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Author McGuan, Ryan

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Los Angeles

Experimental Investigation of Room Temperature Liquid Metal Dynamic Behavior

A dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy in Mechanical Engineering

by

Ryan McGuan

2021

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ABSTRACT OF THE DISSERTATION

Experimental Investigation of Room Temperature Liquid Metal Dynamic Behavior

By

Ryan McGuan

Doctor of Philosophy in Mechanical Engineering University of California, Los Angeles, 2021

Professor Hossein Pirouz Kavehpour, Chair

This dissertation consists of a focused study of the low melting point liquid metal known commercially as Galinstan. This metal is notable for being readily liquid at room temperature, being non-toxic, and forming a peculiar oxide layer that is confined to the surface of the liquid. This study consists of four parts. The first is a literature review of the field of flexible and stretchable electronics. The purpose of this review is to assess the state of the field and to make the case for the value of Galinstan as a primary conducting element in the manufacture of these devices. With this case made, the remaining three parts can be sorted into two overarching concepts: experiments designed to produce data relevant to the drop on demand printing of flexible electronics, and to the study of fundamental fluid mechanics phenomenon, often overlapping throughout. The first study involves the use of tensiometry to measure the effective surface tension, as well as explore the wetting behavior of the liquid metal on glass. For measuring the surface tension, we developed a novel technique that combines principles of both the Wilhelmy plate method, but with a rod modification, with the Du Noüy ring method. After measuring the surface tension, we studied the wetting behavior of the metal, namely the dynamic contact angle and found the advancing contact angle (θ_a), receding contact angle (θ_r), and the contact angle hysteresis $\theta_a - \theta_r$.

Next, we performed droplet impact experiments of liquid metal on glass substrate. Utilizing the wetting information from the tensiometry experiments, we were able to develop a novel model for impact driven spreading of liquid metal on glass for Weber numbers ranging from 10 to 205. This model shows new scaling behavior as compared to other droplet impact models and we compare and contrast these models of impact. This model is also predictive and would serve to modulate voxel size in additive manufacturing operations with Galinstan.

The final set of experiments were of partially coalescing liquid metal droplets in 1 M NaOH. These droplets were observed to bounce on the liquid metal interface and reach different heights as they coalesced into smaller and smaller droplets. We developed a first order model based on the Stokes approximation for droplets in a viscous fluid which we refined with a improved numerical model which was more valid for the range of Reynolds numbers tested. The dissertation of Ryan McGuan is approved.

Jonathan M. Aurnou

Robert N. Candler

Jeffrey D. Eldredge

Hossein Pirouz Kavehpour, Committee Chair

University of California, Los Angeles

2021

To Mom, Dad and to Jacquelyn, the love of my life

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VITA

Education

Master of Science in Mechanical Engineering University of California, Los Angeles (June 2017)

Bachelor of Science in Mechanical Engineering, University of California, Santa Barbara (June 2011)

Professional Experience

California State University, Los Angeles (June 2021 – Present) Lecturer

UCLA Complex Fluids and Interfacial Physics Lab (September 2016 – Present) Lecturer, Teaching Assistant, Graduate Student Researcher

Edwards Lifesciences Corp (September 2015 – September 2016)

Manufacturing Engineer

Publications and Conference Presentations:

McGuan, R., Alizadeh-Birjandi, E., Kavehpour H.P., Experimental and Theoretical Investigation of Impinging Droplet Solidification, International Journal of Heat and Mass Transfer (submitted)

McGuan, R., Candler, R., Kavehpour H.P., Spreading and Contact Line Arrest Dynamics of Impacting Oxidized Liquid Metal Droplets, Physical Review Fluids (submitted)

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Chapter 1: Introduction and Background

1.1 Introduction

Gallium has generated a great deal of research in recent years [1–5] due, in no small part, to the low melting point of the metal, as well as its ability to readily alloy with other low melting point metals. With proper selection of additional components such as indium and tin, a eutectic can be formed which remains liquid at or below room temperature. This family of gallium based alloys are often called room temperature liquid metals (RTLMs) and present exciting opportunities for applications not possible with solid phase metals or other thermal and electrical conductors [6]. One of the most attractive applications of low melting point alloys lies in the field of electronics but questions remain about the behavior of gallium alloys particularly how they flow or interact with other surfaces. The metallic nature of the fluid produces material properties at are very uncommon for everyday liquids, such as very high density and apparent surface tension, as well as new opportunities and challenges in the way that it reacts with ambient air and other substances such as aluminum or steel [7,8].

This manuscript will focus on the study of a room temperature liquid metal known as Galinstan, a eutectic consisting of 68.5% Gallium, 21.5% indium an 10% tin by weight. The motivation of this study is twofold: to study fundamental fluid mechanics and to make advances towards practical applications involving the use of the alloy. For practical applications, the motivating technology is the field of flexible electronics. Section 1.2 consists of a literature review and analysis of the current state of the field as well as a summary of the utility of Galinstan as a component in stretchable electronic devices. Chapter 2: Tensiometry and Chapter 3:



Figure 1-1: Overview of topics covered in this report.

Droplet impact both strive to characterize Galinstan for use in a droplet-based printing method. These also serve to investigate the fundamental fluid mechanics present as noted in Figure 1-1. Chapter 4: Coalescence seeks to present a study of fundamental fluid mechanics, exploiting the unusual material properties of Galinstan in order to observe and model liquid metal droplets bouncing on the free surface in a viscous quiescent medium. This study also serves as an expansion

and validation of previous work by our group involving the partial coalescence process and bouncing droplets by Honey and Kavehpour [9].

1.2 Flexible Electronics, A Review

There is a great deal of interest in the use of liquid metal in the fields of electronics [5], microfluidics [2], and chemistry [1]. For this proposal we will focus on the application of liquid metal in the field of flexible electronics, specifically how the material properties contribute or detract from the manufacturing process.

Innovations in materials engineering and the field of microelectromechanical systems (MEMS) have led to new industrial and academic breakthroughs in the field of flexible and wearable electronics. Circuits that can undergo significant deformation while maintaining complete functionality not only afford new possibilities for engineering applications, but also demonstrate marked increase in ruggedness and resistance to wear and tear as compared to conventional electronics. This ruggedness makes use of this technology ideal in extreme environments such as those endured by soldiers in combat. As such, the military has researched flexible displays for deployment for front line warfighters in the field [10,11]. The combat environment presents extreme conditions where equipment must sustain impacts, vibrations, and constant loading. In these applications the durability of flexible electronics serves as an improvement over rigidly constructed displays and PCBs which may crack from impact, fatigue, or other sources of mechanical stress. The body of research thus far relies on thin film transistors (TFT's) and metal foils deposited onto a flexible substrate to create the flexible circuit. In the time since the initial interest in TFT based flexible circuits some issues with the stability of these types

of circuits as compared to older designs based off a rigid substrate have developed [12,13]. While thin films and foils allow material to bend, stretching, or axial strain requires more innovative approaches for electrically conducting material as metal foils will fail when stretched. The inclusion of stretchability into the field of electronics leads not only to increased durability, but also a wide array of new applications including biomimicry, wearable electronics, functional textiles, haptic sensors, epidermal sensors, sensors matching mechanical properties of surrounding tissue and many more. Recent works have made progreess in resolving many of these issues as well as finding new applications over a broad spectrum of engineering challenges.

1.2.1 Background

The field of flexible electronics has made great strides over the last decade, demonstrating many novel and exciting applications. Among these are applications, one of the first studied (and still being studied) is the production of solar voltaic cells [14–22]. Introducing flexible or stretchable properties makes the cells more versatile and durable, and reduces manufacturing complexity as roll to roll printing becomes viable if the material is sufficiently flexible [20]. The advantage of soft materials cannot be overstated as the devices can be easily integrated into existing structures and easily manufactured with high throughput methods such as roll to roll printing. Roll to roll printing represents a manufacturing method that addresses the scale of manufacturing throughput needed to produce the volume of material needed to use both organic or inorganic technology for energy generation, where organic devices work with lower efficiencies but have proven to be easier to manufacture and cheaper while inorganic cells can be

more complex and expensive but demonstrate much higher efficiencies [19]. In recent years academic research has tended toward the use of Organolead halide perovskites for its favorable optoelectric properties. While cells only a few microns thick yielding efficiencies of around 12% have been demonstrated [15] issues with the stability of the optoeletric materials in a dynamic environment persist. Still, the power generation with respect the weight (23 W g⁻¹) is very high and improvements in environmental stability and over all durability continue. In order to overcome performance related decrease due to mechanical deformation some work has been done to fabricate all polymer solar cells [17]. While this technology is less efficient than others, with an efficiency between 6 and 7%, the flexibility and ability to remain elastic under a high degree of bending are superior. This was demonstrated by measuring the normalized conductance with bending radii down to 1 mm and up to 160 cycles. The organic, all polymer blend, saw very little drop in conductance as compared to the fullerene laden control. Perovskite solar cells have been shown to reach efficiencies as high as 18.1 % on a flexible substrate using hybridization of organic and inorganic technologies [16] which falls short of the 22% efficiency generally achieved by similar organic-inorganic hybrid perovskites (OIHPs) technology on a rigid substrate. Furthermore, efficiency drops significantly for a bending radius less than 4 mm but does retain about 80% efficiency for 1000 bending cycles at a bending radius of 4.4 mm. While efforts continue to overcome the challenges of sufficient flexibility and bendability for solar cells and maximizing efficiency while still maintaining an economic manufacturing process, novel applications of flexible photovoltaic cells have been found. By integrating elastic conductors with spooled titanium wire an electrolyte a linear solar cell can be produced that can readily be integrated into clothing to power wearable electronic devices [22]. Taken even further sufficiently flexible material can be tuned to be close enough to the mechanical properties of the dermis and implanted subdermally. This has led to subcutaneous, implanted solar cells for the powering of electronic implanted devices [21]. Biocompatible devices are a natural progression of flexible electronics technology is one of the most prolific areas currently being studied.

The mechanical challenges and requirements of flexible and stretchable electronics are best illustrated in applications relating to implantable electronic devices or devices worn directly one the body. Devices that can match or mimic the mechanical properties of the skin or surrounding tissue can be implanted and mitigate irritation or inflammation improving patient comfort. Medical devices represent perhaps the most prolific area of study for stretchable electronics today and several applications have already been shown [21,23–37]. By integrating electronics into a flexible substrate, a marriage of flesh and engineering occurs in which the body's natural biological components can be nearly seamlessly integrated into diagnostic and active devices designed in a laboratory. These devices can even be used in soft robots for haptic feedback and tactile sensing. An early example of this concept employed foil as the conducting material and adhered to the surface via Van-Der-Waals forces [30]. This system was able to achieve a linear response with strain up to 15%, a non-linear response up to 30% and irreversible effects beyond that. Most devices mentioned thus far are capable of functioning with strains of up to 30% however epidermally mounted sensors would need to function at significantly high values of strain. Setkani was able to produce large area devices that functioned up to 100% strain, however conductivity was limited to 100 S/m although most functional components were reported to function at lower rates of strain below 50% [33]. Note that this is 5 orders of magnitude lower than copper at 5.96×10^7 S/m meaning that while flexible, functionality of the device must be

designed with the precise electrical constraints in mind and will differ significantly than a circuit patterned onto a stiff substrate. This example and others [27] demonstrate the difficulty of developing circuits that function over a large area. Localized strain values may be quite high, and strain may vary anisotropically. Over large areas greater values of strain mean greater absolute values of stretching and the conducting interconnects become a limiting factor in the overall stretchability of the device.

Different strategies have been formed to undertake the issue of flexibility and stretchability. Figure 1-2 below shows a few common approaches [37]. The first strategy [34] involves (Figure 1-2 (a)) buckling which is a technique in which the elastomer or other flexible substrate is prestrained to a maximum deformation. The flexible electronics are laid on this substrate which is then relaxed and allowed to buckle. The buckling will bulge out of plane and the maximum strain is defined by the pre-strain amount, but this is a simple method of producing stretchable electronics. The second method is known as the rigid islands approach [26,37] in which non stretchable or stiff components are embedded on a stretchable or bendable substrate. This method does require some form of flexible or stretchable electrical connection between islands usually in the form of strategically designed stiff conductors like the out of plane example shown in Figure 1-2 (a) or intrinsically stretchable materials. The method of connecting these stiff islands with stiff conductors with special configurations is known as the deterministic geometries approach. Intrinsically stretchable materials as shown in Figure 1-2 (c) and are materials that can undergo significant strain elastically. The amount to be considered inherently stretchable is not rigorously defined but is generally on the order of 100% strain or more [38].



Figure 1-2: Stretchable Electronics Fabrication Methodologies: [37] (a) Buckling substrate after pre-straining [34]. (b) Rigid Islands on flexible substrate [26]. (c) Intrinsically stretchable conductors [38].

Another consideration is the process of fabrication. As mentioned previously roll to roll printing can be used for simple specific processes for large area devices [18,20] but for most of the devices listed here most require much more complicated, individualized processes. Consideration must be given not just to fit, form or function of the device itself, but manufacturability of the device with attention paid to throughput and cost. The methods available will be limited by the device design; that is to say whether the device relies on pre-strain and buckling, rigid islands, intrinsic stretchability or some combination of the above listed techniques. This report will focus primarily on the application of intrinsically stretchable materials, their dynamic properties and the development of the understanding of the fundamental physics at play in order to progress towards a rapid, economic, and scalable manufacturing process for highly stretchable, tight tolerance electronics.

1.2.2 Intrinsic Stretchability

In recent years much attention has been given towards specific applications of flexible or stretchable biosensors. Additional examples from recent literature include temperature sensing [35], subdermal solar cell arrays for powering implanted devices [21], blood [32] and sweat [25] analysis, pulse tracking [36], measuring intra-ocular pressure [28], and others [31]. Additional applications include solar voltaic cells as mentioned previously, devices worn as accessories [39], circuits printed on foldable paper [40], and even woven into clothing [41]. While much of the current body of research focuses on novel applications or fabrication of specific components, less attention has been paid recently to the conducting material and maximizing the functional device strain. Intrinsically stretchable materials provide a convenient, sometimes overlooked, solution to the competing problems of electrical and mechanical functionality. While not having a rigorous definition, "intrinsically stretchable" generally refers to materials that can undergo tens or even hundreds of percent strain without significant loss of functionality. Many conductors can be strained small amounts but generally this regime is limited before becoming brittle, or undergoing irreversible, plastic deformation. There are several examples of materials meeting these criteria with varying levels of effectiveness as well as different challenges and advantages. Another requirement sometimes specified for intrinsically stretchable materials is that the store mechanical energy when stretched, energy which can be recovered by reversing the imposed strain [42,43].

One form of intrinsically stretchable material involves the use of ionic or electrolytic solutions hydrogels and uses charged ions in a fluid or gel solution in order to transport electric charge [33-35]. Note that while hydrogels may store mechanical energy when strained, fully liquid

electrolytic solutions do not. This also includes organic semiconductors with embedded plasticizers as mentioned previously but the conductivity and elasticity of other methods mentioned here [47]. Yet another example includes conducting composites formed by embedding conductive particles in a stretchable elastomeric matrix. While not intrinsically stretchable in the same way that the other methods listed here are (due to the inhomogeneity of the material), this method has been listed in publication and is reported here for completeness [48]. The focus of this report will be on yet another form of intrinsically stretchable conductor: room temperature liquid metals.

While any metal may be rendered molten with sufficient heat application, the high temperatures required are impractical for use in most cases due to reduction in conductivity, energy and insulation requirements as well as safety. The exceptions to this are metals that melt and remain liquid at or below room temperature. The most metal most commonly associated with a low melting point is of course mercury. While Mercury has many desirable electrical and mechanical properties for flexible circuit applications, namely a low melting point of -39 °C [49], and fairly high electrical conductivity of 1.02×10^6 S/m [50]. Unfortunately mercury and many of its compounds are toxic and this fact combined with a high vapor pressure relative to its toxicity [51] makes mercury unwieldy or unsafe for most applications. An attractive alternative presents itself in the form of gallium, or better, gallium alloys with melting temperatures reduced to below room temperature [52]. Additionally, the vapor pressure of gallium is negligible [53], which indicates that inhalation hazard is low even in non-controlled environments. Gallium is also known to be non-toxic except in rare cases such as gallium halide complexes [54], but is safe for

nearly all devices and many compounds are considered biocompatible for applications such as internal implantation [55].

1.3 Room Temperature Liquid Metals

1.3.1 Gallium Based Alloys

Rigorous study of gallium, mostly from the perspective of chemistry, began in full force in the mid 20th century continuing through the present day [56–58]. The attractiveness of gallium as a conducting material for flexible and stretchable electronics comes from a few factors. Firstly, it's electrical conductivity is slightly better than at of mercury at 3.7 x 10⁶ S/m, its meting point $T_L = 29.9$ °C means that it is liquid just above room temperature and boils far above most practical applications at $T_v = 1983$ °C presenting one of the widest ranges for a metal in liquid state [56]. The advantage of using a liquid conductor as mentioned above is that the conductors themselves have flexibility and stretchability limited only by the method of encapsulation. Furthermore gallium also displays not only high electrical conductivity, but thermal conductivity is high as well with k ≈ 17 W/(m · K) [59] making the substance attractive for not just mechanical and electrical applications, but joule heating or microfluidic based cooling as well.

