



**Trinity
College
Dublin**

The University of Dublin

Droplet Dynamics of Graphene Oxide Suspensions

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A thesis submitted for the degree of

Doctor of Philosophy

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Trinity College Dublin

2024

*Basic research is like shooting an arrow into the air
and, where it lands, painting a target.*

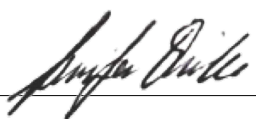
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Declaration

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Abstract

The emergence of printed electronics as an application of Drop on Demand (DoD) inkjet printing has highlighted the importance of understanding the dynamics of this process for non-Newtonian fluids. From jetting to droplet impacts, surface tension and viscosity of printing fluids play a central role in improving the quality and resolution of printed patterns for producing electronic components. Due to the wide range of electrical, thermal and mechanical properties, non-Newtonian 2D nanoparticle suspensions present excellent candidates for such printing applications.

We examined the spreading and splashing behaviour of shear-thinning aqueous graphene oxide (GO) suspensions, and show that the most relevant viscosity in this process for these suspensions during spreading is the high-shear viscosity, and that non-Newtonian behaviour does not influence the critical impact velocity, the impact velocity at which a drop transitions from spreading to splashing. We also found no change in the static surface tension of our samples with GO concentration.

Motivated by the commercial use of magnetic fields to improve crop irrigation, we also probed the dynamic surface tension of water by studying pinch-off dynamics in the presence of magnetic fields. As surface tension is the dominant driving force in the pinch-off dynamics in inkjet printing, any influence on this property due to a magnetic field effect would present important applications in refining the printing process for aqueous nanoparticle suspensions. We show that there is no change in dynamic surface tension under the influence of uniform and gradient magnetic

fields. This study is extended to pinch-off of aqueous GO suspensions and explores the effect of particle concentration on this process, where we observe an increase in concentration results in a slowing of pinch-off.

Acknowledgements

I would like to begin by thanking my supervisor, Prof. Matthias Möbius, for his support and encouragement throughout my PhD project. His thoughtful comments and patient questions pushed this work beyond that which I could have achieved without his guidance. I am extremely grateful to have had the mentorship of an academic so enthusiastic about his work and generous with his time. My experience of pursuing a PhD has been overwhelmingly positive, largely due to the balanced research culture and supportive atmosphere he has cultivated.

This appreciation extends to the rest of the Foams and Complex Systems group at Trinity, Prof. Stefan Hutzler and Prof. Denis Weaire particularly for their helpful insights on both my work on complex fluids and the complex system of academia as a whole. Their expertise on effectively communicating challenging concepts have been instrumental in shaping the clarity and coherence of my work. I would also like to thank Prof. J.M.D. Coey and Prof. Plamen Stamenov for the opportunity to collaborate with the Magnetism and Spin electronics group which I believe elevated and expanded my own research.

I am also grateful to my lab-mates: Dr. Sebastian Barwich for his wealth of knowledge and patience in sharing it, and Arvind Venkatraman for his encouragement and feedback on any issues that arose over the course of my experiments. Thank you both, you truly enriched my experience, and I would not like to have carried out this project without your support and friendship! The rest of the Foams

group who I worked alongside - John, Ali, Stephen, Jens - my heartfelt thanks to you for your collaboration, constructive feedback and camaraderie, which have been invaluable to me over the course of my project.

Despite my research having zero dependence on laser equipment, it would be remiss for me to not thank Chris Smith, Senior Experimental Officer and College Laser Protection Advisor - not for his laser safety expertise, but the for the cumulative *litres* of coffee provided that fuelled the writing of this thesis, not to mention the cheerful friendship and many enjoyable conversations. On that note, I would also like to thank the rest of the 3.24 office gang and miscellaneous tea and coffee comrades – the shared laughter and companionship brightened even the busiest of days. I am thankful for the support of the rest of my friends - you know who you are - but particularly Frances and Stephen, my confidants and companions on the adventure that is graduate studentship. Your empathy and shared experiences navigating life inside and outside of academia has been a much-appreciated source of encouragement and solidarity.

Thank you to all of the technical and administrative staff that assisted me throughout my time at Trinity: Dave Grouse and Pat Murphy for their help with creating and maintaining experimental set-ups, Ken Concannon and Alan O'Meara for their technical support. Thank you to Marie Kinsella and the rest of the staff in both the Finance and School offices for their tireless efforts in supporting the ongoing function of the department which is by no means a small feat.

I also wish to thank the academic staff that were generous enough to allow me to make use of their equipment over the course of my project, Prof. Jonathan Coleman and Prof. Martin Hegner. These opportunities provided important additional insights to my work, and I am immensely grateful.

