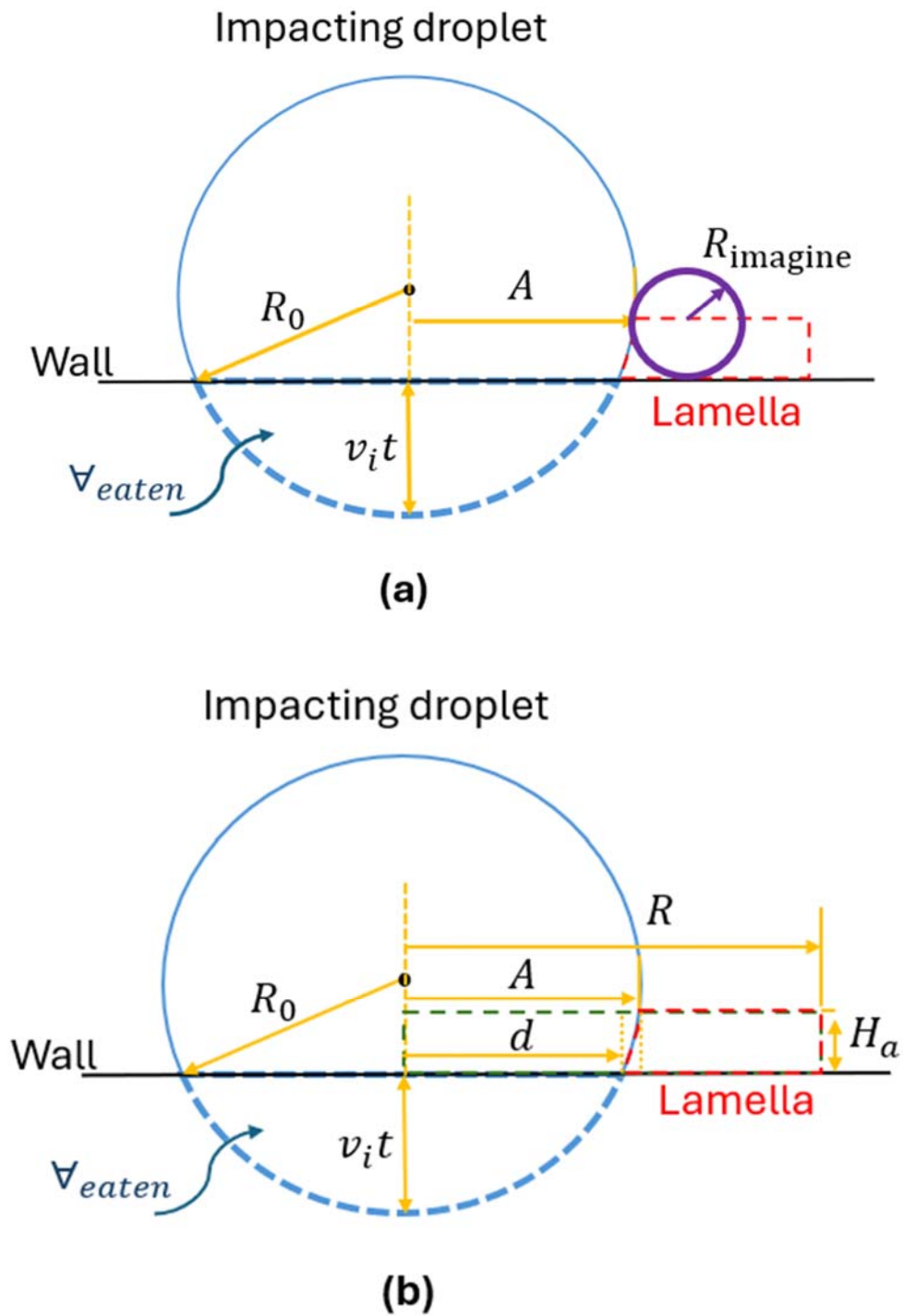


Figure A-1 Schematic of an impacting droplet (a) the jet depicted as an imaginary bulge with increasing curvature (purple circle) rather than a thin flat lamella (red dashed rectangle); (b) the ‘eaten’ portion of the droplet (blue dashed region) forming the lamella (red dashed rectangle). Green dashed lines are to guide the eye.

It should be noted that before t_e , no lamella is observed. Therefore, the ‘eaten’ part of the droplet is not fully converted into the lamella, as calculated in Eq. A-1. The portion that does not contribute to the lamella can be estimated as the difference between the ‘eaten’ volume at t_e and the jet volume at t_e , assuming the jet has a rectangular cross-section with a height and length of $H_{t(t_e)}$:

$$\mathcal{V}_{diff} = \frac{\pi}{3}(3R_0 - v_i t_e)(v_i t_e)^2 - \pi H_{t(t_e)}[(A_{(t_e)} + H_{t(t_e)})^2 - A^2] \quad \text{A-4}$$

Hence, $\mathcal{V}_{eaten}$ must be adjusted by subtracting $\mathcal{V}_{diff}$ to determine the portion that contributes to the formation of the lamella.