The most significant obstacle to utilizing gallium as a fluidic conductor for stretchable electronics is that it is not quite stable as a liquid at or below room temperature. Fortunately, gallium readily alloys with other metals such indium which can, in some ratios, form eutectic gallium – indium (often called EGaIn) or eutectic gallium – indium – tin known commercially as Galinstan to form Room Temperature Liquid Metals (RTLMs). EGaIn has been found to have a melting point as low as 15.7 °C while Galinstan is stable as a liquid even lower with a melting

point of – 19 °C [29]. The thermal and electrical conductivity values for these compounds are nearly equivalent to those listed for gallium above on a first order basis so a distinction will not be made for the remainder of this report. For clarity RTLM will refer to Galinstan or a chemically and metallurgically equivalent of eutectic unless stated otherwise.

1.3.2 Fluid Properties and Applications

The focus of the proposed work is dynamic properties of RTLM, the complicated nature of the flow of these materials, and how the fluid properties can be exploited or accounted for when designing for manufacturing of devices incorporating this material. In recent years there has been great interest both in the physical properties of RTLMs [1,60–63] and many innovating and emerging applications in the fields of additive manufacturing, microfluidics, and of course, stretchable electronics [2,3,5,11,20,23,64–74]. For example, as mentioned above one of the most prominent applications of flexible electronics include soft devices that can undergo high levels of strain in order to improve durability or mimic material properties of surfaces such as soft tissue. Figure 1-3 below demonstrates a biaxial stain gauge and pressure sensor embedded on a flexible substrate.

Using liquid metal as the conductor, functional strain values of 250% have been achieved, Figure 1-3 demonstrates a biaxial strain gauge and pressure sensor capable of 250% strain [23]. This device is intended as an artificial skin an consists of an elastomer matrix with microchannels filled with the RTLM EGaIn. Changes in conductivity of the channels due to deformation are read as biaxial strain measurements as well as pressure detection in the normal plane.



Figure 1-3: Biaxial Strain Gauge and Pressure Sensor [23].

Most applications exploit many of the favorable materials properties of liquid metal such as those reported for Galinstan in Table 1-1below:

Table 1-1: RTLM Galinstan Material Properties

| Gallium based Eutectic Galinstan Material Properties [75,76] Typical Composition: Ga: 68.5% In : 21.5% Sn: 10% | | | | | | | |
|---|------------------|-------------------------|----------------------------|--|--|--|--|
| Boiling Point | 1300 °C | Melting Point | -19 °C | | | | |
| Vapor Pressure | > 1.33 x 10⁻6 Pa | | 6 44 - 13 | | | | |
| (500 °C) | | Density (20 °C) | 6.44 g/cm ³ | | | | |
| Viscosity (20 °C) | 0.0024 Pa·s | Specific Heat | 295 J/kg·K | | | | |
| Surface Tension | 0.501-0.718 N/m | Surface Tension | 0 535 + 0 011 N/m | | | | |
| | | w/out oxidation [60] | 0.000 1 0.011 10/11 | | | | |
| Thermal Conductivity | 16.5 W/m·K | Electrical Conductivity | 3.46 x 10 ⁶ S/m | | | | |

Table 1-1 illustrates many of the attractive qualities of liquid metal for electrical and microfluidic applications, but also some of the challenges. The alloy has a low melting point of - 19 °C and a high boiling point at 1300 °C making its liquid state attractive for most ambient or high temperature devices. The density is high compared to many liquids at 6.44 g/cm³ which is

about 6.5x that of water while the viscosity is comparatively lower at 0.0024 Pa·s, only about 2x that of water. This means flows of the metal have a higher predilection towards inertially dominated dynamics than viscous forces as compared to many geometrically similar flow conditions. Furthermore, the surface tension is very high, it is often reported as 0.718 N/m, however is a product of the formation of gallium oxides at the surface, when measured in an inert environment consisting of nitrogen, argon or different inert gas with oxygen purged to below ppm concentrations, the oxide layer formation can be prevented and the measured surface tension in this case is 0.535 ± 0.011 N/m [60]. In either case, this value is very high and is very important with small scale applications where the curvature of the flow may be significant or in lower speed flows where the capillary number *Ca* is given by [77]:

$$Ca = \frac{V\mu}{\sigma}$$
 1.1

Where V is the contact line velocity for a spreading fluid, μ is the viscosity, and σ is the surface tension. Many existing applications and patterning techniques seek to minimize or overcome the capillarity driven flows as RTLM's do not wet many surfaces (this is true for the bulk material however in the case of oxidation at the surface this will change, to be discussed later), however faster, more dynamic flows such as inkjet methods may improve scalability and cost of manufacturing with this material. The high thermal conductivity combined with the fluid nature of RTLM also make it a very valuable candidate for cooling or heating double so with the application of joule heating through the conductivity of the metal.
Returning to the topic of initial discussion: flexible and stretchable devices, the advantage of using liquid metal for electrically conducting material and components becomes immediately obvious. It is generally solid components exhibit material stiffness, meaning the stress response is proportional to the degree of strain given by the Young's Modulus [78], fluids, that is true fluids, not viscoelastic material, has no stress response due to strain but rather a response due to the shear rate from viscous forces [79]. The consequence of this is that the conducting material provides no mechanical resistance as a result of the degree of stretching, and the limitations for how far or for how many cycles a device can stretch is only a function of the substrate and encapsulating material. This of course is providing that there is sufficient volume of fluid to undergo the stretch however even if the device is over stretch and the continuity of the fluid is broken, the electrical circuit may self-heal once the strain is relaxed due to capillarity [80]. The advantages of liquid metal over other solutions for flexible electronics is best articulated by comparing the relative conductivity and maximum functional strain rate of various stretchable electronics solution. Dickey summarized the strain vs conductivity relationship well in figure 3 [5,81-85].

Here it is clear that of the 'intrinsically stretchable' (where stretchable in this context is defined as the maximum functional strain and the intrinsic property indicates that special geometric considerations are not needed to attain stretchability) options liquid metals are the best option in providing both maximizing the functional strain region and high electrical conductivity. Only solid metals are more conductive while being far less 'stretchable' and while ionogel may approach liquid metal in terms of maximum strain, it is 5 orders of magnitude less electrically conductive. Some conductive inks approach liquid metal in terms of either stretchability or conductivity but

even in the most idealized cases liquid metal is superior in both regards. Additionally, as the bulk fluid is not viscoelastic, the Young's Modulus is naturally zero so liquid metals offer no stress response proportional to the strain, only the strain rate from viscosity.

Liquid metals represent the ideal case of balancing stretchability with electrical conductivity. As a liquid, strain is limited only by the cross section of the electrical connection as well as the surrounding material. Even if a device is strained to the point of breaking electrical connection, the metal wires will self-heal once the material is relaxed (assuming the encasing material is not damaged). Figure 1-4 below shows that gallium alloys represent the highest electrical performance at maximum strain as well as the potential for the highest maximum strain value.



Figure 1-4: Electrical Conductivity at Maximum Strain: Adapted from [5], hollow squares are conductive inks [81], the orange square is an ionogel [82], the blue plus is a functionalized composite [83] the red triangle [84] and green circle [85] are liquid metals embedder in elastomer.

This removes the conductor as a variable in the final device's mechanical properties and the properties of the surrounding matrix may be tuned without worrying about the conducting material. One of the few limitations of RTLM intrinsic to their fluidic nature is that they must be fully encapsulated, or the metal would flow freely off the device rendering it useless. Gallium RTLM does in fact have some inherent advantages in the fabrication of these channels or encapsulation [2], [86] but that is generally beyond the scope of this project. The biggest challenge in fabrication liquid metals is the layer of gallium oxide that forms of the surface. This layer forms very quickly and drastically changes the static, dynamic and chemical properties of the fluid.

1.3.3 Surface Oxide Properties and Effects

Initially many saw gallium or alloys of gallium as an alternative to mercury or solid metals as detailed above. However much of the initial excitement damped quickly due to the seemingly confounding surface chemical formation of gallium oxides. This oxide layer has some unique properties.



Figure 1-5: RTLM droplet in flight

Figure 1-5: RTLM droplet in flightshows a droplet in flight captured by a Phantom v7.2 High speed Camera (Vision Research). Note the distinctive tail of the droplet in flight, nominally a low velocity droplet in free fall will assume a quasi-spherical shape in order tin minimize the free surface energy given by [87]

$$dG = \sigma dA \tag{1.2}$$

Where dG is the differential Gibb's free energy and is shown to be proportional to the surface tension σ multiplied by the differential area dA. By the second law of thermodynamics a system in equilibrium will assume the lowest available energy state and, neglecting work done by air resistance this should be a sphere as a sphere has the lowest ratio of surface area to volume. Some work presents this oxide layer as an impediment to the minimization of Gibb's energy at the surface [6] which indicates that the excess energy must, in fact be, stored at the surface. The implication of this hypothesis is that the surface can store a finite amount of energy in the form of compressive strain which, in turn, would indicate the surface is not fluid. As stated before RTLM surface tension is often reported as $\sigma = 0.718$ N/m however this is the apparent surface tension as measured by the pendent drop method [60] in an atmospheric environment. Counterintuitively surface tension is a strong function of interactions in the bulk fluid, but the resulting interactions are a result of the different surfaces the bulk fluid is in contact with. Although many papers characterize RTLM in an oxygen rich environment as a viscoelastic [88] it can also be thought of a two phase flow with two distinct flow regions (or rather mechanically inhomogeneous regions as the oxide layer does not readily flow). In this case the two phases are not liquid flowing with a different thermodynamic phase, but rather a highly localized, chemical inhomogeneity. The

surface is quite thin, on the order of 1 nm [89] and we have observed that the surface may be ruptured by not only sufficient stress as is expected, but sufficient strain. The thin nature of the surface is key as it indicates that the skin is a highly efficient insulator for oxygen and the unusual material properties are localized at the surface. It is tempting to categorize this as a viscoelastic fluid but because the nature of these material properties is localized at the surface, that is the non-oxidized fluid is decidedly Newtonian which was shown by Xu, et al [62] by insulating the metal from atmosphere with HCl which also reduces the surface, before preforming rheological measurements. These complicated interactions between the fluid and skin are difficult to quantify in a static or quasi-static environment, but even more so in a dynamic flow. Understanding the fluid mechanics of RTLM is essential for the leap from theory to practical, scalable manufacturing such as ink jet printing, as well as achieving the resolution and precision needed to be a tenable solution.

Another interesting facet of this liquid metal oxidation is that while the apparent surface tension is very high, capillary effects are actually retarded by the oxide layer. Figure 1-6 below shows the jet breakup and lack thereof in the presence of argon gas.



Figure 1-6 Droplet generation in normal air (a) and with inert argon line attached (b). Plateau-Rayleigh Breakup is retarded by the presence of the oxide layer [90].

When the liquid metal is streamed in an air environment the stream forms a continuous jet. Normally fluids with high surface tension have a higher propensity to breakup in jets due to the plateau Rayleigh instability [91]. In Lord Rayleigh's derivation the fastest growing wavelength growth rate is given by:

$$\omega = 0.34 \sqrt{\frac{\sigma}{\rho R_0^3}}$$
 1.3

Where ω is the growth rate R_0 is the jet radius and ρ is the fluid density. The inverse of this is a scaled form of the so-called inertial time scale for capillary phenomena and actually represents the breakup time for the stream.

$$t_{breakup} \approx 2.91 \sqrt{\frac{\rho R_0^3}{\sigma}}$$
 1.4

As shown from equation 1.6, the expected breakup time decreases rapidly for greater surface tension. For the liquid metal if surface behaved like other liquids the breakup time would be approximately on the order of 10 ms. This discrepancy is due to the elasticity at the surface conferred by the oxide skin. When the skin formation is prevented by argon as shown in Figure 1-6 the stream breaks up almost immediately. This creates a difficult to understand material. In some dynamic scenarios, namely when external work is done on the surface, the surface tension acts as expected and appears very high. However other phenomena that result from most fluids tending to conserve surface area tend to be suppressed by mechanical energy storage in the oxide.

1.4 Droplet Impact

Droplet impact experiments provide opportunity to create dynamic flow behavior, and through control of impact parameters, gain understanding of the relative importance of inertial, viscous and capillary, or in this case simply interfacial, forces. Our initial observations working with this fluid come primarily from working with a Gallium- Indium-Tin eutectic (Ga: 68.5% In: 21.5% Sn: 10%) as mentioned earlier which is ideal primarily for its low melting point of -19°C which is the lowest composition available. Otherwise eGaIn, a similar eutectic without tin and even elemental gallium present many similar properties, notably oxidation at the surface. One

note however, only certain compositions of gallium alloys are eutectics which is a desirable trait for practical applications.

Droplets impacting a solid surface is a well-established field, Yarin has written an extensive review of publications through 2005 [92]. Some have even looked to metals as metals represent an extreme case in terms of kinetic energy at impact and surface tension [6,93–95]. The field has seen a renaissance of sorts in the last view decades due to the increasing advances and availability in high speed imaging due to the advent of digital photography. There is a wealth of information about the mechanics of fluids hidden between blinks of the eye such as the impacting and spreading process, the effects of viscosity as a form of dissipation, wetting in a dynamic spreading environment or the effect of capillarity of resisting the flow, as well as crown instabilities and splashing. For drop on demand (DOD) or ink jetting processes we want to encourage the deposition mode of impact as shown in Figure 1-7 below [96] :



Figure 1-7: Deposition Mode of Droplet Impact [96]. Droplet sequence begins with droplet near the surface then an initial thin layer forms. This spreads to the maximum radius with some capillary waves and the droplet is pinned at or near the maximum diameter.

The droplet impacts cleanly and spreads uniformly without ejection of satellite droplets, splashing or receding or bouncing. In the world of printing this means no contamination of the substrate as well as well-defined geometry within specified tolerances. In the analysis of droplet impact and spreading several important parameters dictate the dynamics of the flow the first being the Reynolds Number:

$$Re = \frac{\rho V D_0}{\mu} = \frac{inertia\ forces}{viscous\ forces} = \frac{\sqrt{We}}{Oh}$$
1.5

Where ρ is the density, V is the impact the velocity (which scales with the spreading velocity), D_o is the droplet flight diameter and μ is the viscosity. For a highly inertial flow (low capillarity) the impact energy will drive spreading while viscosity will dissipate this energy [97]. With fluids like RTLM where surface tension is very high the Weber Number is particularly important:

$$We = \frac{\rho V^2 D_0}{\sigma} = \frac{inertia\ forces}{capillary\ forces}$$
1.6

Where all variables are as mentioned thus far. The Weber number represents a ratio of the inertia forces and capillary forces. For a high surface tension liquid like RTLM the surfaces forces serve to resist and arrest the spreading of the liquid, however normally these types of interactions would producing a rebounding or even bouncing droplet [92,98,99], but for RTLM impacting glass an unusual spreading behavior is observed to be discussed. The final number of relevance is the Ohnesorge number:

$$Oh = \frac{\mu}{\sqrt{\rho \sigma D_0}}$$
 1.7

The Ohnesorge number is of particular interest for characterizing the jettability of a fluid. It is often reported as the ratio of the viscous forces to the square of inertia and capillary forces, but it can be recast per Ohnesorges's own work [100]. If we define a viscous time scale $t_{visc} \sim \mu L/\sigma$ this gives a capillary velocity:

$$V_{cap} \sim \frac{L}{t_{visc}} = \frac{L}{(\mu L/\sigma)} = \frac{\sigma}{\mu}$$
 1.8

From this we can show Ohnesorge Number represents a modified Reynolds Number (ratio of inertial forces to viscous forces) for flows where surface tension is important:

$$\frac{inertia\ forces}{viscous\ forces} = Re^* = \frac{\rho V_{cap}L}{\mu} = \frac{\rho \left(\frac{\sigma}{\mu}\right)L}{\mu} = \frac{\rho \sigma L}{\mu^2} = Oh^{-2}$$
1.9

Where L is a characteristic length scale usually the droplet diameter when dealing with impacts or other capillary phenomena. Note that the Reynolds number may also be cast as the square root of the Weber Number divided by the Ohnesorge number: $Re = \sqrt{We}/Oh$. With regards to inkjet printing the importance of the Ohnesorge number cannot be overstated, however the Weber number, and by extension the Reynolds number, are important too. Figure 6 shows the interaction of these variables from a prominent review performed by Derby [101]. Note that the x axis contains an error the numbers in red indicate the correct values as confirmed by calculation and by Abbott and the source materials [100–102]. At low Weber numbers the fluid is too viscoius to produce an individual jettable droplet all together. Beginning at Re 10 satellite droplets become a risk due to the inertial forces at impact and capillary instabilities. This can be mitigated with lower surface tension as evidenced by the second dotted line which indicates that higher Weber numbers indicating that capillary breakup is less likely. Criteria is generally given as $0.1 \le Oh \le 1$ for whether the substance is jettable and the Weber number provides an upper and lower bound for droplet impact velocities. In any case there is an onset of splashing threshold when the kinetic

energy is high enough. This would permit a jettable droplet size on the order of $0.12 \,\mu\text{m}$ however this is complicated but the dynamic nature of the surface tension as the droplet is forming and ejection the oxide layer will be forming.