I want to thank all the staff I worked with throughout my time as a teaching assistant in the Junior Fresh laboratory, James, Nigel, Romina, Chris, Joe and Dave.

It has been a pleasure to work alongside you.

I would like to acknowledge Science Foundation Ireland for funding this work. I am extremely grateful to have been afforded the opportunity to pursue a PhD in a research area I love.

Finally, I want to thank my family for their unwavering support, home-cooked meals, and abundant encouragement without which I would not have been able to see this project through to its conclusion. Mum, Dad and Rachel, you have seen me through the most difficult times with grace and understanding, and I am eternally grateful. I love you all.

Covid-19 Impact Statement

I began my PhD in September 2019 with the Foams and Complex systems group and spent the first three months getting familiar with the equipment I needed to use, namely the high-speed camera and rheometer. As extensive droplet impact experiments had not been carried out previously in the group, much trial and error was involved in determining the optimal experimental set up and procedures. We began a collaboration with Professor J.M.D Coey and the Magnetism and Spin electronics group in December 2020, designing our experiment set up, and again obtaining preliminary measurements until March 2020.

At this point, the closure of all colleges was announced by the Irish government, and I no longer had access to the laboratory. Over the period from March to late May 2020 I was unable to carry out experimental research which significantly hindered my progress in my PhD. At this point, I had very little usable data and ultimately spent this time reviewing the literature and optimizing my data analysis techniques.

The laboratory was reopened in a limited capacity during the summer of 2020. Upon the reopening of campus, lab occupancy in my lab was reduced to one person, however the lab was needed for use by two students – myself and a student from Prof. Coey’s group, who we collaborated with and used our tensiometer extensively. While I was now able to recommence the capture of experimental data this took place in a significantly reduced capacity and not in the full time capacity required.

In October 2020, the high-speed camera upon which all my research depends

broke down. While equipment failure can happen over the course of a research project, reduced staffing caused by the pandemic and consequent slowdown in communication resulted in a significant delay in the camera repair, which required shipment to the US for the repair to be completed. The level five restrictions that were once again put in place in December 2020 also contributed to this, resulting in the return of the camera in February 2021. This understandably had major ramifications on my progress on my PhD project. Over the course of this period I made a concerted effort to carry out any measurements I could that did not require high-speed imaging - namely surface tension measurements - along with working on optimizing my image processing techniques and MATLAB scripts.

Restrictions on lab capacity continued until September 2021, and the addition of another group member who also required access to the lab in January 2021 meant the available hours in the lab remained reduced. After this point, I was able to resume normal activity and progress more quickly with my project.

Overall, COVID-19 had a significant impact on my ability to run experiments and capture data, resulting in a delay in submission from August 2023 to March 2024. I used any delays to optimize my data analysis and image processing techniques to the best of my ability but ultimately my progress was hindered. Thankfully I managed to achieve the original goals we had for the project with the addition of a five month extension provided by the Higher Education Authority, but this would not have been possible without the extra time.

List of Publications

S. Poulouse, **J. A. Quirke**, P. Stamenov, M. E. Möbius, and J. M. D. Coey,
“Deformation and necking of liquid droplets in a magnetic field,” *Physics of Fluids*,
vol. 34, no. 11, p. 112 116, 2022

J. Quirke and M. Mobius, *The spreading and splashing of graphene oxide
dispersions*, presented at APS March Meeting, Chicago, IL, USA, March 2022,
Abstract: <https://ui.adsabs.harvard.edu/abs/2022APS..MARS11012Q>

L. C. Fan, K. McConn, M. Plataki, S. Kenny, N. C. Williams, K. Kim,
J. A. Quirke, Y. Chen, M. Sauler, M. E. Möbius, K. P. Chung, E. Area Gomez,
A. M. Choi, J. F. Xu, and S. M. Cloonan, “Alveolar type II epithelial cell FASN
maintains lipid homeostasis in experimental COPD,” *JCI insight*, vol. 8, no. 16,
2023

J. M. D. Coey, L. Coburn-Moran, and **J. Quirke**, “Influence of Magnetic Field on
Evaporation of Water and Ionic Solutions,” in *2023 IEEE International Magnetic
Conference - Short Papers (INTERMAG Short Papers)*, 2023, pp. 1–2

J. A. Quirke and M. E. Möbius, “Spreading of graphene oxide suspension
droplets on impact,” *Physics of Fluids*, 2024 (in review)

J. A. Quirke and M. E. Möbius, “Splashing outcomes for droplet impacts of graphene oxide suspensions,” 2024 (in preparation)

J. A. Quirke and M. E. Möbius, “Pinch-off dynamics of graphene oxide suspensions,” 2024 (in preparation)

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Chapter 1

Introduction

1.1 Fluid Dynamics Across Timescales

In the realm of fluid dynamics and material science, the pace at which discoveries unfold often varies, ranging from the deliberate, nearly imperceptible descent of a pitch drop in long-term experiments, such as the renowned Pitch drop experiment here at Trinity College Dublin, to the rapid, dynamic interactions observed in droplet impacts that necessitate the use of high-speed photography to capture. This dichotomy serves as a metaphor for the diverse timescales inherent in the study of fluid behavior.