Figure 1-8 Ink Jettable Regoion for droplets as a function of Weber and Reynolds Numbers [101]. The blue region indicates the region too viscous to produce a droplet. At higher Reynolds numbers the risk of satellite droplets and splashing increase. Note that the figure contains an error and was corrected with the red numbers.

We also observed a few advantages of the oxide layer formation both as a source of stability in impact, and a more favorable wetting characteristics on the glass substrate. This illustrates the necessity of developing a time scale of oxide layer formation as well as a quantitative model for the dynamic surface properties including, *but not limited to*, surface tension. We performed droplet impacts of RTLM on glass to establish a baseline of the mechanical and dynamic response of the metal.

An additional metric that is very important to understand, particularly with respect to applications such as inkjet printing is the spread factor $\xi_{max} = D_{max}/D_0$ where D_{max} is the maximum spreading diameter and D_0 is the diameter of the droplet in flight, equivalent to D' for liquid metal droplets. Pasandideh-Fard derived a commonly cited model for ξ using a conservation of energy approach, balancing the kinetic energy of impact with viscous dissipation and work of spreading to determining the following relation [103]:

$$\frac{D_{max}}{D_0} = \xi_{max} = \sqrt{\frac{We + 12}{3(1 - \cos\theta_a) + 4(We/\sqrt{Re})}}$$
1.10

Where θ_a is the advancing contact angle. It can be shown that if $We \gg \sqrt{Re}$ and if $We \gg$ 12 then the relation becomes $\xi_{max} = 0.5Re^{0.25}$ or alternatively $\xi_{max} \sim V^{0.25}$. This derivation model assumes that surface energy and viscous dissipation are of approximately the same magnitude. Clanet arrived at a similar relation between spread factor and impact velocity in the study of droplets impacting on a superhydrophobic surface [99]. In modeling the droplet as largely inviscid and balancing a capillary length enhanced by inertial forces and applying volume conservation arrives at the relation $\xi_{max} \sim We^{0.25}$ which is of note as it also can be written as $\xi_{max} \sim V^{0.5}$ quite a different relation equation (7). This is in line with work done by Schiaffino which characterized droplet impact into four distinct regions as shown in Table 1-2 below [97]. Region I indicates an impact driven event resisted primarily by inertia, meaning that the impact largely spreads out to fully wet unless the solid surface and the liquid have very unfavorable wetting characteristics. Region II represents a capillarity driven (or resisted) force when the maximum spread is largely determined by the wetting characteristics between the liquid and solid phases due to the minor effects of viscosity. Region III represents a capillarity driven, or resisted impact resisted primarily by viscosity where forces at the contact line may be secondary to dissipation in the bulk.

Region IV represents an impact driven spread resisted by viscosity or a flow that may be best characterized by the Reynolds number as shown in Table 1-2. In this table U represents the characteristic velocity and τ is the characteristic time scale. Due to the high surface energy, high density and comparatively low viscosity liquid metal tends to have a very low Ohnesorge number for droplets on the order of millimeters in diameter. Droplet impact experiments with liquid metals will virtually always fall deeply into region meaning spreading is nearly inviscid. Unlike the conclusion drawn by Schiaffino in the above table however, the resisting force for spreading could instead be understood to be the transformation of the kinetic energy at impact to surface energy. In fact, in the paper by Clanet mentioned above, a simplified model was proposed where kinetic energy was fully converted to surface energy as $\rho D_0^3 V^2 \sim \sigma D_{max}^2$ which was not supported by experimental results and in fact has not been observed in prior experiments. Table 1-2: Droplet Impact Regions from Schiaffino and Sonin [97]. Region one indicates an impact driven event resisted primarily by inertia, meaning that the impact largely spreads out to fully wet. Region II represents a capillary driven (or resisted) force when the maximum spread is largely determined by the wetting characteristics between the liquid and solid phases. Region III represents a capillarity driven impact resisted primarily by viscosity where forces at the contact line may be secondary to dissipation in the bulk. Region IV represents an impact driven spread resisted by viscosity.

| | Condition | | | | Driving | Resisting |
|--------|------------|-------------------|--------------------------------------|--|--------------------|-----------|
| Region | 1 | Condition 2 | U | τ | Force | Force |
| I | We≫1 | $Oh \ll We^{1/2}$ | V | D ₀ /V | Impact Pressure | Inertia |
| П | We \ll 1 | $Oh \ll 1$ | (2σ/ρD ₀) ^{1/2} | (ρD ₀ ³ /σ) ^{1/2} | Capillarity | Inertia |
| Ш | We \ll 1 | $Oh \gg 1$ | σ/μ | μD₀/σ | Capillarity | Viscosity |
| IV | We \gg 1 | $Oh \gg We^{1/2}$ | ρV²D₀/μ | μ/ρV² | Impact Pressure | Viscosity |

This would imply a very strong relationship between impact velocity and spread factor and would scale as $\xi_{max} \sim V$. This would suggest an elastic response to the impact not unlike a mass-spring system. Due to the high density, low viscosity and unique surface properties of Galinstan we hypothesized that if any material could demonstrate this behavior, it would be a gallium RTLM.

1.5 Coalescence

Coalescence is a process than occurs before in our lives nearly every day, usually too fast to be seen by the human eye. It is a complex phenomenon involving all of the common force regimes found in fluids: gravitational body force, inertial forces, surface tension, and viscous forces [104,105]. Everything part of the process from the onset of coalescence [106], to the mechanism of a drop joining the bulk fluid [107], to the cascade of partial coalescence into smaller and smaller droplets, as well as external effects such as electric fields [108], or even the cascade of partial coalescence events into increasingly small droplets [9], are all of great interest in current research. Due to the rapidity of the coalescence process, as well as the difficulty in timing the onset of the event, observing this phenomenon was not readily possible until technological leaps in highspeed video were achieved, notably being able to shoot video in a high enough frame rate, and at a long enough time. This required both advances in the camera technology itself, as well as advances in digital storage technology.

Understanding the coalescence process, while valuable simply for advancing the field of fluid dynamics is important for a few key applications as well. Complex and non-linear materials such as those in the merging field of biological additive manufacturing require a very granular of the effects of material properties on the process [109]. The field of microfluidics often involves drop-drop coalescence, or, conversely, the joining of bubbles in a fluid circuit such as the microfluidic bubble logic shown in Figure 1-9.

There are also fundamental phenomena where coalescence serves as an important process such as pouring and drinks and mixing liquids or the formation of raindrops leading to precipitation. Of great interest is the process of partial coalescence wherein after the initial droplet begins to coalesce into the free surface instead of draining completely into the bulk fluid, the capillary bridge pinches off a smaller droplet, often called a daughter droplet. This smaller droplet has a downward velocity due to capillary and, if present, gravity forces and rebounds off the free surface. Developing an understanding of this process is crucial for microgravity applications where, in the absence of gravity, new forms of control are needed to prevent ejection of droplets during printing for process like those shown in Figure 1-10 [111]. The device shown in the figure utilizes electromagnetic fields to control droplet flight path against gravity.



Figure 1-9: Microfluidic bubble logic device [110] which utilizes bubbles as bits and develops logic gates including AND/OR/NOT gates as well as other digital logic functions.

In a true microgravity environment the high degree of capillarity present in liquid metal can result in resistance to coalescence due to stable lubrication layers developing can be which can be further complicated by the presence of thermal effects [112,113]. One strategy may be to attempt to use a vacuum instead of an inert gas however this can complicate the cooling process. Both solutions still require a deep understanding of the coalescence dynamics as the very high surface tension of molten metals makes thermal effects dominate other phenomena which can result in droplets bouncing off the free surface and be being ejected by the print.



Figure 1-10: Gravity suppression additive manufacturing device [111]. Electromagnetic fields produce body forces designed to act opposite of gravity.

Chapter 2: Tensiometry

2.1 Introduction

Tensiometry serves as a tool used to directly measure contact angle, wetted length, or surface tension of various liquids on solids as well as density of liquids. The principle is simple: a carefully chosen probe is inserted into the test liquid and retracted while force and position data are continuously recorded. Knowing three of the above four parameters, contact angle, wetted length, surface tension or density allows for the calculation of the remaining parameter. Some methods such as the Wilhelmy Plate method do not require values of density. Techniques involving tensiometry are useful for characterizing the surface tension of liquids [114,115], the interfacial tension between two different liquids [116], wetting properties of individual fibers or textile materials [117,118], determine the work of adhesion between a liquid and a solid [119], the characterization of complex fluids and surfaces [120,121], and a litany of other uses.

While there is a vast array of possibilities when it comes to tests with a tensiometer, the most popular methods are the ring method and plate method. In our work we make use of the principles involved with both methods and will introduce novel test procedures that utilize concepts employed in both types of measurement. We take measurements of the room temperature liquid metal (RTLM) Galinstan utilizing a carefully selected probe design. For these experiments utilized a Krüss K100 tensiometer for measurement. The measurement capabilities of the K100 tensiometer are described in TABLE 2-1 [122].

TABLE 2-1: Krüss K100 Tensiometer measurement capabilities

| Force Resolution | 10 nN | Measurement Rate | 50 Hz |
|------------------------------|------------|----------------------------|-----------|
| Position Resolution | 16 nm | Rod Method Surface Tension | 0.02 mN/m |
| Plate Method Surface Tension | 0.002 mN/m | Plate Method Contact Angle | 0.01° |

2.1.1 The Du Noüy Ring Method

The Du Noüy ring method was created in 1919 by Pierre Lecomte du Noüy as a new method for measuring surface tension, and later adapted to measure interfacial tension as well [123,124]. The method is transient, which differs from the Wilhelmy plate method discussed below. This can be seen as a disadvantage in cases with changing surface tension such as surfactant ladened fluids, but can also prove useful to characterize the surface tension of the new surface as a function of time [125]. The advantage of this method is that the ring probe has a comparatively larger wetted length compared to other probes of similar size making for more accurate measurements on a given tensiometer.

The ring method is detailed in Figure 2-1. The ring is lowered into the liquid and slowly withdrawn creating a lamella above the free surface. Ideally the ring is composed of platinum which has a very high surface energy which causes many liquids to have low contact angles. As the lamella raises it forces the contact angle towards 0° as shown in step 7 of the figure. After which point the lamella begins to break and the contact angle dips below 0°. For older tensiometers this was the end of the test but for the K100 as it is a digital tensiometer it can

detect the force maximum and relax the lamella by a prescribed amount before making an additional measurement.



Figure 2-1: Du Noüy Ring Method: 1 the weight of the ring is zeroed. 2 the ring contacts the surface and initial positive force is detected from wetting. 3 ring is depressed into fluid and negative force is detected due to inversion of surface tension 4 small positive or negative force is observed due to buoyancy (negative) or surface tension on supporting structure (positive). 5-6 Ring is lifted through the surface and force increases as lamella is lifted from surface. 7 maximum force is measured equal to the surface tension force and the lamella weight. 8 The lamella begins to rupture and the force decreases. [126].

The surface tension can then be expressed with the following formula:

$$\sigma = \frac{F - W_l}{2\pi(r_i + r_o)}$$
2.1

Where r_i and r_o are the inner and outer radii of the ring respectively, W_l is the weight of the lamella and F is the force as measured by the tensiometer. The weight and shape of the lamella causes some complication and can be estimated by a few established methods such as the Harking-Jordan method [127], the Hun-Mason method [128], or the Zuidema – Waters method [129].

2.1.2 The Wilhelmy Plate Method

The Wilhelmy plate method was developed in 1863 by Ludwig Wilhelmy with the intention of studying surface tension as well as the adhesion and cohesion of fluids [130,131]. The plate method gave an effective way to measure the work of adhesion which is the energy required to create or destroy a liquid solid interface [132]. This expression is given by:

$$W_{ls} = \sigma_l (1 + \cos \theta_c)$$
 2.2

Where W_{ls} is the work of adhesion, σ_l is the surface tension and θ_c is the contact angle. This expression indicates that a lower contact angle indicates a higher degree of adhesion between the liquid and solid surface as the work of adhesion follows $W_{ls} = 2\sigma_l$ for $\theta_c = 0$ which is equal to the work of cohesion meaning that the liquid phase molecules favor the solid surface as much as they favor each other [133]. Equation 2.2 derives from the famous Young equation which defines the relation between the solid surface energy σ_{sg} , the surface tension or liquid vapor surface energy σ_l , and the liquid solid surface energy σ_{ls} . The Young Equation ca be written as follows [131] and each term is shown in Figure 2-2:

$$\sigma_{sg} - \sigma_{sl} - \sigma_l \cos \theta_c = 0 \tag{2.3}$$



Figure 2-2: Fluid on surface with various surface energies and their influence on the contact line.

The solid liquid surface energy is difficult to determine empirically so equation 2.2 is derived from equation 2.3 by finding the minimum of the expression for the derivative of free energy with respect to area [132]. The convenience of this expression is that it reduces the work of adhesion to functions of the contact angle and surface tension, both values that can be readily measured with the Wilhelmy plate method. This method also sees a high degree of use in studying complex [134], the behavior of the triple line [135], and contact angle hysteresis which can be used to quantify surface roughness [136].

There are three primary measurement methods with the Wilhelmy plate method: The static surface or interfacial tension measurement, the static contact angle method and the dynamic contact angle method which includes advancing and receding contact angle

measurements. Figure 2-3 shows the setup for the plate method. Surface tension can be found with the following equation:

$$\sigma = \frac{F}{(2w+2d)\cos\theta}$$
 2.4

Where all values are as listed in equation 2.1 and w is the plate width while d is the plate thickness. Equation 2.4 can also be manipulated to solve for the wetted length or contact angle as well and presupposes that the plate is not immersed in the fluid. When measuring the static surface tension or contact angle the plate is first immersed in the liquid then brought to the level of the liquid surface. This requires a wetting fluid in order to make a measurement so once again platinum is the ideal material due to its high surface energy and it is often roughened to increase its wetting potential. Liquids that are not fully wetting can still be measured but the contact angle must be known *a priori* in order to measure the surface tension as noted in equation 2.4. Of course, the contact angle may be measured separately such as with the sessile drop method and then combined with the Wilhelmy plate method to characterize both surface tension and contact angle.

Contact angle hysteresis is defined as $\theta_a - \theta_r$ where θ_a and θ_r are the advancing and receding contact angles respectively and can be attributed to contaminants on the surface or surface roughness as well [138]. A classic example of this phenomenon is a raindrop on a vertical window [139]. Gravity pulls on the raindrop which creates a wetting asymmetry, the contact angle on the dop of the drop decreases, while the contact angle on the bottom decreases. This asymmetry is at equilibrium with gravity, provided that the drop volume is small enough, and allows the droplet to remained pinned to the glass. As such the degree of contact angle hysteresis can be a useful tool for characterizing surface roughness as well as the degree of



Figure 2-3: Wilhelmy plate method [137]. The z axis represents the depth below the surface.

apparent drag of the surface on the droplet. For example, water on superhydrophobic surfaces is known to have high contact angles but low hysteresis when in the Cassie-Baxter state as higher hysteresis is associated with sticking to surfaces [140].

The procedure for measuring contact angle hysteresis is also known as the dynamic contact angle measurement. This method consists of lowering the probe into the liquid while recording displacement and force. As the probe advances into the liquid, the advancing contact

angle is achieved. The plate is lowered to the prescribed maximum depth, where the test may dwell for an optional prescribed period to account for any unsteady or inertial effects. The plate is then retracted to the minimum depth, during which period the receding contact angle is achieved. During this entire process, the contact angle is measured as follows:

$$\theta = \cos^{-1} \frac{F + \rho g \Psi}{(2w + 2d)\sigma} = \cos^{-1} \frac{F + \rho g (wdz)}{(2w + 2d)\sigma}$$
2.5

Where θ is the dynamic contact angle, advancing or receding depending the on the sequence, and $\rho g(wdz)$ is the buoyant force which must be accounted for in real time, and F is the force value as measured by the K100 sensor, and z is the immersion depth. The K100 is capable of providing continuous contact angle measurement throughout the process if the liquid surface tension and density are known. For our experiments we selected glass rods to exploit the material properties of the liquid metal. Figure 2-4 demonstrates the dynamic contact angle test for three runs with precision machined glass rods 2 mm in diameter. The first three plots show the contact angle while the next three show the raw force measurements.



Figure 2-4: Dynamic contact angle measurements for 2 mm diameter glass rod in deionized water. Are paired by contact angle and force for the same trial in each row.

Each plot represents three separate passes per rod with the red circles being the first, the green triangles the second and the blue squares are the third. For these cases, the initial pass gave a mean advancing angle of $\theta_a = 70.78^{\circ} \pm 1.76^{\circ}$ and for passes 2 and 3 the advancing contact angle was $\theta_a = 76.19^{\circ} \pm 2.75^{\circ}$. The difference between the advancing angle in pass 1 as compared to passes 2 and 3 can be attributed to the fact that the prob is dry on the first pass and is prewetted on passes 2 and 3. The receding contact angle was consistent across all three passes and was found to be $\theta_r = 50.29^{\circ} \pm 0.70^{\circ}$. Note from the force diagrams that the force remains positive throughout the majority of the sequence due to the surface tension but dips into the negative region at maximum depth. This is attributed to the buoyant force which provides a negative force to the sensor, netting a positive effect for the contact angle per equation 2.5.

There are a few key features of Figure 2-4 to take note of. First, note that the contact angles are consistent throughout immersion and withdrawal sequences, particularly the receding contact angle. Also note that there is a region where the contact angle must change over from advance to receding and vice versa around 1 mm of immersion and 5 mm of immersion, the minimum and maximum immersion depths, respectively. This figure will serve as the basis for normal wetting behavior on the 2 mm glass rods. Note that for the rods equation 2.5 can take a modified form:

$$\theta = \cos^{-1} \frac{F + \rho g(\pi D^2 z)}{\pi D\sigma}$$
 2.6

Where *D* is the diameter of the glass rod.

2.2 Liquid Metal Tensiometry Experimental Setup

2.2.1 Static Surface Tension

The first method of characterizing the Galinstan we employed was to utilize a modified version of the static Wilhelmy method. Glass was chosen since it has been shown that galliumbased alloys adhere strongly to glass due to the external oxide layer. Due to the mechanical properties of the oxide, indirect methods of surface tension measurement such as the pendant drop or contact angle methods have produced results ranging from 0.501 N/m to 0.718 N/m as summarized by Liu et al [60]. To avoid complications associated with these methods we sought to measure the mechanical response directly. However, this proved problematic as Galinstan does not "wet" surfaces in the conventional sense. In fact, Liu's group observed a range of contact angles from 7° to 165° however the tests were incomplete due to insufficiencies of the sessile drop method for making the measurement. As such there is no established value of equilibrium contact angle for use in the equation:

$$\sigma = \frac{F}{\pi D \cos \theta_c}$$
 2.7

The stiffness of the skin may provide a solution here. Due to the skins ability to store energy it has a form of "memory", more properly described as elasticity. This can be exploited by changing the initial immersion depth before returning to the surface level. This will change the lamella height off the free surface $h_{lamella}$ as shown in Figure 2-6 (a). It is assumed that this height is equal to the immersion depth, but this is limited to a maximum value as the skin may break, causing the metal to dewet. We setup the rod with an immersion depth of 4 mm and quickly realized that the results would not be consistent enough with this method. This led to a refined method as detailed in section 2.2.2. Setup for this static method (and subsequent dynamic method) is shown in below.



Figure 2-5: (a) Glass rod tensiometry experiment setup with Krüss K100 tensiometer and 2 mm diameter rod. (b) Rod immersion sequence. (c) Rod retraction sequence.

2.2.2 Dynamic Surface Tension Measurement

Since the contact angle of the liquid metal on glass is a function of the applied load, then the Du Noüy ring method became an attractive alternative since raising the probe out of the liquid pool until the force reached a maximum would force the contact angle to 0. The main obstacle for directly applying the ring method is the probe itself. The standard Krüss ring is composed of platinum, however this is problematic as Galinstan forms an amalgam with many metals and could possibly degrade the ring, a costly prospect [57]. Designing a ring out of glass could possibly have worked, but again would be a costly and timely endeavor, and a thin glass ring would be a very delicate instrument to use. Instead, the rod again proved to be the ideal choice as the mechanical elasticity of the skin could be exploited to force the contact angle towards 0. The K100 was set to run the standard ring protocol, but the glass probe was loaded into the machine instead per Figure 2-5 (a). The rod was then immersed and brough tot the free surface per Figure 2-6 (a). But the process then continues raising the probe out of the liquid to height *h*. This height is determined automatically by the K100 software. Once the force reaches a maximum and begins to decrease as shown in Figure 2-1 in steps 7 and 8 the rod is lowered 10% to relax the lamella and the maximum force is recorded. This process is then repeated for the prescribed number of measurements.



Figure 2-6: Tensiometry using rod. (a) Nominal static position of glass rod. Bottom of rod is coplanar with the unperturbed free surface. The true height of the lamella, $h_{lam, true}$, is a function of the immersion depth and the material properties of the liquid metal. (b) Rod during tear off procedure. Rod is raised to height h_{lam} as measured by the K100 Tensiometer. The true lamella height, $h_{lam, true}$, is this height plus the initial wetted height on the rod. (c) The initial contact angle θ_c . Due to the nature of the oxide layer this value is a function of the immersion depth. (d) The contact angle θ_c tends towards 0 due to mechanical forces. The maximum measured force of F_{σ} multiplied by the wetted area represents the apparent surface tension.

This method of recording the maxium force forces the contact angle to 0 as shown in Figure 2-6 (c) and (d). Since only the force values are being recorded, the calculation for surface tension must be done manually. This calculation is very similar to the principles laid out in equation 2.6 with a a key difference:

$$\sigma = \frac{F - \rho g \pi D^2 h}{\pi D}$$
 2.8

Here the lamella conntibution is in the opposite direction as the buoyant force of the displaced liquid in equation 2.6. The K100 outputs values of lamella height, which corresponds to the bottom of the rod, h, the time, and the force. We manually combined these values to meaure the effective surface tension.

2.2.3 Contact Angle Hystersis

The final set of tests were conducted in order to further understand the wetting behavior of the liquid metal by measuring the contact angle hysteresis. These tests rely on the results from the dynamic surface tension tests as in input parameter. Once again, the rod was used as the implement and the K100 dynamic contact angle module was taken advantage of. Since the density, $\rho = 6440 kg/m^3$, and effective surface tension were known the K100 can calculate contact angle continuously at each immersion point. The software in this case automatically calculates the buoyancy force and solves the following equation:

$$\theta = \frac{F + \rho g \pi D^2 z}{\pi D}$$
 2.9

Where z once again is the depth below the free surface as shown in Figure 2-3. The Hysteresis measurements were taken six times with three passes per trial. Both the force and contact angle information were obtained as functions of the immersion depth as shown in Figure 2-4. The range of immersion depths was the same as the water case with 1 mm minimum immersion and 5 mm maximum which are the default values for the K100 module. The same glass rods were used for these experiments and each trial represents a different rod. Between all three types of measurements the rods needed to be cleaned thoroughly as the metal left a distinct wetted layer. The were first cleaned with 1 M NaOH to reduce the oxidized film and strip it. Then the probes were thoroughly cleaned with DI water, then with 70% isopropyl alcohol before being wiped clean and dry with lint free Kimwipes. This cleaning procedure was found to enable repeatable results across all test methods.

2.3 Results and Discussion

2.3.1 Static Surface Tension

Measuring the static surface tension quickly presented an issue. Equation 2.7 makes it clear that the equilibrium contact angle θ_c must be known in order to measure the surface tension. This is complicated by the fact that the liquid metal has no apparent equilibrium contact angle and instead assumes an angle that is a function of how it came into contact with the substrate. For this test, the immersion depth determines the contact angle at the time of measuring. The problem with this is that it would require a timely procedure to determine the contact angle where more efficient methods exist.



Figure 2-7: Static surface tension vs time. Each marker represents an individual measurement. Each separate color and symbol represent a distinct trial run.

Figure 2-7 shows the static surface tension measurements vs the time for 4 mm immersions. Each separate symbol represents an individual trial. The measured value of surface tension is given by $\sigma_{eff} = 0.556 \pm 0.022 \ N/m$. However, there were a few issues with this data. As stated, before the contact angle was not known so this above surface tension is incomplete. Furthermore, we observed that the liquid metal left a very clear film after wetting the rod. This seemed to change the wetting behavior of the metal and the surface tension clearly

decreases in time as seen in the figure with each subsequent retest. Since there is no reason to believe that the surface tension should be a function of time as the oxidation time scale is much faster than the time between tests, this means that rewetting the rod affects subsequent tests. We desire data that is consistent in time.



2.3.2 Dynamic Surface Tension

Figure 2-8: Calculated surface tension as a function of lamella height for 2mm diameter glass rod in Galinstan. Red dashed line is the mean value $\sigma = 0.628 N/m$.

Figure 2-8 shows the measured surface tension measurements for the dynamic method. The average value was found to be $\sigma = 0.628 \pm 0.037 N/m$. These results were consistent across time and with lamella height. This value is withing the range of values reported in the literature of 0.501-0.718 N/m and in fact falls close to the middle of the range. An interesting feature of these tests can be observed in the x-axis of Figure 2-8. As the test sequence continues the rod continued to get higher with each test indicating the maximum occurred at a greater height each time. This can either be attributed to the pre-wetted rod changing the wetting mechanics between each measurement, or a relaxation period allowing for the skin to reach a new equilibrium. Either way the result indicates that the surface tension is *not* a function of the lamella height so the force on the rod is only a function of wetted length and not the degree of strain. This is an important result as it will allow this value to be used for droplet impacts modeling in chapter 3. The data in Figure 2-8 can be viewed on a per trial basis in Appendix I in Figure AI-0-2. This figure makes it clear that the surface tension does not vary with time or lamella height in any given test sequence.

The summary of the lamella height data vs time can be found in Figure 2-9. Recall that the lamella height is determined by the K100 software and found when the force is maximum, so the increase indicates that the change in height is due to response from the liquid. As seen in the figure the response increases linearly with each measurement. It is likely that with each subsequent measurement the surface has time to reach a new equilibrium and a similar amount of strain is required to reach the maximum force value.



Figure 2-9: Lamella height vs time. Each symbol designates a different trial sequence. This figure is a selection of a few trials. The full set can be found in Figure AI-0-3 in Appendix I.

The mean height differential Δh was found to be 0.17 mm and the standard deviation was 0.06 mm. This indicates that an induced strain on the order of 100-200 µm is required to have the skin come to tension. This distance is small for most applications but can add up for repetitive tests such as those shown in the figure.
2.3.3 Contact angle hysteresis

For the dynamic contact angle measurements, the liquid metal displayed unique behavior, particularly when contrasted with a more common wetting liquid such as water as detailed in Figure 2-4. Here, Figure 2-10 shows the contact angle as a function of immersion depth for six trials with three passes for each trial. Figure 2-12 shows graph 1 in greater detail including annotation of the direction of the plate and indication of advancing and receding contact angles. The results were quite striking for the initial pass the advancing contact angle was found to be $\theta_a = 180^o$ for all six passes. This indicates the strong effect of the film after the initial pass which affects the wetting behavior for subsequent passes. For this first pass there is also a short period approximately from 1-2 mm of immersion where the contact angle ramps up to 180° before reaching this value at around 2 mm. This is the process of the probe first entering the liquid and establishing the advancing angle. This also indicates the strong function of mechanical work on the contact angle since the hysteresis was quite significant. Figure 2-11 shows the force measurements from the K100. The first pass has a negative value of around -4 mN which includes the buoyant force (which is measured as negative) and the surface force. This value is consistent during the first pass.

For passes 2 and 3 the advancing behavior changed quite dramatically. The contact angle initially begins relatively low, around $\theta_a = 50^\circ$. As the plate advances the contact angle increases to an inflection point of $\theta_a = 90^\circ - 100^\circ$ which occurs nearly exactly at the capillary length of $l_c = 3.15 \ mm$.

51



Figure 2-10: Contact angle vs Immersion depth for 2mm glass rod in Galinstan. Each chart represents a different trial run with 3 passes each and corresponds directly to Figure 2-11.



Figure 2-11: Force vs Immersion depth for 2 mm glass rod in Galinstan



Figure 2-12: Detailed view of graph 1 of Figure 2-10. Arrows indicate directions of test progression for advancing and receding portions of the contact angle tests.

This behavior is highly unusual as compared to normal fluids such as the water where the advancing angle is constant or nearly constant throughout the advancing process. This further reinforces the roll of the elasticity of the skin and how mechanical work informs how the metal wets the surface. The force value can be seen reaching 0 near this point but it is slightly offset due to the buoyant force calculation. The advancing contact angle then continues to a value of $\theta_a = 150^\circ - 165^\circ$ before beginning the receding process. During this portion, the concavity of the graph is no concave up as opposed to concave down.

For the receding contact angle portion of the tests the behavior is the same for much of the test for all 3 passes with the exception of the final millimeter of travel. Once again, the concavity changes near the capillary length and the receding contact angle and force diagram is very nearly the mirror image for passes 2 and 3. The contact angle then switches to concave down and approaches the final, minimum contact angle. For the first pass the final contact angle was roughly $\theta_a = 30^o$ for all 6 trials. Then for passes 2 and 3 the final angle decreased, tending towards 0 with each subsequent pass. For all 6 trials the 3rd pass saw a final contact angle at or near 0 while the 2nd pass saw a final receding contact angle between $\theta_r = 0^o - 17^o$. This is indicative that prewetting strongly affects the subsequent wetting behavior. For a newly cleaned probe, the metal appears to be highly non-wetting. As the metal passes up and down the probe it leaves visible residue in the form of a dark grey tint. For subsequent passes the contact angles, particularly the advancing after the first pass and the final receding with each pass all become markedly lower. Amazingly this liquid metal demonstrates full hysteresis of 180° the maximum value that is possible. This also indicates that the liquid metal will resist any change once equilibrium is established. When wetted and sheared it will assume lower and lower contact angles increasing the effective wetting. When unwetted and sheared it will assume a maximal contact angle in order to resist wetting.

2.4 Conclusion

In this chapter we have performed a number of tests with the Krüss K100 tensiometer. First we performed a measurement with using the standard Wilhelmy plate method but substituted a rod for a plate at the cost of accuracy due to issues with the plate geometry and the metal. Using this method, we measured a surface tension value of $\sigma_{eff} = 0.556 \pm 0.022 \ N/m$ but σ_{eff} is inaccurate as it does not account for the contact angle. This led to the conclusion that this method was insufficient for obtaining the surface tension.

Using the glass rod probe, we developed a new method of measuring the surface tension for materials with elasticity in the skin. Due to the skins ability to hold its shape and resist wetting or dewetting we combined the principles of the Wilhelmy plate method with the Du Noüy ring method. By withdrawing the rod from the liquid pool over the free surface the metal was forced to wet the surface allowing for the measurement of the surface tension with $\theta_c = 0^o$. The calculation was performed manually including accounting for the weight of the lamella. The value for surface tension measured was $\sigma = 0.628 \pm 0.037 N/m$. This value is new to literature, but falls within the range of values previously published.

Finally, we performed dynamic contact angle hysteresis measurements from 1 mm to 5 mm depth. For the first pass the metal proved to be fully non-wetting giving a contact angle of $\theta_a = 180^\circ$. As the rod developed a film the advancing contact angle dropped but it still varied through the test indicating that the fluid likely remained pinned. For the receding cases the contact angle followed a similar behavior, varying throughout the retraction sequence and tending towards low values of θ_r . In some cases, but not all, the contact angle terminated at 0° indicating complete hysteresis of $\theta_a - \theta_r = 180^\circ$. This wetting behavior is quite novel and indicates the importance of considering the complicated mechanics of the skin when using Galinstan or similar metals for research or application.

Chapter 3: Droplet Impact

3.1 Introduction

Gallium alloys have received a great deal of attention due to their vast array of applications particularly in the fields of flexible and stretchable electronics, microfluidics, biomedical engineering, and chemistry [1,2,141–144]. They are often called Room Temperature Liquid Metals (RTLM), a term coined by Dickey whose group has done a great deal research about these alloys [80,145,146]. These metals tend to be gallium based and are often combined with indium, usually called EGaIn, as well as tin, commercially known as Galinstan [3,147]. This research focused on a eutectic alloy comprised of 68.5% gallium, 21.5% indium, and 10% tin known commercial as Galinstan and is available commercially from Geratherm Medical AG in Germany or RG Medical Diagnostics in the US. This formulation is ideal as it is a eutectic with one of the lowest melting points at -19 °C as well high electrical and thermal conductivities of 2.30 x 10⁻⁶ S/m and 16.5 W·m⁻¹·k⁻¹ respectively. Furthermore, Galinstan has a low vapor pressure and is considered non-toxic making in an attractive candidate for research and practical applications [54,60]. While there have been studies of certain properties of RTLM such as viscosity μ , and the effect of oxidation and reduction on interfacial properties such as surface tension σ , there is still a need to understand the effects of oxidation at the surface for dynamic events and to develop a predictive model for these effects [62]. Li, et al were able to generate liquid metal droplets from Galinstan utilizing HCl as a reducing agent and leveraged Plateau-Rayleigh instabilities to break-up the stream into droplets. However, the finished print warrants improvement in terms of consistency and resolution [148]. Xu, et al performed droplet impacts

with a similar liquid metal EGaIn but focused on the effect of acid wash vs the oxidized case [95]. That study utilized rheology to quantify elastic effects in order to modify the impacting Weber number to fit the data. In this work we take a different approach in studying a different alloy and in how we model the skin effect, instead treating it like a mechanical spring and achieve different results. The focus of this manuscript is on the impacts of droplets and how features such as the droplet volume Ψ and the impact velocity V_0 affect the spread factor $\xi_{max} = D_{max}/D_0$, spread time t_s and to present a model for this behavior. This will also be cast in terms of the Weber number We = $\rho V^2 D_0 / \sigma$ and Reynolds number Re = $\rho V D_0 / \mu$ where ρ is the liquid metal density and other variables are as mentioned previously.