The Pitch drop experiment, initiated in 1944, is one of the world's oldest ongoing scientific experiments. It demonstrates the extraordinary viscosity of pitch, a material that appears solid at room temperature but flows like a liquid over long time scales. The experiment consists of a sample of pitch held in a funnel at the bottom of which drops form and fall on a timescale of years, as shown in figure 1.1.

Movement of the Trinity pitch drop over time can be observed in figure 1.2a. This illustrates the gradual descent that has captivated scientists and the public alike for decades. After imaging the drop every one to two months over the course



Figure 1.1: Pitch drop experiment at Trinity College Dublin, March 28th, 2023.

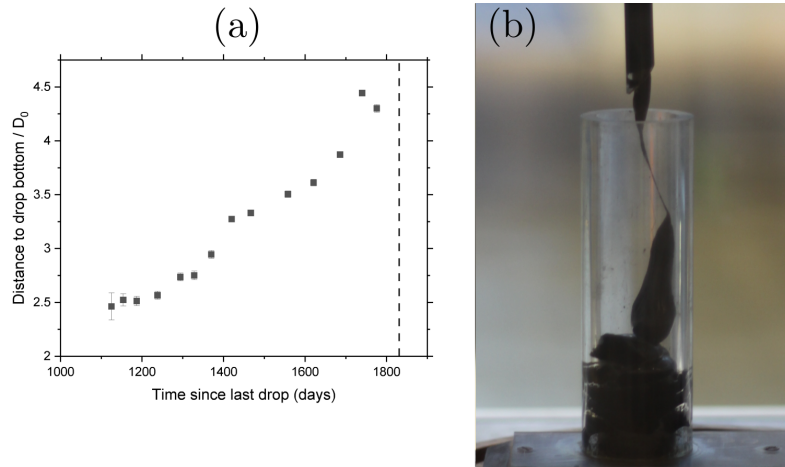


Figure 1.2: (a) Distance from funnel to drop bottom over time, made dimensionless by dividing by the funnel diameter. The vertical dashed line lies at day 1813, indicating the date the drop fell in 2024. (b) Pitch drop experiment at Trinity College Dublin, October 25th, 2024, one day after the most recent drop fall.

of my time at Trinity, through times of pandemic and otherwise, I arrived to capture the latest photo of the drop on October 25th, 2024, only to find the drop had fallen. I was informed by library staff that the drop had fallen the previous day. The image captured of the drop that day is shown in figure 1.2b. This event of the last pitch drop provides a poignant example of the unpredictable yet inevitable nature

of scientific phenomena.

1.2 High-speed Imaging

In addition to the historical and scientific significance of the pitch drop experiment, its metaphorical resonance extends to the study of droplet impacts and jetting, the focus of this thesis. Just as the controlled observation of pitch drops has contributed to our understanding of fluid behavior over extended periods, the meticulous investigation of droplet dynamics plays a crucial role in advancing technologies reliant on fluid manipulation.

Recent decades have witnessed remarkable technological advancements that have revolutionized the study of fluid dynamics and material science, enabling researchers to probe complex phenomena with unprecedented precision and detail. One such advancement is the development of high-speed imaging techniques which have provided researchers with a powerful tool to study rapid fluid dynamics phenomena, such as droplet impacts and jetting events. Current imaging capabilities for exploring the dynamics of fluids have advanced significantly from the earliest studies, such as those conducted by Lord Rayleigh and Worthington in the late 19th century, utilizing plate photography in its earliest form and presenting sketches of their findings [1, 2]. Modern digital high-speed cameras can now achieve time resolutions of 10,000,000 frames per second at moderate resolutions [3].

By recording the entire droplet impact process at a high frame rate, researchers can unravel the underlying physics governing droplet behavior, shedding light on phenomena that occur on timescales as short as microseconds. Similarly, in the study of jetting phenomena, high-speed imaging has proven invaluable in capturing the transient dynamics of fluid jets with exceptional clarity. By visualizing the evolution of jet morphology and instability patterns at high frame rates, researchers can elucidate the underlying mechanisms driving jet breakup, dispersion, and mixing.

This insight is crucial for optimizing industrial processes reliant on fluid jetting, such as additive manufacturing and microfluidic device fabrication.