Figure 3-1. (a) (Left) RTLM droplet in flight with 2 mm scale bar. Shape is maintained through entire falling sequence. The tail is a result of elastic stresses in the skin resisting the minimization of surface area due to cohesive forces in the bulk. (Right) Water droplet in flight with 1 mm scale bar. (b) Diagram of oxide layer. F_s represents the oxide skin force which is not necessarily in tension while F_c are the cohesive forces in the bulk.

3.1.1 Surface Characterization

Critical to understanding the behavior of RTLM's is the study of oxidation occurring at the surface of the fluid. There is some disagreement about the surface tension of this commonly used formulation with the value presented as between 501 mN/m and 718 mN/m [60,63]. Many authors

attribute this difference to different formulations of the material (e.g from additives) but it also may be due to a failure to quantify and account for different levels of oxidation and/or reduction at the surface, as well as the use of different techniques for measuring apparent surface tension. The gallium oxides that form at the surface form a "skin" that is self-limiting, insulating the bulk material from further oxidation and generally remains between 0.5-3 nm thick [149,150]. Despite being very thin this oxide layer stores strain energy and resists typical capillary phenomena such as the minimization of surface area as shown in Figure 3-1 (a). This skin layer has dramatic effects regarding both the way the fluid flows and interfacial phenomena such as surface minimization, Plateau-Rayleigh instabilities, and coronal instabilities [6,90]. Figure 3-1 (b) shows the presence of the skin as well as the proposed forces at work, a distributed cohesive force, F_c that would normally be modeled as surface tension, and a separate mechanical stress in the skin, F_s, which can be either in tension or compression.

It is often erroneously reported that gallium alloys wet glass and other similar surfaces when in fact, RTLM's do adhere to glass due to the skin but they do not spread due capillary forces, only due to gravity and mechanical work. In fact, when oxidation is prevented, such as in an inert environment, the advancing contact angle θ_a is 146.8° and the receding contact angle θ_r is 121.6 indicating a highly non-wetting liquid [60]. Note that this oxide layer can be reduced with strong acids and strong bases such as sodium hydroxide, NaOH, and hydrochloric acid, HCl as studied by Handschuh-Wang, et al [151].

Correctly quantifying surface vs bulk forces is important when understanding the mechanics of RTLM. $\sigma = 0.718$ N/m is commonly reported as the surface tension of oxidized Galinstan due to the oxidation the apparent surface tension is a strong function of the method used

as well as the method by which the droplet surfaces are created [67]. For example, in another study Vaclav Kocourek found the surface tension of this composition to be $\sigma = 0.517$ N/m using a contact angle method [152]. This leads a range of values spanning 200 mN/m in the literature. To account for this disparity, we chose to measure the mechanical stress using a direct method, tensiometry, rather than sessile droplet or pendant droplet methods. We utilized a Krüss Scientific K100 tensiometer and employed a common method of tensiometry known as the Whilemy plate method. Due to gallium's propensity to form amalgams with many metals, this method was modified to utilize a glass rod which mimics the substrate material on which the impacts occurred. It was also found the rod geometry produced more repeatable results than a plate geometry due to material remaining adhered to the edges of the plate. The value for the effective surface tension σ_{eff} was found to be $\sigma_{eff} = 0.628 \pm 0.037 N/m$. The variability of the data can be attributed to the relatively small wetted length of the rod vs the plate methods. This value falls withing the range established by literature, appearing about right at the midpoint for reported values. $\sigma_{eff} = 0.628$ N/m is the value we used for calculation in this manuscript and this value as well as other material properties are listed in

Table 3-1: Material properties of liquid metal eutectic. Formulation is 68.5% Ga, 21.5% In and 10% Sn [63,76].

| Boiling Point | 1300 °C | Melting Point | -19 °C |
|-----------------|------------------|------------------|-------------|
| Vapor Pressure | < 1.33 x 10-6 Pa | Density | 6.44 g/cm3 |
| Surface Tension | 0.628 N/m | Viscosity (Bulk) | 0.0024 Pa.s |

3.2 Droplet Impact Background

The study of impacting droplets provides an opportunity to investigate the relative effects of various fundamental forces in fluid mechanics including viscous, capillary and interfacial, gravity, and inertial forces [101]. It is also useful designing and fine-tuning droplet based methods of manufacturing with metals [153,154]. The most common model for droplet impact and the spreading ξ was derived by Pasandideh-Fard et al [103]:

$$\frac{D_{max}}{D_0} = \xi_{max} = \sqrt{\frac{We + 12}{3(1 - \cos\theta_a) + 4(We/\sqrt{Re})}}$$
3.1

Which was derived by equating the impacting kinetic and surface energies with the viscous dissipation as well as the work of spreading. This relationship can be reduced as follows:

$$\xi_{max} = 0.5 Re^{0.25}$$
 or, $\xi_{max} \sim V^{0.25}$ 3.2

Equation 3.2 applies for cases where $We \gg \sqrt{Re}$ and if $We \gg 12$. Pasandideh-Fard derived this by modeling the work of spreading per Carey, who notes that non-wetting liquids require much more work to spread given by [132]:

$$W_{sn} = \sigma A (1 - \cos(\theta_a))$$
3.3

Where A is the wetted area and W_{sp} is the work associated with spreading. This model is applicable for many typical surfaces however it underpredicts the power law scaling term of the

spreading if the surface is sufficiently non-wetting. For example, water on a hydrophobic surface will scale differently from the model in equation 3.2 for a given impact velocity, and by extension, Weber and Reynolds numbers. Clanet, et al. studied water drops impacting on solid surfaces with super-hydrophobic coatings [155].

In this analysis they were able to determine that viscosity had a negligible effect, likely due to slip length at the interface, and constructed a model based on the capillary length with the impact deceleration taking the place of gravity producing a "gravity puddle". The result was found to scale as:

$$\xi_{max} \sim We^{0.25}$$
 or, $\xi_{max} \sim V^{0.5}$ 3.4

With the coefficient of proportionality to be 0.9 Equation 3.4 indicates as the Weber number, We, increases, there is a decidedly different change in ξ_{max} as compared to equation 3.2. It also should be noted that due to the hydrophobicity ξ_{max} does not represent the final diameter as the droplets would rebound and even bounce at sufficiently high enough impact velocities [98]. Of note is that Clanet's paper did speculate that in an elastic impact $\xi_{max} \sim We^{0.5}$ or $\xi_{max} \sim V$, but was not able to confirm this empirically and then went on to derive the aforementioned model.



Figure 3-2: Impact sequence of liquid metal droplets at We = 42.6 (above) and DI water droplets at We = 41.6 (below) on hydrophobic substrate. Time stamps are 0 ms, 0.4 ms, 0.9 ms, 1.7 ms, 3.5 ms, and 15.4 ms for both sequences. Scale bar indicates 1 mm.



Figure 3-3: Impact sequence shown in Figure 3-3 normalized by D_{max} note that ξ_{max} is not the same for both data sets.

Although the results listed in equation 3.4 seem to indicate an effective conversion of kinetic energy to maximum spread the process of complicated by the rebounding and bouncing nature after maximum deformation. The ideal impact for printing applications is a droplet impact where the droplet impacts and becomes arrested at ξ_{max} without splashing or fingering, often called a *deposition* style impact [92]. In this regard, RTLM are highly desirable. One might expect the fluid to rebound due to high surface tension like in Clanet's work, but the oxide layer adheres to the glass. Furthermore the oxide layer has a degree of elasticity and provides mechanical stability for the deposited material and has been demonstrated to produce free standing liquid

structures [67,71]. There has been very little study of these liquids in the field of droplet impact. Xu, et al. studied an alloy, EGaIn, however they observed a different relationship than our work found either due to the different material composition or perhaps chemical reaction with the needle as gallium readily forms an amalgam with most metals [56].

Figure 3-2 shows the impact sequence for a liquid metal droplet on a glass substrate and DI water on a hydrophobic substrate. The droplets were matched by Weber number and the impact sequences look quite similar until $D = D_{max}$ at which point the water begins to rebound while the metal droplet is pinned in place due to the oxide glass adhesion. This is a sign that bulk viscosity plays a small or negligible role similar to Clanet's observations. Schiaffino and Sonin studied droplet impacts over a range of We and Ohnesorge numbers, Oh, and created 4 categories of droplet impact by the resisting and driving forces and based on the material properties of the RTLM and the impact conditions all of the impact sequences tested could be considered impact driven (as opposed to capillarity) and inviscid as shown by Region I below. [97].



Figure 3-4: Droplet impact regions as defined by Schiaffino and Sonin [97]

3.3 Experimental Setup

Our test setup for the droplet impact testing included stepper motor-controlled Z-axis in order to adjust the height and impact velocity. A Phantom V7.2 (Vision Research) high speed camera was mounted to an optical table and lit with a high-power LED backlight and diffuser. A Kent Scientific Genie Plus syringe pump was used to pump RTLM out of needles composed of composites polytetrafluoroethylene (PTFE) or polypropylene in order to ensure there was no chemical reaction between the metal and dispensing needle. 3 needle sizes were used in order to modulate the droplet volume, a 20-, 25- and 30-gauge needle. We also performed comparative

experiments of water droplets impacting a hydrophobic substrate. These results were comparted to Clanet's work and found to fit the model. Every impact sequence was shot at 10000 frames per second and image analysis was carried out with ImageJ software with spatial resolution of 17 μ m – 20 μ m. The setup is shown in Figure 3-5.

Due to the oxide layer's presence the droplets in flight did not minimize surface area and assume spherical shapes as previously mentioned. In fact, the droplets had different shapes when dispensed from the different needle sizes but did remain consistent in shape and volume from any given needle. In order to account for shape effects, the droplet volumes were used and a sphere equivalent diameter D_0 was chosen as follows:

$$D_0 = \left(\frac{6}{\pi} \mathcal{V}\right)^{1/3} \tag{3.5}$$

Where the volume Ψ was determined by image analysis using the ImageJ software. For all background information and for DI water impacts in this document D_0 refers to the droplet flight diameter.



Figure 3-5: Experimental set up for droplet impact experiments.

For RTLM specifically, D_0 is given by equation 3.5 but refers to the nominal diameter when discussing other droplets such as the water droplet. The three needle sizes, 20G, 25G and 30G were chosen in order to study the effects of droplet volume. The average volume for the 20G was 22.38 µl giving $D_0 = 3.50$ mm, for the 25G was 10.73 µl giving $D_0 = 2.74$ mm, and for the 25G was 6.85 µl giving $D_0 = 2.35$ mm.

The droplet impacts were carried out for a range of conditions 12.1 .7 \leq We \leq 205.5 and 4270 \leq Re \leq 19979. For all impacts there were no satellite droplets observed and only minor fingering at the lamella at the highest Weber numbers. The adhesion of the oxide layer to the substrate meant the final diameter was equal to D_{max}, in other words there was no retraction or rebound. The test conditions are summarized in TABLE 3-2.

| $D_0 (\mathrm{mm})$ | Weber No. | Ohnesorge No. | Reynolds No. |
|---------------------|---|--|---|
| 2.28 | 10.7 | 6.3 x 10 ⁻⁴ | 4270 |
| 3.52 | 205.5 | 7.9 x 10 ⁻⁴ | 19979 |
| 2.67 | 84.1 | 7.3 x 10 ⁻⁴ | 11753 |
| | D ₀ (mm) 2.28 3.52 2.67 | D ₀ (mm) Weber No. 2.28 10.7 3.52 205.5 2.67 84.1 | D_0 (mm)Weber No.Ohnesorge No.2.2810.7 $6.3 \ge 10^{-4}$ 3.52205.5 $7.9 \ge 10^{-4}$ 2.6784.1 $7.3 \ge 10^{-4}$ |

TABLE 3-2: Galinstan Impact Conditions

3.4 Impact Model

Due to the fact that oxidation is confined to the surface, the dynamics can be considered quite complicated if fully parsed out. There is adhesion between the elastic skin and the glass substrate, there are the mechanical properties of the skin to account for, there is the interfacial energy between the oxide skin and the non-oxidized bulk, as well as the bulk viscosity and inertia to contend with. As is often the case a simplified model is sufficient to explain this complicated interaction.

We begin by assuming that the net result of these forces is a restoring force, F_{rest} , that acts at the contact line that follows scales as the Hookean model with the length of the contact line and the effective surface tension [156]:

$$F_{rest} \sim \sigma_{eff} \pi (D - D_{eq})$$
 3.6

Where D_{eq} represents the equilibrium position, the state of zero tension or compression. As the diameter *D* increases the restoring force increases linearly, albeit with an offset. D_{eq} . This offset can be observed empirically by depositing the droplets directly onto the substrate so that $V_0 \approx 0$ and therefore We = 0. In doing this we found the equilibrium diameter as a function of D_0 to be $D_{eq} = 0.6D_0$. We then seek to develop the energy associated with this term as the droplet spreads, we do this by integrating the force over the path:

$$E = \int F_{rest} dx = \sigma_{eff} \pi C \int (D - 0.6D_0) d(D - 0.6D_0) = \frac{\sigma_{eff} \pi C}{2} (D - 0.6D_0)^2$$
 3.7

Where C is constant that will serve as a scaling term to be determined form the experimental data. Note that expression 3.7 relies on the results from Chapter 2 in that it assumes the advancing contact angle is 180°. This model is a familiar Hookean model of a mass-spring system as shown in Figure 3-6. Here the surface tension represents the spring stiffness while the friction coefficients are $\mu_k = 0$ for spreading and μ_s is very large at arrest. This shows that the

surface tension serves to limit the maximum spread and the large μ_s serves to capture the contact line arrest at ξ_{max} .



Figure 3-6: Liquid metal mass-spring analogy

This expression can be used in a conservation of energy equation following the method described by the energy balance described in Chandra's work [157] while dropping the viscous term and including the term from equation 3.7.

$$KE_1 = KE_2 + \Delta SE \tag{3.8}$$

At maximum spread $KE_2 = 0$ and the SE term is taken at $D = D_{max}$ giving the following expression:

$$\frac{1}{2}\rho \Psi V_0^2 = \frac{\sigma_{eff} \pi C}{2} \left(D_{max} - 0.6D_0 \right)^2$$
 3.9

By leveraging the definition of $\xi_{max} = D_{max}/D_0$ and solving for ξ_{max} , equation 3.9 becomes:

$$\xi_{max} = A(0.41)We^{1/2} + 0.60$$
3.10

Where A is a constant of proportionality that will be fitted from the data equivalent to $1/\sqrt{C}$ from equation 3.7. Strikingly, the scaling for this model is quite different than both those of Pasandideh-Fard's group or Clanet's and instead follows the scaling relationship:

$$\xi_{max} \sim We^{0.5}$$
 or, $\xi_{max} \sim V$ 3.11



Figure 3-7: Spread factor ξ_{max} vs Weber number. Black line is the power law fit and the markers are the data points from the droplet impacts.

Another facet of this elastic relationship is that the spread time is independent of the impact velocity as is seen in Figure 3-9. The droplets impacts are clustered per needle gauge and by extension their volume or D_0 . The velocity independence of time not only conforms to predictions by the model as listed in equation 3.11, but also matches the results for Clanet's work mentioned previously. The average t_s was found to be 2.6 ms for the 30-gauge needle, 2.7 ms for the 25-gauge needle and 4.4 ms for the 20-gauge needle.



Figure 3-8: Comparison of spread factor scaling models. Green, red and orange dashed lines are the Pasandideh-Fard model for normal surfaces [103] for advancing contact angles of 1, 90 and 180 respectively, the solid blue line is the Clanet model for water on a superhydrophobic surface [155], and the solid black line is this work.

Impact and initial spreading velocities are assumed to scale with each other so the spread factor would increase linearly with velocity if spread time is constant for a given D₀. This conforms to the linearly elastic assumption applied to derive equation 3.10 since time to maximum is a function of mass and, presumably in this case, σ_{eff} only and independent of V₀. The one caveat with this model is that the contact line is pinned at maximum. This we believe is due to the adhesive nature of the skin and not due to dissipation of energy due to viscosity as the droplet can be seen to oscillate even after reaching a maximum value and becoming pinned.



Impact Diameter D₀ (mm)

Figure 3-9: Droplet spread time vs Impact Diameter D₀.

The predicted spread time from linear elastic theory would scale as $t_s \sim \sqrt{m/k}$ or, in this case, $t_s \sim D_0^{3/2} \sigma_{eff}^{1/2}$ which is depicted in Figure 3-9. Figure 3-10 shows 6 different impact events chosen to represent two groupings of We and showcasing the range of volumes tested.

3.5 Results and analysis

Figure 3-7 shows the data from the droplet impact experiments plotted with impact Weber numbers vs the spread factor ξ_{max} . The model was fit with the Igor Pro Software from Wavemetrics and obeys the fit equation $\xi_{max} = y_0 + B(We)^{pow}$ with B found to be 0.32 ± 0.02 and *pow* found to be 0.48 ± 0.03 . This corresponds to a value of A to be 0.743 from equation 3.10. This linear relationship with velocity contrasts starkly with the other models as detailed in Figure 3-8.

This figure shows all three models including a range of advancing contact angles for the Passandideh-Fard model. Our model performs similarly to the Clanet model at lower Weber numbers but predicts greater spreading than all 3 as the We \rightarrow 200. This conflicts with reality for a substance that is fully wetting but it should be noted that the Passandideh-Fard model loses utility as $\theta_a \rightarrow 0^+$ and is included only to show the extrema of the model.

The figure shows that the spread behavior is similar for droplets of similar volumes regardless of We. For example, the larger droplets take much longer to spread as compared to the lower droplet volumes regardless of impact velocity. The different droplet volumes also group well by We number. This similarity of spread behavior for droplets of similar mass independent of impact velocity, is characteristic of the linear elasticity we posited. An interesting aspect of the

liquid gallium can be seen near the end of the spread sequence after ~6 ms for all cases. At that time, the droplets see virtually no retraction of the contact line. They are pinned at maximum spread due to the adhesion of the oxide layer to the glass substrate. This is counterintuitive sincestatic and dynamic contact angles of the liquid metal both indicate it is non-wetting. This illustrates the complicated dynamic nature of the alloy mentioned previously.



Figure 3-10: Spread factor ξ vs time for 6 different impacts. Red represents the 20G needle with filled circles corresponding to 22.8 µl droplet at We = 22.3 and open circles are 21.8 µl at We = 106.9. Blue represents the 25G needle with filled triangles at 10.6 µl and We = 27.4 and open triangles at 10.6 µl and We = 117.8. Green represents the 30G needles with filled squares at 6.2 µl at We = 27.4 and open squares at 6.5 µl and We = 114.1

Referring to Figure 3-6, we made the specific decision to state that while $\mu_k = 0$, and μ_s was large, we intentionally did no state $\mu_s \rightarrow \infty$. The further the droplet spreads, the greater the restoring force per equation 3.6. We found that at above the upper Weber Numbers reported, above 205, coronal instabilities began to occur. The restoring force also proved greater than the adhesive force causing a retraction of the metal deposition. This is depicted in Figure 3-11 where both the fingering at the contact line is evident as is the retraction of the droplet. There is clear evidence of the initial impact point on the retracted sample and at the apex of each finger instability there are streaks that track back to the center. This behavior may warrant further study.



Figure 3-11: Liquid Metal Droplet Retraction

3.6 Conclusion

In summary we have conducted droplet impact experiments of a RTLM alloy consisting of 68.5% Ga, 21.5% In and 10% Sn by weight over a range of Weber numbers from $10 \le We \le$ 205. In doing so we observed a strong correlation between the maximum spread parameter ξ_{max} and the impact velocity V_0 , indicating a linear relationship which is an unusual relationship for droplet impacts. These impacts were modeled with a 1-D mass-spring approximation which affirmed the linear relationship between spread factor and impact velocity as well as independence of spread time and impact velocity. The stiffness associated with this model was chosen by directly measuring the stress response using a tensiometer and specially chosen cylindrical glass probe and found to be 628 ± 37 mN/m. We performed a comparison of this model to existing models from Pasandideh-Fard, et al [103] and Clanet, et al [155] and noted that near lower Weber numbers around 10-80, ξ_{max} is lower for metal than the other models but begins to grow larger as the Weber number exceeds 100. behavior over the range of Weber numbers tested. This model is predictive and can serve to modulate voxel size of liquid metal droplets when used applications such as in drop on demand additive manufacturing processes.

Chapter 4: Coalescence

4.1 Introduction

Coalescence is an enticing phenomenon for study by the fluid dynamicist as it involves several of the major force contributions seen in the field namely capillary, viscous, inertial and gravity forces. The study of coalescing fluids has allowed for advances in microfluidics [110], additive manufacturing in microgravity [111], bioprinting of living tissue [109], the ink jet printing of electronics [158], and even the study of natural phenomena such as rain [159]. Coalescence can largely be separated into drop-drop coalescence [160–162], bubble coalescence [163–166], onset or initiation of coalescence [113,167], and drop-planar coalescence [106,168,169] which is the focus of this study. At planar surfaces coalescence can take occur two ways: partial or full coalescence. Full coalescence is characterized by complete drainage of the droplet into the free surface while partial coalescence produces a smaller so called "daughter" droplet [104].

Lord Rayleigh first characterized the breakup of fluid columns or jets to droplets, a mechanism driving the, partial coalescence process back in 1878 [91]. This analysis serves as the foundation for work through the 20th century continuing even through the present day. The importance of viscosity in determining the parameters of a coalescence event and has been studied at planar surfaces by Gillespie and Rideal [170] who's work focused on the drainage time of the coalescing droplets as well as the condition for droplet rupture, finding it occurred when film at the drop-surface interface was 10⁻⁵ to 10⁻⁶ m thick. A foundational study of planar coalescence, including partial coalescence can be found in the well-known works by Charles and Mason which

serve as a basis for much of the subsequent work [171,172]. These studies were conducted in a viscous quiescent fluid with the first taking a hydrodynamic approach to studying the onset of coalescence at a planar surface as well as the coalescing time. The second paper focuses on partial coalescence, on which this paper will focus as well, comparing the ratio of daughter droplets $r_i = R_2/R_2$, where R_1 is the father droplet and R_2 is the daughter, to the viscosity ratio of the droplet fluid and quiescent fluid. This work also established a framework for the production of a daughter droplet using linear stability analysis finding an amplitude for the most dominant wavelength successful in producing the droplet using the method established by Rayleigh. Tomotika [173] established a working model for the parameter π/Z_0 or the ratio of circumference to optimum wavelength which was found to be about 0.68 by Charles and Mason for mercury, the substance that is most comparable to the liquid metal chosen for our study. Using a simplified model, the derived a readily usable equation for this parameter given by:

$$Z_0 = \left(\frac{3}{2}r_i^{-3}\right)^{1/2}$$

Tomotika's study created a theoretical framework that produced a model for π/Z_0 as a function of the viscosity ratio $p = \mu_i/\mu_o$, where μ_i and μ_o are the inner and outer velocities respectively, for a range of $0.001 \le p \le 100$. The result of this analysis was a model that predicted a maximum value out a viscosity ratio of p = 0.28 with the tail ends reaching 0 as the viscosity ratio tended towards 0, the case of an inviscid inner fluid, or towards infinity, for an inviscid outer fluid. While this work is often cited for drops coalescing in a quiescent fluid, many studies conducted since have produced data that do not match Tomotika's model [171,174]. This indicates a more complicated, or at least a different relationship between the propensity to partially coalesce,

the parameter Z₀, and by extension r_i, than the viscosity ratio alone. For example Fedorchenko and Wang [175] conducted experiments of droplets impacting on liquid surfaces and observed a partial coalescence cascade including bouncing of the daughter droplets. The found a regime defined by the dimensionless capillary length $l_c^* = l_c/D$ and determined the regime for partial coalescence effects to begin at $l_c^{*2} > 1$ and end at a critical value of 28.3. While their experiments are complicated by the effects of the droplet impact, they indicate the importance of capillary forces in the dynamics of the generation and subsequent behavior of the secondary droplets. This relationship can also be interpreted as the regime where We < 2 Fr and 0.1 < Fr < 200, where We and Fr are the Weber, $We = \rho VD/\sigma$, and Froude, $Fr = V/\sqrt{gD}$ numbers respectively, emphasizing the important contribution of capillarity in overcoming gravitational body force effects. Here and throughout this manuscript ρ , μ , σ , V, and D will refer to the density (kg/m³), dynamic viscosity (Pa·s), surface/interfacial tension (N/m), characteristic velocity (m/s), and characteristic length (m) and refer to the inner fluid unless stated otherwise. Characteristic lengths and velocities will be specified as needed.

The Ohnesorge number, $Oh = \mu/\sqrt{\rho\sigma D}$, is a parameter that has seen a great deal of focus for the limit of partial coalescence. The importance of Oh with respect to applications such as inkjet printing, which involve both coalescence and droplet breakup which is dynamically very similar to partial coalescence, has been noted by many works such as the study by Derby [101,176]. These works set a limit of Oh < 1 for droplet breakup, beyond which the fluid is too viscous. This becomes intuitive if one assumes that capillary force is a driving force in the breakup process while viscous forces serve to stabilize the fluid column.



Figure 4-1: Partial Coalescence Generation of the Daughter Droplet of liquid metal Galinstan in 1 M sodium hydroxide. In order of appearance: 1. Droplet resides at interface. 2. Capillary wave initiates from the interface between the droplet and NaOH/Metal surface. 3. Capillary continues to propagate to the top of the droplet. 4. Fluid column forms as droplet drains into metal pool. 5. Plateau-Rayleigh style punch off can be observed near base of column. 6. Pinch off continues and daughter droplet is apparent. 7. Daughter droplet is formed with initial downward velocity V_0 .

Blanchette and Bigioni [177] focused on the Ohnesorge number as a criteria for pinch off when the Bond number was sufficiently small. Through both simulation and experiments using ethanol they found a critical value for the Ohnesorge number $Oh = 0.026 \pm 0.001$ when the Bond number, $Bo = \Delta \rho g D^2 / \sigma$, was less than 0.1. Above this critical Oh the authors assert that only full coalescence can occur. Previous work by our group [174] utilizing a number of liquids coalescing in planar surfaces in air showed coalescence occurring up to the Oh <1 threshold with the droplet ratio obeying the following relationship: $r_i = (1 - 0.75\alpha - 0.75\beta Oh)^{1/3}$ where α =1.13 and β =.25 are empirically determined constants. This comes from considering that inertial effects dominate until Oh \rightarrow 1⁻ at which point viscous forces become important.

The timescales of coalescence are also of interest where viscous and inertial regimes are differentiated, with some literature naming a third regime where inertia is important. Inviscid theory predicts that coalescence time will scale as $R \sim t^{3/2}$ due to the inertial timescale taking the form $t_i = \sqrt{\rho R_1^3 / \sigma}$ [107]. Xia et al. [178] explored the effect of crossing over from the viscous regime to the inertial regime by studying the relative timescales for each type of behavior, using Oh as a basis for differentiating them. This work was able to affirm that in the inertial regime, the coalescence time scales with the radius to the power of 1/2 while in the viscous regime coalescence time scales linearly with the radius. This built upon previous work such as that by Paulsen et al. [179] which also included a third regime in which both viscous and inertial forces are important. The scaling of $R \sim t$ for viscous regime and $R \sim t^{3/2}$ for the inertial/capillary regime are generally the accepted scaling parameters for the coalescence processw. These works serve to affirm the importance of the Ohnesorge number in properly stratifying the dynamic regimes of coalescence.

For this study we will build on our work previously exploring the phenomenon of a bouncing, partial coalescing droplet in air as studied previously by Honey and Kavehpout [9] and expand to a viscous quiescent fluid. The partial coalescence process imparts a downward velocity

 V_0 on the generated daughter droplet due to capillary and body forces. This process is detailed in Figure 4-1 and modified from Honey's work to include buoyancy effects.

As shown in the figure, first the droplet of radius R₁ resides on the interface, supported by a thin lubrication layer of the surrounding NaOH. At 1 ms the capillary wave can be seen initiating from the base and continues upward as shown in the image at 3 ms. The fluid forms of column of diameter $2R_0$ where $R_0 = \sqrt{2r_i/3}R_1$ which is found by equating the volume of the daughter droplet to the fluid column [171]. This column will then begin to breakup per Rayleigh's model with the pinch-off at the neck first shown in Figure 4-1at 7 ms. At first the neck begins at radius R_0 but pinches off over a time as described by [180]. During this time capillary and gravity forces both act downward on the droplet. We can write an equation for the force balance on the fluid mass that will become the eventual daughter droplet as follows:

$$\left(m\frac{dV}{dt}\right)_{drop} = F_{grav} + F_{cap} = \frac{4}{3}\Delta\rho\pi R_2^3 g + 2\pi R(t)$$

$$4.1$$

Where R(t) is given by the aforementioned work by Clanet and Lasheras. The neck continues to shrink as shown in Figure 4-1 in the 6th image over a period governed by the inertial timescale $t_i = \sqrt{\rho R_1^3 / \sigma}$. The final image in the figure shows the daughter droplet of radius R_2 which is generated with an initial downward velocity of V_0 . The size is related to R_1 by:

$$R_2 = r_i R_1 \tag{4.2}$$

By integrating equation 4.1 over t_i the equation for the downward velocity V_0 can be obtained:

$$V_0 = \frac{1}{e} \sqrt{\frac{3\sigma}{2\rho r_i^3 R_1}} + \frac{\Delta\rho}{\rho} g \sqrt{\frac{\rho R_1^3}{\sigma}}$$

$$4.3$$

Equation 4.3 will serve as an important initial condition for the model we will use for bouncing droplets in a viscous medium. Note that this model relies on Rayleigh's inviscid model for breakup. While a viscous dispersion relation developed by [181] does exist, it can be unwieldy and yield very similar results to the inviscid model [182]. Furthermore, this work will focus exclusively on low Ohnesorge numbers $Oh \ll 1$ so the inviscid model will suffice.

4.2 Room Temperature Liquid Metal Interfacial Properties

Gallium based alloys have become popular in recent years due to several desirable material properties notably their low melting points, low toxicity, and high thermal and electrical conductivities [3,54]. The properties of these alloys make them ideal candidates for applications such as stretchable electronics [5], practical chemistry [1], and microfluidics [2]. Here we seek to use a specific formulation consisting of 68.5\% gallium, 21.5\% indium and 10\% tin, known commercially as Galinstan and is commercially available from Geratherm Medical AG in Germany with RG Medical Diagnostics distributing in the US. The material properties for this formulation are listed in Table 4-1. This material is a eutectic alloy which remains liquid well below room temperature, solidifying at -19° C. This combined with the negligible vapor pressure and high boiling point make this room temperature liquid metal (RTLM) an ideal candidate for many practical and laboratory applications.

| Density (20° C) | Viscosity (20° C) | Apparent surface tension | |
|----------------------------------|------------------------------------|-----------------------------|--|
| Density (20°C) | viscosity (20°C) | (oxidation) | |
| 6440 kg/m ³ | 0.0024 Pa · s | 0.571 N/m | |
| | | | |
| Surface Tension (no | Interfacial tension (w/ 1 M | Interfacial Tension (w/ 1 M | |
| oxidation) | HCL) | NaOH) | |
| 0.535 N/m | 0.455 N/m | 0.4042 N/m | |
| | | | |

 Table 4-1: Interfacial and bulk material properties of RTLM Galinstan [60,151]

While this eutectic is often compared favorably to mercury in terms of its usefulness, like mercury there exists a significant challenge when working with the material. For mercury the toxicity is often cited as a primary challenge, for gallium alloys, the problem is oxidation at the fluid surface. While some have found uses or workarounds for this surface layer such as Ladd et al [67] who were able to exploit the stiffness introduced by the skin to create free standing structures, most either lose interest in the material or seek a workaround. Alloys containing gallium will react with ambient oxygen to produce gallium (III) oxide or gallium (I) oxide at the surface of the liquid [183]. This layer is extremely thin, on the order of ~5 Å and insulates the bulk fluid quite well from additional oxidation [89]. Despite being very thin the oxide layer significantly impacts the dynamics of the moving fluid, particularly the wetting, spreading and other capillary behaviors. Jia et al. [90] showed that the presence of the oxide layer inhibits Plateau-Rayleigh instability breakup of gets which as mentioned previously is important for the partial coalescence process. The surface tension of this RTLM is usually reported as 0.718 N/m, but this is a facet of

the measurement technique and more rigorous methods have found it to be $0.517 \text{ N/m} \pm 6\%$ [152]. This indicates that the presence of the oxide layer must be attended to in order to properly study the phenomenon.

Fortunately, a solution exists to study capillary effects with RTLMs through either the prevention of oxidation through the use of isolation and inert gasses such as nitrogen or argon. The difficulty here is that oxidation may have occurred before the sample is isolated. In order to ensure that the oxide layer is not present at any time, the layer may be reduced using a strong acid or base. The most commonly used candidates are hydrochloric acid (HCl) and Sodium Hydroxide (NaOH). Table 4-1 depicts several of the values of surface or interfacial tension reported in literature (SFT/IFT). Handschuh-Wang et al. [151] studied the IFT of Galinstan in NaOH and HCl as a function or molarity and time. For HCl, even in higher concentrations, the IFT took at least 1 minute to converge to a steady value. For NaOH in concentrations of 1M the value of IFT converged to 404.2 ± 3.5 very quickly and as such we chose 1 M NaOH in water as the quiescent fluid for these experiments. We also confirmed the IFT value of the RTLM with 1 M NaOH with a procedure detailed in section 4.3.

4.3 Experimental methods

The basic experimental setup is depicted in figure \ref{fig:setup}. All components were mounted to an optical table to ensure leveling and minimize vibration. This is particularly important as the droplets are prone to skate around and out of frame if there are errors in leveling or ambient vibration. A high-powered LED light source provided illumination and an optical diffuser was used to insure uniformity of lighting in the test area. The syringes were mounted to a custom-made
vertical z-stage which was mounted to the optical bed with tubing connected to a Kent Scientific Genie Plus Syringe pump. The needle was inserted into the 1 M Sodium Hydroxide and brought in proximity to the liquid metal surface. We triggered the high-speed video camera, a Phantom v7.2 High Speed camera (Vision Research) when the partial coalescence event began. The video data was then saved as individual frames in the TIFF image format and exported to ImageJ software where measurements could be made for droplet diameters and bounce height. A few details on each component:



Figure 4-2: Coalescence experiment setup. All components shown are mounted to optical bench. The need assembly is affixed to a motor-controlled z stage that is not shown.