1.3 Additive Manufacturing with Nanoparticle Suspensions

The precise control of fluid jetting and splashing is integral in many industrial applications, from inkjet printing to rapid spray cooling [4]. Considerable work has been carried out over the last 100 years to understand the dynamics governing these events, further refining control of industrial processes. Drop-on-demand (DoD) is the most common form of inkjet printing. In this method a transducer, piezoelectric or thermal, pushes fluid out of a chamber in the printhead through an orifice. A column of fluid emerges, which, driven by surface tension, pinches off into a droplet, typically 20 - 50 μm in size [5]. The ejected droplet, with an ejection velocity of 10-20 m/s, impacts on the printing substrate which may lead to splashing, dependant on the properties of the fluid, substrate and surrounding gas. If splashing occurs, it reduces the resolution of the printed pattern and is as such undesirable in the printing process. Secondary satellite droplets may also form during the pinch-off, as can be seen in figure 1.3. These satellites may recombine with the primary droplet, or may also deposit on the substrate, further reducing the quality of the printed pattern.

The rapidly evolving area of nanofluids presents further potential applications in printing. Since the discovery of single layer graphene, 2D nanomaterials have been highlighted for their broad ranges of thermal, electrical, and mechanical properties. The implementation of inkjet printing with suspensions of 2D nanoparticles such as graphene, MoS_2 , boron nitride and black phosphorus has resulted in the capacity to produce printed electronic components. From flexible supercapacitors for flexible energy storage [6] to flexible sensors for wearable electronics [7], a thorough under-

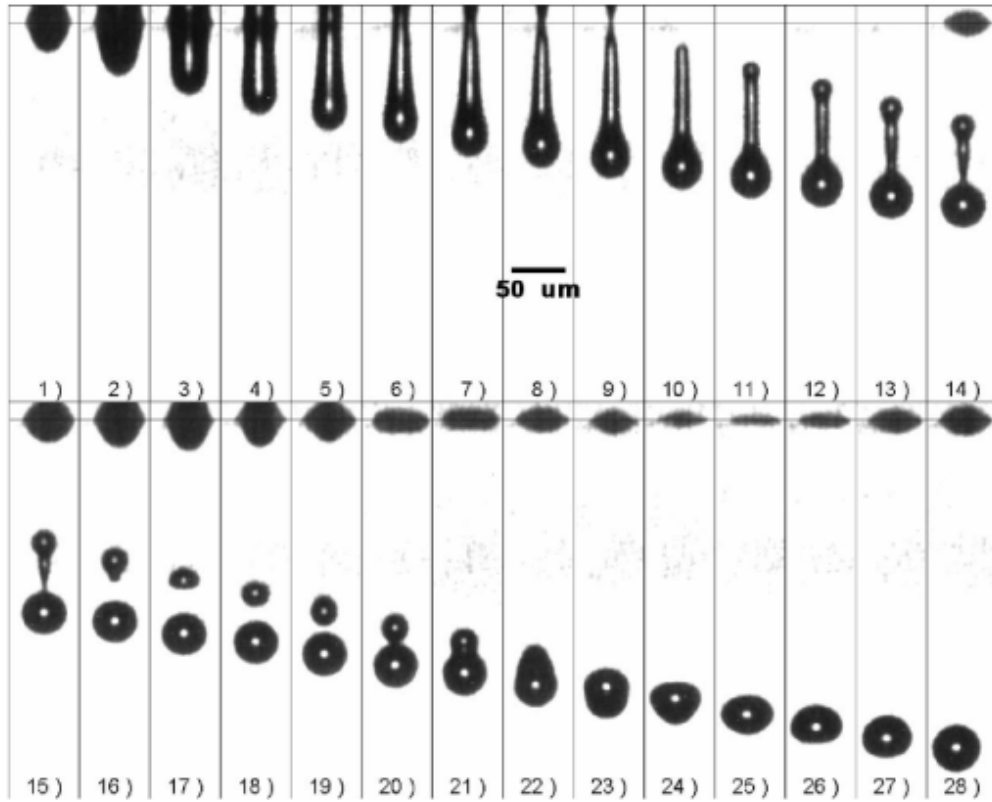


Figure 1.3: Formation of a DoD inkjet droplet, Dong *et al.* (2006) [5].

standing of the dynamic behaviour of 2D nanofluids is paramount to improving the quality of printed-electronic applications.

While it has become easier to produce pristine graphene nanosheets in recent years, they and most other nanosheets were dispersed in toxic solvents such as N-Methyl-2-pyrrolidone (NMP) which presents hazards in the experimental investigation of jetting and splashing behaviours. More recently, Isopropyl Alcohol (IPA) has been used, but such dispersions are not stable. We chose to investigate graphene oxide (GO) nanosheets which are readily dispersible in solutions of ethanol and water and are stable over our experimental timescales.