The high-speed camera was mounted to the table and leveled to the liquid interface. The resolution for video is 640x480 for all tests. The frame rate was somewhat limited as the cascade process can be quite long, on the order of whole seconds. The camera memory is limited so the frame rate must be balanced with the recording window in order to capture as much of the process as possible. The frame rate for all tests is between 5000 and 6024 frames per second. The spatial

resolution is 0.014 px/mm for all tests. The exposure time was kept constant at 98 μ s in order to ensure uniformity of lighting conditions on all tests. Note that figure Figure 4-1: Partial Coalescence Generation of the Daughter Droplet of liquid metal Galinstan in 1 M sodium hydroxide. In order of appearance: 1. Droplet resides at interface. 2. Capillary wave initiates from the interface between the droplet and NaOH/Metal surface. 3. Capillary continues to propagate to the top of the droplet. 4. Fluid column forms as droplet drains into metal pool. 5. Plateau-Rayleigh style punch off can be observed near base of column. 6. Pinch off continues and daughter droplet is apparent. 7. Daughter droplet is formed with initial downward velocity V₀. uses a separate setup and is for demonstrative purposes only, the results do not include data from that particular setup.

The NaOH used in every experiment was 1 M in concentration and the solution consisted of water as the solvent. The density used is taken to be $\rho_o = 1040$ kg/m and the viscosity is $\mu_o =$ 1.3×10^{-3} Pa · s. The RTLM is composed of 68.5% Ga, 21.5%, In and 10% as mentioned above. The values we use in calculations match those in table with the density and interfacial tension verified prior to testing. The density was measured with a laboratory scale and found to match the expected value. The interfacial tension was measured with a KRÜSS Scientific Drop Shape Analyzer-DSA100. Using the pendant drop method, the IFT was found to be in full agreement with the value reported in the Table 4-1 of $\sigma = 404$ mN/m.



Figure 4-3: Detailed sequence of the partial coalescence process. This figure shows the generation of two daughter droplets. The scale bars represent 1 mm.

The needle was actuated via stepper motor to be as close to the interface as possible as to minimize any inertial effects from the generation of the initial droplet. Additionally, the flow rate from the syringe pump was kept at 0.50 μ L/s. In order to prevent reaction with both the RTLM and the NaOH, polymer needles were used either polytetrafluoroethylene (PTFE) or polypropylene depending on the needle size. A few sizes of needle were used ranging from 21G to 30G. Some consideration was needed in choosing the as well. The container was a rectangular prism and was placed so that one face was normal to the camera to prevent optical distortion.

Due to the material cost, it was desirable to minimize the volume of liquid metal needed in the container. However, eliminating effects from the side walls and bottom panel were also important. For the bottom panel, the minimum fluid height needed to be above the so called "shallow water" condition which is defined as the case $ky \rightarrow 0$ where k is the wave number $k = 2 \pi / \lambda$, where λ is the wavelength, and y is the depth [184]. The largest droplet had a diameter of 2.881 mm so taking this as the conservative estimation of wavelength the was vector is k =2180. This led to the choice of a depth of 22 mm which was gave a value of ky = 48 which we deemed sufficient to avoid shallow water effects. The capillary length provided an additional complication as the value for RTLM in NaOH is $l_c = 2.76$ mm. The reduced metal is highly nonwetting on the plexiglass so the curvature at the walls was severe. If the container were not large enough the curvature would affect the free surface and the droplets would skate off on the lubrication layer between the two metal surfaces. Because of this a 38.1mm x 38.1mm base contained was selected. This was found to produce a sufficiently flat surface to mitigate the issue of droplets skating out of frame or focus.



Figure 4-4: Droplet travel and bounce sequence (a) depicts the downward portion with initial conditions $x_1(t_1 = 0) = 0$, $V(t_1 = 0) = V_0$ where V_0 is given by equation 4.3 with gravity and drag forces acting on the droplet. Droplet then impacts at time t_i before rebounding. (b) A new datum h is introduced and new time t_2 such that at $t_2 = 0$, h = 0, $\dot{h} = V_b$. Where V_b is the impact velocity times the restitution coefficient. The droplet travels up until reaching maximum height h_{max} .

ImageJ software was used to perform all measurements with the needles serving as the physical reference scale. The droplets were then measured before and after each coalescence event for their diameter which was halved to give R_1 and R_2 . The bounce height h was also measured with the undeformed free surface used as a reference for all height data. Time is measured by combining

the frame number with the known frame rate creating a known time interval between frames, which was used to determine the coalescence time.

4.4 Mathematical Modeling

4.4.1 Stokes Model

For this study, our primary focus is to confirm the velocity of the daughter droplet as given by equation 4.3 and develop a model for the dynamics of the droplet as it impacts the interface, rebounds, and climbs to a maximum height. This process is shown in more detail in

Figure 4-3. The first image of this figure represents the initial droplet of radius R_1 residing on the free surface. The capillary wave then initiates and travels up the drop surface until a fluid column is formed at 6.4 ms in the figure. Capillary forces and gravity act on the mass of fluid that will become the daughter droplet and the image at 8.6 ms depicts the droplet immediately before pinch-off has occurred. The droplet then descends with initial velocity V_0 before impacting the surface, rebounding, and reaching a maximum height h_{max} as shown in the 7th image in the sequence at 31 ms. The droplet then descends to the interface and begins a new residence time. During this time the outer fluid is squeezed out slowly, and at 612.8 ms the capillary wave can be seen propagating again as the cascade continues. The smaller droplet is reassigned the role as father droplet for this new sequence and its radius becomes the new value of R_1 .

In order to analyze this phenomenon, it is convenient to break the bouncing sequence into two parts: the downward portion and the upward portion. Figure 4-4: Droplet travel and bounce sequence (a) depicts the downward portion with initial conditions $x_1(t_1 = 0) = 0$, $V(t_1 = 0) =$ V_0 where V_0 is given by equation 4.3 with gravity and drag forces acting on the droplet. Droplet then impacts at time t_i before rebounding. (b) A new datum h is introduced and new time t_2 such that at $t_2 = 0$, h = 0, $\dot{h} = V_b$ Where V_b is the impact velocity times the restitution coefficient. The droplet travels up until reaching maximum height h_{max} (a) depicts the downward sequence. We will begin by using the famous model for creeping flow on a sphere as derived by Stokes in 1851 [185]. This will require a modification to the effective viscosity since the inner droplet is a liquid and not a rigid sphere. An effective or net viscosity μ_{net} can be found and is expressed as follows per White and Cofield [186]:

$$\mu_{net} = \mu_o \frac{1 + 2\mu_o/3\mu_i}{1 + \mu_o/\mu_i} \tag{4.4}$$

For the fluids used here equation 4.4 gives a value of $0.880\mu_o$ or $1.11 \ge 10^{-3}$ Pa·s. The drag on a droplet can then be modeled as $F_d = F_{d,s} = 6\pi\mu_{net}R_2V$. This allows us to write the equation of motion for the droplet undergoing gravity forces and Stokes' drag:

$$\rho \forall \ddot{x_1} = F_g - F_d = \Delta \rho \forall g - 6\pi \mu_{net} R_2 \dot{x_1}$$

$$4.5$$

Here Ψ is the volume of the droplet of radius R_2 and the variables x_1 and t_1 are the spatial and time systems for the downward portion. At $t_1 = 0$ the droplet is subject to the following initial conditions: $\dot{x_1}(0) = V_0$, $x_1(0) = 0$. The initial velocity V_0 is calculated via equation 4.3. Equation 4.5 can be readily integrated analytically to yield equations of motion for the droplet:

$$x_1 = \beta' g t_1 - \beta (\beta' g - V_0) \left[1 - exp\left(\frac{-t_1}{\beta}\right) \right]$$

$$4.6$$

$$\dot{x}_1 = \beta' g - (\beta' g - V_0) exp\left(\frac{-t_1}{\beta}\right)$$

$$4.7$$

Where

$$\beta = \frac{2\rho R_2^2}{9\mu_{net}}, \quad \beta' = \frac{2\Delta\rho R_2^2}{9\mu_{net}}$$

$$4.8$$

The equations 4.6 - 4.8 are familiar equations associated with the stopping distance of small spheres at low Reynolds Numbers. Specifically we are are looking for for the conditions at which the droplet impacts the interface which is found by setting $x_1 = 2R_1 - 2R_2 = 2R_1(1 - r_i)$, the initial height from the surface. Equation \ref{downpos} is then solved, numerically to find the impact time $t_1 = t_{impact}$. This time is plugged into equation \ref{downvel} to find the velocity at impact such that $\dot{x}_1(t_{impact}) = V_i$, the velocity at impact. This impact velocity will provide the initial condition to calculate the bounce height. However, energy is not conserved in the impact with the interface. Jayaratne and Mason [187] studied the impact of droplets with a free surface. They modeled the impact as a simple harmonic and proposed a coefficient of restitution, A, which is defined as:

$$A = \frac{V_b}{V_i}$$
 4.9

Jayaratne and Mason found this value to be 0.22 for water droplets impacting a free surface, also of water, which corresponds to a loss of 95% of kinetic energy from the rebound. This gives

a way to determine V_b which will provide the means to integrate the upward portion of the bounce as defined in Figure 4-4 (b). This portion uses a new coordinate and time scale to keep the calculation simple, as well as allowing us to neglect the time period associated with deforming the interface. In the figure h = 0 represents the plane of the undeformed free surface and t_2 is a new time variable that begins as the droplet leaves the surface. This results in a slightly different equation of motion that equation 4.5:

$$\rho \forall \ddot{h} = -F_g - F_d = -\Delta \rho \forall g - 6\pi \mu_{net} R_2 \dot{h}$$

$$4.10$$

Due to the fact that both drag and gravity now act against the direction of motion. Equation 4.10 can be analytically integrated and subjected to the initial conditions h(0) = 0, $\dot{h}(0) = V_b$ to yield:

$$h = -\beta' g t_2 + \beta (\beta' g + V_0) \left[1 - exp\left(\frac{-t_2}{\beta}\right) \right]$$

$$4.11$$

$$\dot{h} = -\beta' g + (\beta' g + V_0) exp\left(\frac{-t_2}{\beta}\right)$$

$$4.12$$

Where β , β' are still given by equation 4.8. The maximum height is found when $\dot{h} = 0$ and is found to be:

$$t_{max} = \beta \ln \left(\frac{V_b}{\beta' g} + 1 \right)$$
 4.13

Plugging this into equation 4.11 yields an equation for h_{max} :

$$h_{max} = -\beta' g \left(\beta \ln\left(\frac{AV_i}{\beta' g} + 1\right)\right) + \beta(\beta' g + V_0) \left[1 - exp\left(\frac{\left(-\beta \ln\left(\frac{AV_i}{\beta' g} + 1\right)\right)}{\beta}\right)\right]$$

$$4.14$$

Note that this equation has substituted V_b for AV_i per equation 4.9. Equation 4.14 is convenient in that it is the result of analytical integration and provides a value h_{max} that can readily be measured. However, this model is incomplete in that it is predicated on the Stokes Law which can only be faithfully applied up to Reynolds Numbers $Re \ll 1$. This is insufficient for this system which may see Reynolds numbers above this threshold. While Stokes' Law may not be valid throughout the full sequence, it does provide the basis for a more precise solution.

4.4.2 Numerical Model

Beard and Pruppacher [188] published empirically derived results for drag on droplets from the Stokes regime to Re = 200. Later Greene et al. [189] were able to validate these results and extend the validity of the model to $Re \sim 1000$ The drag relationship is as follows:

$$\frac{F_d}{F_{d,s}} = \frac{1 + 0.102Re^{0.955}, \quad 0.2 < Re < 2.0}{1 + 0.115Re^{0.802}, \quad 2.0 < Re < 21.0}$$

$$4.15$$

$$1 + 0.189Re^{0.632}, \quad 21.0 < Re < \sim 1000.0$$

Where F_d is the drag and $F_{d,s}$ is the Stokes drag. Equation 4.15 can be combined with the first parts of equations 4.5-4.10 to give a better estimate for the dynamics of the bouncing droplet. The weakness of this approach is that the equations become non-linear and no longer can be integrated analytically. In order to deal with this, the equations were integrated numerically using

an RK4 scheme with step size $dt = 1 \times 10^{-6}$ s. The solution procedure is similar to the Stokes procedure as detailed in Figure 4-4. First, the equations are integrated until the stopping condition of $x_1 = 2R_1(1 - r_i)$ is reached and the corresponding velocity at this time step is read off. The coefficient of restitution was determined by comparing the measured height data to the upward portion and using the shooting method to solve for A. This was done separately from plotting h_{max} which was done using the average value for the restitution coefficient from the data. The stop condition for integration on the upward portion is reached when the velocity was less than or equal to 0.



Figure 4-5: Solution procedure using the Beard numerical model.

Figure 4-5 details the solution procedure using the numerical model. The experiment results are taken first then the problem is transformed from a boundary value problem to an initial value problem with h_{max} serving as the boundary check and A giving the initial velocity $V_b = AV_i$. The average value of A determined from this part is then used to plot the overall model.

Results and Analysis

The bounce height was calculated using the Stokes drag and equations 4.4-4.14 and is plotted in Figure 4-6. In the same figure the equations of motion were integrated using the Beard model and an RK4 scheme and plotted along with the measured experimental data.



Figure 4-6: Bounce height h_{max} vs initial droplet radius R_1 . Blue line is the numberical model featuring Beard's drag model and the solid black line is the Stokes approximation.

The behavior of the model can be segmented into three distinct regions. In this figure, the restitution coefficient A and the droplet ratio r_i were held constant at A = 0.27 and $r_i = 0.47$ which were extracted from the data. depicts a hypothetical fluid system where in the inner fluid has the same fluid properties as the liquid metal but the net viscosity is varied over several orders of magnitude to demonstrate the importance of the viscosity of the quiescent fluid on the bouncing behavior of the droplet. The inviscid case is equivalent to the model our group previously

developed for modeling bouncing droplets in air [9]. Both Figure 4-6 and Figure 4-7 are best interpreted reading the x-axis from right to left as this as the direction in which the partial coalescence cascade occurs.



Figure 4-7: Viscous bouncing droplet model for different quiescent fluid viscosities. Black line indicates the inviscid case as demonstrated by Honey and Kavehpour [9]. As the quiescent fluid becomes more viscous the capillary region disappears and the viscous region eventually dominates the gravity region as well.

The first region in figure Figure 4-6 exists for $R_1 > 1.11$ mm which corresponds to a Bond Number Bo > 0.16. This region can be considered the gravity dominant region. As droplets get too large the model loses usefulness as the droplets can no longer be approximated as spheres. It can be seen that in this region a larger droplet results in a higher bounce height, which can be interpreted to the gravity dominance of the region contributing a higher initial velocity to droplets that are larger and therefor are more massive. For the region where $Bo \leq 0.16$ gravity effects begin to become unimportant, and capillarity becomes the driving force for the droplet behavior.



Figure 4-8: Coefficient of Restitution A vs dimensionless radius R_1^* . Where $R_1^* = R_1/l_c$. Additional materials listed are all in air and were taken from previous work from my lab following the procedure detailed here.

In the inviscid case, depicted in black in Figure 4-7, the droplet will bounce higher and higher in perpetuity until the drop fully coalesces. When a viscous quiescent fluid is introduced at a certain point viscous forces being to dominate at a certain threshold. The region bounded by 0.38 mm $< R_1 \le 1.11$ mm we call the capillary region where the bounce height increases as the partial coalescence cascade leads to smaller and smaller droplets. It is not appropriate to characterize this regime by the Bond number as gravity is no longer as important as viscosity or capillarity, so we bound it by the Ohnesorge number, choosing the net viscosity, μ_{net} and calling this specific version of the number Oh_{net} . This gives a region bounded by 4.76 x $10^{-4} \le Oh_{net} < 8.13$ x 10^{-4} . As can be seen in figure Figure 4-7 the viscosity strongly governs the size of the capillary regime. At $\mu = 10^{-2}$ the capillary regime is barely apparent and at $\mu = 10^{-1}$ it is lost entirely, and the gravity vs viscous regimes have no distinct division between them.

As the partial coalescence cascade continues past the final local maximum at $R_1 = 0.38$ mm the bounce height only decreases as viscous forces dominate the motion of the droplet. This region is defined by $R_1 < 0.38$ mm or $Oh_{net} \ge 4.76 \times 10^{-4}$. The Ohnesorge number is still quite small as the cascade proceeds into the viscous region. Assuming that the partial coalescence will proceed as $Oh \rightarrow 1^-$ as seen in our previous, inviscid experiments [174], the partial coalescence cascade would proceed until the droplet radius was 1 nm however per the model, the bounce height decreases faster than the radius of the droplet and at $R_1 = 900$ nm the bounce height is only $h_{max} =$ 90 nm, an order of magnitude lower, so any noticeable bouncing would cease as the droplet radius approaches the ~ 1 μ m scale. Unfortunately, the cascade was observed to continue past the reported values, but the resolution of the camera was insufficient to capture the droplets. Observing this cascade into the micro and possibly nano scales will be the subject of future research.



Figure 4-9: Droplet ratio r_i vs vs dimensionless radius R_1^* . Where $R_1^* = R_1/l_c$. Additional materials listed are all in air and were taken from previous work from my lab following the same procedure detailed here.

The relative performance of the Beard and Stokes drag models can be readily compared in figure Figure 4-6 as well. Both models agree in the gravity region which is expected as gravity body forces dominate viscous forces which is the facet of the models that is unchanged between them. The Beard model then performs much better in the capillary region near the local minimum as well as in the viscous region. The local maximum separating the viscous and capillary regions is shifted to the right in the numerical model as compared to the Stokes model as well and more

closely matches the data. This is due to the fact that the Stokes model under-predicts the magnitude of drag in regions where the Reynolds number is near or above unity. The Stokes model does perform slightly better in the mid capillary region which is surprising and warrants further investigation. Figure 4-8depicts the restitution coefficient as a function of the dimensionless radius R_1^* where R_1^* is the radius divided by the capillary length $R_1^* = R_1/\sqrt{\sigma/\Delta\rho g}$. For these individual values, the restitution coefficient was found using the shooting method, with the h_{max} from the data serving as the corresponding boundary value.

The value for the RTLM was found to be $A = 0.27 \pm 0.06$. While this value is higher than the value of A = 0.22 as measured by Jayaratne and Mason, it does fit with the data from our previous work published which found values of $A_{meth} = 0.21 \pm 0.08$, $A_{water} = 0.27 \pm 0.01$, $A_{SiOil} = 0.27 \pm 0.03$ for methanol, water, and silicone oil respectively. This restitution coefficient corresponds to a 93% loss of kinetic energy as opposed to the 95% loss noted previously. This could be due to improvements in measurement equipment, or to the fact that Jayaratne and Mason were limited to study droplet impacts at oblique angles and estimating the coefficient for normal impacts which we were able to observe directly. While the values of A were generally slightly higher for larger values of R_1^* , the difference was not significant, and no part of the theory predicts a function of droplet size affecting the bounce velocity ratio.



Figure 4-10: Ratio of capillary and gravity energy vs total energy. E_{cap} and E_{grav} indicate the energy associated with the generation of the daughter droplet per equation 4.5. Note that the figure does not reflect the proportion of energy of each term, but rather if each term was the only source of kinetic energy for the daughter droplet.

Figure 4-9 depicts the drop ratio coefficient as a function of dimensionless radius R_1^* . The mean value was found to be $r_i = 0.47 \pm 0.037$ which is in good agreement with the remaining data plotted which includes $r_{i,meth} = 0.65 \pm 0.08$, $r_{i,water} = 0.58 \pm 0.06$, $r_{i,SiOil} = 0.52 \pm 0.05$ for methanol, water, and silicone oil respectively. The droplet ratio for RTLM was lower than the other three liquids but performed fairly similarly to silicone oil.

Of additional interest to this study is further investigation of equation 4.3 the initial downward velocity of the daughter droplet of radius R_2 . By inspection, the equation has two parts: one gravitational term and one capillary term. To understand the relative contributions of each force we model the kinetic energy of the droplet of each contributing force in the absence of the other, in other words a pure capillary driven droplet vs a pure gravity driven droplet:

$$E_{cap} = \frac{1}{2}\rho \left(\frac{1}{e}\sqrt{\frac{3\sigma}{2\rho r_i^3 R_1}}\right)^2, \quad E_{grav} = \frac{1}{2\rho} \left(\Delta\rho g \sqrt{\frac{\rho R_1^3}{\sigma}}\right)^2$$
 4.16

And the total kinetic energy is found from the entirety of equation 4.3 to give:

$$E_{tot} = \frac{1}{2}\rho \left(\frac{1}{e}\sqrt{\frac{3\sigma}{2\rho r_i^3 R_1}} + \frac{\Delta\rho}{\rho}g\sqrt{\frac{\rho R_1^3}{\sigma}}\right)^2$$

$$4.17$$

The relative contributions of equation 4.16 to the total energy as given by equation 4.17 are plotted in figure Figure 4-10. Predictably the crossover occurs at the capillary length $l_c = 2.76 \text{ mm}$. Below the capillary length surface forces quickly begin to dominate the driving energy of the bouncing sequence. Gravity only plays an important role in very large droplets and as the partial coalescence process very quickly reduces the droplet size, the importance of capillary forces in driving the process cannot be overstated.

Figure 4-11 shows the coalescence time plotted against the initial droplet radius. Thoroddsen and Takehara [107] predicted this was governed by the capillary time t_{cap} . In fact, when the coalescence time data is plotted and fitted with a power law fit the data matches very well. Affirming the result from Thoroddsen and Takehara as well as other prior work that related the capillary time to coalescence time. As $Oh \rightarrow 1^-$ the viscous time scale is expected to begin to govern the coalescence behavior, but this was not observed due to the low Ohnesorge numbers present in this work. Residence time was also noted for the droplets however there was no discernable pattern to the duration between coalescence events indicating a high degree of nonlinearity in the residence period before the onset of the subsequent event.



Figure 4-11: Coalescence time t vs initial droplet radius R_1 . Theory from Thoroddsen and Takehara [107] predicts the relationship $t \sim R_1^{3/2}$.

Figure 4-12 shows the bounce height normalized by the droplet radius R_2 vs the normalized radius $R_2^* = R_2/l_{cap}$. This plot shows the importance of the capillary. The gravity dominant region

is approximately defined here as $0.47 \le R_2^*$ (or $1 \le R_1^*$) and the normalized bounce heights increase as the droplets get larger due to the larger potential energy contribution. Below the capillary length, surface tension dominates in the region defined as $0.020 \le R_2^* < 0.47$, and the normalized bounce height increases as the normalized radius decreases. Below this point $R_2^* <$ 0.02 the viscous forces can be seen to dominate and the normalized height decreases.



Figure 4-12: Non-Dimensional height h_{max}/R_2 vs normalized radius $R_2^* = R_2/l_{cap}$.

As the plot shows the droplet of radius R_2 may travel up to 4 times its diameter high above the surfaces. In Appendix II, Figure AII-0-1 conveys this normalized height data vs R_1^* but normalizes the height vs R_1 . This plot shows that the droplets bounce up to 1.835 times the initial diameter or $2R_1$ which indicates the importance of the capillary force in providing the kinetic energy for the bounce effect.

As a final note the value of π/Z_0 , ratio of the circumference over the wavelength, was calculated per equation 4.1 for all partial coalescence events. The Tomotika model predicts a value $\pi/Z_0 = 0.548$ but the value from this work was found to be $\pi/Z_0 = 0.840 \pm 0.10$. Previous work reached similar conclusions about Tomotika's model [171,174]. Taken together this information indicates that the viscosity ratio is likely not the best predictor of the normalized wavelength for partial coalescence.

4.4.3 Coalescence in other media

As part of a complete investigation we also investigated the coalescence process of Galinstan in air and water. However, since oxidation was allowed to occur the oxide layer was present. This layer served mainly to impede the normal capillary driven nature of the process and instead the droplet drained directly into the liquid metal pool. In the case of water, the droplet seemed to collapse directly into the pool, with no neck at all. In the case in air, coalescence began immediately with no observed residence time. The procedure generally occurred in two stages which can be seen in Figure 4-13. The red plusses represent a 21 gauge needle as opposed to the other colors and symbols which correspond to the smaller 30 gauge needle. For the 30 gauge the drainage was observed to occur in two phases. The first in which the rupture grew until

about 3 ms at which time the surface forces stabilized the rupture for 1-5 ms before the droplet ruptured again and drained into the pool. For the larger droplet, the inertial forces seemingly overcame the surface forces, and the drainage is one continuous process with no discernable stages.



Figure 4-13: RTLM free surface coalescence in air. Each data set is from a 30 gauge needle with the exception of the red plusses which are form a 20 gauge.

4.5 Conclusion

In this manuscript we performed drop-planar partial coalescence experiments that resulted in droplets bouncing on the interface of room temperature liquid metal alloy with 1 M sodium hydroxide as a quiescent fluid. These resulted in a range of drop sizes from 0.039 mm $\leq D_1 \leq$ 1.440 mm. We further validated the model for droplet initial velocity first proposed by Aryafar and Kavehpour [174] and demonstrated the importance of the capillary force in creating the conditions for droplet bouncing to occur. Furthermore, we developed a numerical model to simulate the dynamics of a bouncing droplet by applying the drag force as attained by Beard abd Pruppacher [188] and integrating the equations of motion over the downward and then subsequent upward trajectory of the drop. In doing so we were able to identify three distinct regions for the bouncing phenomena. The first region is bound by Bo > 0.16 and is known as the gravity dominant region. The second is bound by the conditions $Bo \leq 0.16$ as well as $4.76 \times 10^{-4} \leq$ $Oh_{net} < 8.13 \text{ x } 10^{-4}$ where Oh_{net} is the Ohnesorge number with the combined viscosity per equation 4.4 serving as the viscosity. This region is known as the capillary region as interfacial forces dominate it. The third region is given by $Oh_{net} < 4.76 \text{ x } 10^{-4}$ and is known as the viscous region as the droplet's behavior is dominated by viscous forces. The restitution coeffcient as defined by Jayaratne and Mason [187] was also determined numerically via the shooting method and found to be $A = 0.27 \pm 0.06$ a result that is in line with previous research [9]. The droplet ratio was found to be $r_i = 0.47 \pm 0.037$ a result that is slightly low compared to other substances with similar Ohnesorge numbers. The coalescence time was also compared to existing theory that finds $t_c \sim R^{3/2}$ which conforms to existing theory posed by Thoroddsen and Takehara [107]. We would expect this to change as the drops got smaller and $Oh \rightarrow 1^-$. Finally, we tested the ratio of the droplet circumference to the wavelength π/Z_0 vs the theory posed by Tomotika [173] and found a value of $\pi/Z_0 = 0.840 \pm 0.10$ vs the predicted value of 0.548 further affirming that the viscosity ratio is not sufficient to model the droplet breakup wavelength. Taking this all together we have built upon the invisicd model for a bouncing droplet and extended it to apply to a viscous quiescent fluid in cases where the interfacial tension is high enough to result in bouncing.

Chapter 5: Conclusion

This manuscript serves as integrative study of a single liquid metal alloy: Galinstan and alloy consisting of 68.5% gallium, 21.5% indium and 10% tin by weight. This metal alloy is unique in that it is readily liquid at room temperature, is non-toxic, and forms a layer of oxidized gallium at the liquid surface. This dissertation sought to provide adequate background for the motivations of study, as well as a combination of phenomenological fluid fundamental experiments and practical models for real world applications. The initial chapter was written to discuss the background and motivation for studying room temperature liquid metals. This consisted of a literature review that focused on the existing body of flexible and stretchable electronics technologies. These technologies were summarized, and the utility of Room Temperature Liquid Metal (RTLM) was found to be potentially very high in the field, as liquid metal presented the best performance in terms of combined conductivity and intrinsic stretchability. It also represents a simpler and more straightforward method of implementing flexible electronics than some of the more involved methods surveyed.

Upon establishing the value of studying Galinstan we sought two different tracks to be taken in parallel. The first track was one pursuing practical application and producing data that would have value for implementing Galinstan based manufacturing. Chapter 1 established the motivation to pursue electronics and from there we elected to work towards droplet-based manufacturing methods. This required a two-pronged approach, a study of the surface material properties in chapter 2 and implementing a predictive model for droplet spread factor ξ_{max} in chapter 3. Both of these, while serving as steps towards an end goal of a Galinstan based

manufacturing system both fall in the category of fundamental fluid mechanics and thus can be categorized as both.

In chapter 2 we established a value for the effective surface tension of the oxidized RTLM. This was achieved by building upon the static Wilhelmy technique for measuring surface tension and developing a novel technique that exploited the stiffness of the oxide layer in order to force full wetting. Through the use of this technique, we were able to ascertain a value of $\sigma = 0.628 \pm 0.037 N/m$ which, while a new value, falls within the range of established values from literature. This information was the utilized along with the liquid density to perform dynamic contact angle analysis to find advancing, receding, and contact angle hysteresis values θ_a , θ_r and $\theta_a - \theta_r$ respectively. A few notable observations included the fact that the advancing contact angle was $\theta_a = 180^{\circ}$ although this value decreased on subsequent passes once a film developed. Another interesting result was that the hysteresis was maximal, in some cases a full $\theta_a - \theta_r = 180^{\circ}$ which demonstrate the propensity of the metal to *resist* wetting when dewetted and *resist* dewetting when wetted.

In chapter 3 we built upon this wetting information and performed droplet impact tests. By modulating the drop volume and the impact height we varied the Weber numbers over a range of 10 -205. The unique wetting behavior of the oxide layer led to a specialized model that treated the spreading as a Hookean spring where a force was applied at the contact line resisting the spread and the advancing contact angle was assumed to be $\theta_a = 180^o$ based on the results from chapter 2. This produced a model with a novel scaling relationship between the impacting velocity and the maximum spread where they scaled linearly together, a result not seen in prior literature. The fruits of these experiments are a predictive model for liquid metal droplet impacts that may be implemented in Drop on Demand systems in the future as well as a better understanding of wetting with an elastic interface.

The final topic was fully focused on fundamental fluid phenomena: the partial coalescence of droplets at a flat surface. In this study we were able to observe droplets bouncing on the interface of RTLM and NaOH despite the viscous medium. We developed a model to model the drag on these droplets and integrated the process numerically which allowed for the discretization of three distinct regions: the gravity dominant region, the capillary dominant region and final the viscous dominant region.

5.1 Future research

There is no shortage of possible research with this remarkable material. The wetting behavior merits additional study. This could include hysteresis over different ranges as well as studies of the contact angle and wetting behavior of the reduced alloy. This reduction could be done with NaOH, or the metal oxidation could be prohibited and carried out in a fully inert environment such as argon. An additional variable is the reaction rate of the oxidation at the surface. As this is not known *a priori*, certain fluid phenomenon may occur on timescales that are short enough that the oxide may not have time to form so even in oxygen the process may carry out as if the metal is reduced or some combination of oxidized and reduced.

For practical applications we have developed a model for studying the impact process, so the next logical step is to study the generation of droplets. The paradox with the liquid metal is that the oxide creates favorable wetting conditions for printing, without it the droplets would rebound, but the skin also inhibits the capillary phenomena necessary to produce a droplet in the first place. Since instabilities such as the Plateau-Rayleigh breakup are suppressed by the elastic skin an ideal setup would have the droplets produced by a skinless metal but be allowed to oxidize in flight to allow for adhesion to the print surface. Critical to a design like this is to understand the reaction rate of oxidation, so that remains an important step for progress in the field.

For the coalescence, an interesting follow up would be to explore the partial coalescence process in an argon chamber. The lack of viscosity of the surrounding medium would produce some very dynamic bouncing behavior that would be interesting at the very least. An additional avenue would be to use enhanced imaging technology. If the Ohnesorge limit for coalescence holds then the partial coalescence cascade should continue until the droplet radius is $R_1 =$ 1.3 nm! This is a very small droplet and corresponds to a capillary pressure of 616 mPa or over 6000 atmospheres. This really underscores the energy of capillarity and the energy density if this process truly does continue to the Ohnesorge limit would be tremendous.

The final suggested topic of future research is not explored in this dissertation but was observed incidentally: chemically induced dewetting. By exposing a droplet of wetted Galinstan to a droplet of 1 M NaOH. This interaction is shown in Figure 5-1. At first nothing appears to happen but rather quickly a wave initiates from the side that was reduced and propagates towards the dry side of the metal. This process was very starch and produced beautiful capillary waves and Marangoni motion at the surface. This is fertile ground for studying surface tension gradients as well as how the affect wetting behavior.



Figure 5-1: NaOH impacing on wetted liquid metal droplet.

In conclusion, there are a wealth of Galinstan related topics that remain to be explored. Whether they be the development of new and novel applications, or the leveraging of the material properties to study unexplored areas of fundamental fluid phenomena. This metal presents an opportunity for any researcher that is sufficiently creative and patient enough to deal with its sometimes-difficult properties.

Appendix I: Additional Tensiometry Plots



Immersion Depth (mm)

Figure AI-0-1: Force vs Immersion Depth for single trial for glass rod in Galinstan



Figure AI-0-2: Surface tension vs time for several tear off measurements of surface tension. (Full set)



Figure AI-0-3: Tear off probe height vs time for several measurements on tensiometer (full set)



Figure AI-0-4: (a) First measurement for surface tension on a given trial probe is clean prior to this measurement. No observed link between initial tear off height and measured surface tension. (b) Final, 10th, measurement where rod is the most pre-wetted. Final tear off heigh it higher but there is still no observed relationship between the tear off height and measured surface tension. (c) Initial vs final surface tension.

Appendix II: Additional Coalescence Plots



Figure AII-0-1: Non-Dimensional height h_{max}/R_1 vs normalized radius $R_1^* = R_1/(_{cap}.$
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