1.4 Mechanics of Fluids and Soft Matter

1.4.1 Understanding the Fluid Mechanics of GO Suspensions

Understanding the fundamental principles of fluid mechanics and soft matter is crucial for analyzing and interpreting the behavior of GO suspensions. These suspensions exhibit complex flow behaviors that are influenced by their unique physical and chemical properties. Given this, it is important to garner an understanding of the basic mechanics of simple and complex fluids. In the following section, we will explore the basic mechanics of elasticity and viscosity, Newtonian fluids, non-Newtonian fluids and viscoelasticity, to provide a theoretical foundation on which to build our study of GO suspensions.

1.4.2 Basic Mechanics of Solids and Fluids

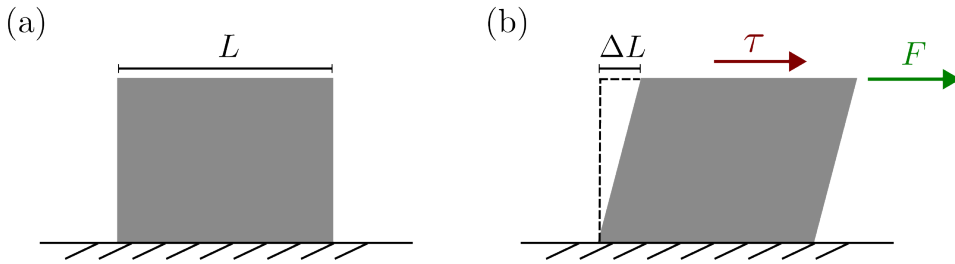


Figure 1.4: (a) Solid object at rest on surface, (b) object undergoing shear force F .

Figure 1.4 illustrates the application of a shear force (perpendicular to the normal surface) to a solid object at rest on a surface. This causes a shear stress, τ , to arise in the object which results in a deformation. The shear stress is defined as the force per unit area $\tau = F/A$, where the area, A , in this case corresponds to the top surface of the object. The shear strain, γ , is the relative deformation of the object, and in this case $\gamma = \Delta L/L$. We now impose that this solid object is *elastic*. This infers that if the shear force is removed, the object will return to its original shape. This

ideal case of a perfectly elastic solid obeys Hooke’s law,

$$\tau = G\gamma, \quad (1.1)$$

where G is the shear modulus, a measure of the elastic shear stiffness of the material [8]. A Hookean solid is commonly illustrated with the example of a spring as shown in figure 1.5a [9].

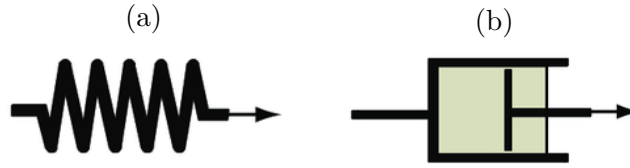


Figure 1.5: (a) Spring and (b) dashpot diagrams to represent Hookean solids and Newtonian liquids respectively. Adapted from Hodge *et al.* (2012) [9].

Let us now consider a fluid between two parallel plates separated by a thickness h . Suppose a shear force F is applied to the upper plate, causing it to move at a velocity U , while the lower plate remains stationary. We enforce a “no-slip” boundary condition in which the fluid in contact with the boundary moves with the same velocity as that boundary, i.e. the portion of fluid in contact with the lower plate has a velocity $v = 0$, while the portion in contact with the upper plate has a velocity $v = U$. This results in a velocity gradient within the fluid, as indicated in figure 1.6. We define the shear rate as the rate of change of this velocity gradient, $\dot{\gamma} = \frac{dv}{dh}$ [10]. Newton’s law of viscosity defines the ideal viscous fluid,

$$\tau = \mu\dot{\gamma} \quad (1.2)$$

where μ is the fluid viscosity, a measure of the fluid’s resistance to flow [8]. In some respects, an ideal viscous fluid is the opposite of a perfect elastic solid in that after a force is applied to the fluid and then removed, the fluid will remain in the deformed state. This is often illustrated using a dashpot diagram, as shown in figure 1.5b [9].

As a constant force is applied to the piston, the piston will move at a continuous velocity. When the force is removed, the piston will remain stationary at it's current position.

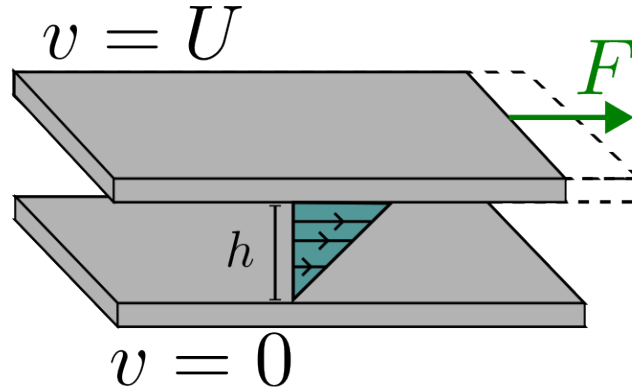


Figure 1.6: Shear force applied to a fluid between two parallel plates.

Newtonian and Non-Newtonian Fluids

Viscosity is the defining property in distinguishing Newtonian and non-Newtonian fluids. In everyday life we have an intuitive sense of what viscosity is - we know that honey flows with more resistance than water.

For a Newtonian fluid, the value of viscosity is independent of the rate of change of velocity when the fluid undergoes shear, or the shear rate. For example, water flowing in a pipe undergoes a shear stress but the viscosity of the water is not affected, remaining at a value of approximately 1 mPa s.

This is not the case, however, for a non-Newtonian fluid. Figure 1.7 shows an example of the relationship between viscosity and shear rate for a Newtonian fluid and two types of non-Newtonian fluids. In the case of the Newtonian fluid, the relationship is linear and the viscosity is independent of the shear rate. If we observe the relationship for the two non-Newtonian fluids, we can see this is not the case. For one fluid, we see the viscosity increases with increasing shear rate – this is known as shear-thickening. For the other non-Newtonian fluid, we see the viscosity

decrease with increasing shear rate – this is known as shear-thinning.

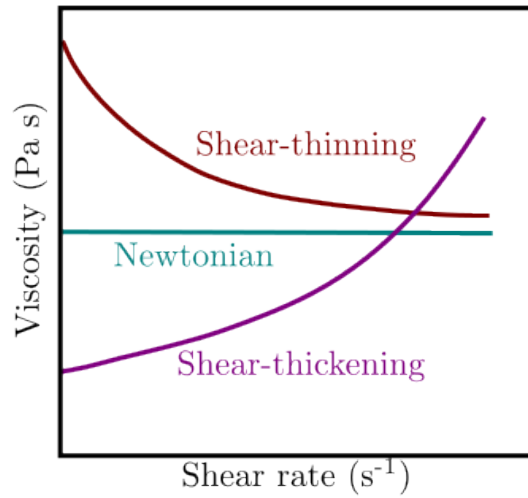


Figure 1.7: Viscosity dependence on shear rate for Newtonian and non-Newtonian fluids.

Another example of a non-Newtonian fluid is a thixotropic fluid, in which viscosity decreases over time under constant shear, for example ketchup or paint, and is a case of a time-dependent shear-thinning. Conversely, in a rheopectic fluid, viscosity increases over time under constant shear, and is a case of time-dependent shear-thickening. Measurements of a material's viscosity dependence on shear rate are typically carried out in a rheometer. In a stress controlled rheometer, the sample is loaded between two parallel plates, the bottom of which is fixed and the upper rotates. The rotations are carried out over a range of shear rates, and the materials response is monitored.

1.4.3 Viscoelasticity

Real materials often do not exhibit solely elastic or viscous behaviour. Such materials are referred to as viscoelastic, and additionally exhibit a dependence on timescale, with a delayed response to an applied stress and its removal.

Viscoelastic liquids are materials that remain partially deformed after the application and removal of a force. A basic model of such materials is the Maxwell

model, given by

$$\dot{\gamma} = \frac{\tau}{\mu} + \frac{\dot{\tau}}{G}. \quad (1.3)$$

This model is illustrated using a combination of a spring and dashpot, where the spring and dashpot are joined in series, as shown in figure 1.8a [10].

Viscoelastic solids are viscoelastic materials that have a reversible deformation process. The Kelvin-Voigt model describes this behaviour,

$$\tau = \mu\dot{\gamma} + G\gamma \quad (1.4)$$

In this case, the behaviour is illustrated by a spring and dashpot in parallel, as shown in figure 1.8b [10].

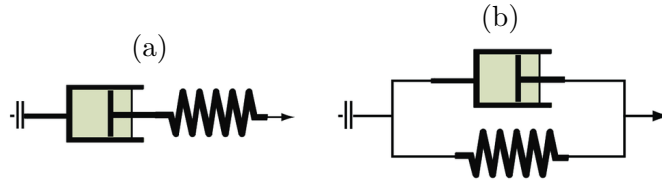


Figure 1.8: (a) Maxwell and (b) Kelvin-Voigt dashpot diagrams to represent viscoelastic liquids and solids respectively. Adapted from Hodge *et al.* (2012) [9].

Creep tests are an excellent way to distinguish between viscoelastic solids and liquids [8]. In a creep test, a step stress is first applied and maintained for a set time interval and then is removed and the strain response of the material is measured. Figure 1.9 shows a creep test for both a viscoelastic solid and liquid. At time t_0 , a stress is instantaneously applied to the material, and maintained at a constant value until time t_1 . At this point, the stress is immediately removed and remains so permanently. In the case of the viscoelastic liquid, a certain amount of deformation remains in the material at the point t_2 . For the viscoelastic solid, the material returns to its initial state after a delay. Both the viscoelastic solids and liquids discussed here can be referred to as Linear viscoelastic. This means that they have viscoelastic properties under small deformations where strain varies linearly with

the applied stress.

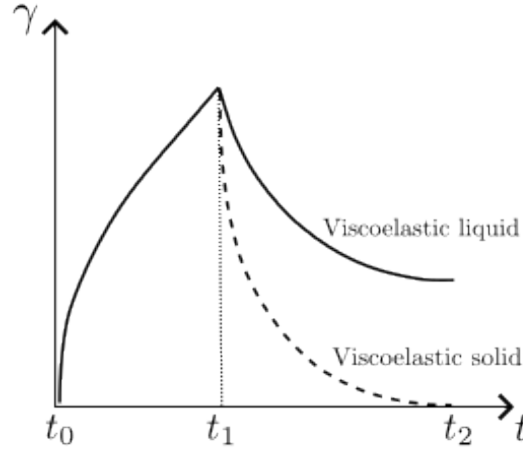


Figure 1.9: Creep test for a viscoelastic liquid and viscoelastic solid.

Oscillatory measurements are key to examining the viscoelastic behaviour of materials. In a strain controlled oscillatory test, an oscillating shear force is applied to the material and the materials response is measured. A sinusoidal strain is applied of the form $\gamma(t) = \gamma_0 \sin(\omega t)$, for strain amplitude γ_0 and frequency ω , and from the resultant torque a sinusoidal curve is output. The angle delta represents the phase shift between the strain input into the system during the oscillation and the resulting stress in the material, visualised in figure 1.10 [8]. For ideal elastic behaviour, $\delta = 0^\circ$, for ideal viscous behaviour, $\delta = 90^\circ$, and so for viscoelastic behaviour, $0^\circ < \delta < 90^\circ$.

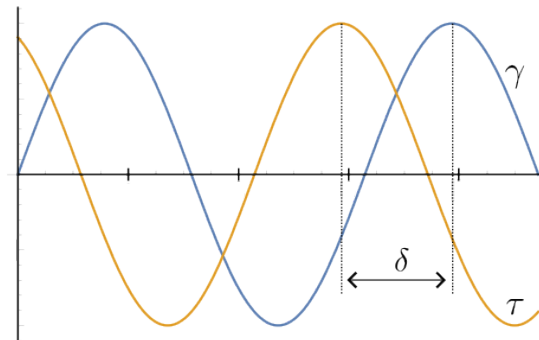


Figure 1.10: Stress and strain over time in an oscillation test.

This viscoelastic response is characterised using the complex shear modulus

$$G^* = \frac{\tau(t)}{\gamma(t)}, \quad (1.5)$$

where both the stress and strain are time dependant due to the nature of the oscillation measurement [10]. The complex modulus can be broken down into two components, the storage modulus, G' , and the loss modulus, G'' , as $G^* = \sqrt{G'^2 + G''^2}$, and $\tan\delta = \frac{G''}{G'}$, indicated in figure 1.11 as a vector diagram.

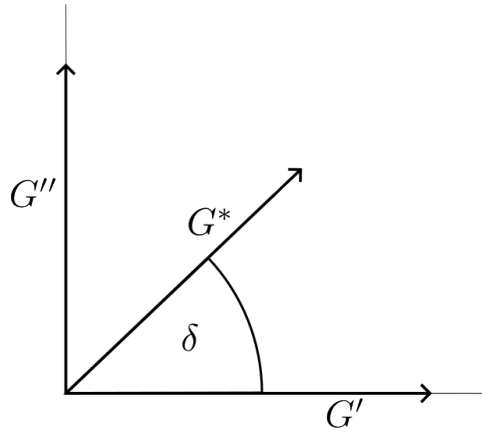


Figure 1.11: Vector components of the complex modulus, G^* .

In an amplitude sweep, such an oscillatory test is carried out over a range of strain amplitudes. At low amplitudes, the resulting G' and G'' will display a plateau in a region known as the linear viscoelastic (LVE) range. Comparison between these plateaus can help us identify the viscoelastic behaviour of a material. For materials with $G' > G''$ in the LVE range, elastic behaviour is dominating, and the material behaves like a gel or a solid at low amplitudes. If $G' < G''$, viscous behaviour dominates and the material is more like a liquid.

1.5 Thesis Overview

In adding nanoparticles to an aqueous solution, the fluid becomes non-Newtonian, with the viscosity going from a constant value to shear-rate dependant. Addition of nanoparticles can also alter the surface tension of a fluid. This study aims to investigate how droplet impacts depend on the GO concentration - which can have a significant effect on the the fluid properties - in order to understand how to optimize inkjet printing with such suspensions.

Surface tension is an important parameter to consider in droplet impacts. Tuning of surface tension in an impacting drop could further improve printing resolution by reducing the likelihood of splashing outcomes. In collaboration with the Magnetism and Spin Electronics group at Trinity College Dublin, a study was conducted to investigate if the surface tension can be influenced by a magnetic field. Preliminary measurements of using magnetic fields in crop irrigation have shown an effect on the droplet size distribution, namely the suppression of droplets in the sub 50 μm range [11]. As surface tension is one of the dominating factors in the mean droplet size of sprays [12], we explored whether magnetic fields affect the dynamic surface tension of water, which can be inferred from droplet pinch-off experiments.

Expanding on this study, we examined the pinch-off process in GO suspensions. By varying the particle loading, we probed how the addition of 2D nanoparticles can affect the rate of droplet detachment, along with how they affect filament morphology as the point of droplet detachment is approached.

The outline for this thesis is as follows: in chapter 2, the makeup of the GO suspensions employed in this study is reviewed, along with the characterisation of the fluid parameters for each sample of varying GO concentration. A summary of the structure of GO is given along with it's synthesis methods, and the sample preparation methods utilized in this study are described. The surface activity of GO suspensions is outlined and results for surface tension measurements of our

sample set are given, where we see negligible change in surface tension with increased particle loading. The rheology of the GO suspensions are also examined, with its shear-thinning and yield stress behaviour are illustrated through viscosity ramps and oscillatory measurements.

Chapter 3 examines the spreading behaviour of the suspensions, investigating whether a Newtonian spreading model can be used to predict their spreading behaviour. The current understanding of the spreading behaviour of Newtonian fluids is outlined, and we show that a new Newtonian energy balance model can capture the spreading behaviour of our non-Newtonian GO suspensions.

In chapter 4, the study of the splashing threshold of GO suspensions is detailed, where we outline the current Newtonian models for the transition of spreading to splashing. We show that this transition for GO suspensions cannot be predicted by Newtonian splashing models. We also observe the suppression of splashing within our experimental limit of an impact velocity of 5 m/s for both GO suspensions and Newtonian samples of water-ethanol-glycerol mixtures.

The collaboration on magnetic field effects on surface tension is detailed in chapter 5. Here we find that uniform magnetic fields have no effect on dynamic surface tension, and that any affect resulting from the presence of a gradient field is negligible over the course of drop pinch-off.

Chapter 6 examines the pinch-off study for suspensions of different GO particle loadings, where we observe a retardation of droplet detachment with increasing GO concentration and remark upon similarities in the filament profiles with those of non-Brownian spherical colloidal suspensions.

We conclude in chapter 7 with an exploration of the outlook for this work and detail the further work that would provide additional insights into the droplet dynamics of 2D nanoparticle suspensions.

Chapter 2

Materials & Characterisation

2.1 Introduction

Understanding the physical properties of aqueous graphene oxide (GO) suspensions is pivotal for predicting their behaviour in the context of splashing, spreading, or jetting. This chapter delves into the 2D nanomaterial itself and characterization methodologies essential for comprehending the intricate dynamics of droplets of such suspensions. 2D nanoparticle suspensions hold promise in various applications [13], but predicting the behavior of drops of an aqueous suspension is contingent upon understanding the fundamental physical properties of the suspension. GO itself may not be as useful in such applications as other 2D nanoparticles, but serves as a model system for other suspensions.

The initial section of this chapter provides a comprehensive background on GO, including its structure and synthesis methods. Subsequently, the sample preparation technique for GO suspensions utilized in experiments in chapters 3, 4 and 6 is outlined.

Finally, the chapter addresses the characterization of samples of aqueous GO suspensions of varying GO concentration to measure the dependence of important

physical properties on nanoparticle concentration, particularly surface tension and viscosity, along with assessing the viscoelastic properties of the suspensions.

2.2 GO Structure and Synthesis

GO is a 2D material, comprised of atomically thin micron-length flakes, first synthesised in 1855 [14]. It has the typical graphene hexagonal carbon lattice, with its basal plane and edges containing oxygen-based functional groups [15]. The exact structure of the nanomaterial is undetermined, with several potential models seen in the literature [16], but the complex combination of oxygenated functional groups makes the task of ascertaining the structure non-trivial. There is wide variation in the structure of GO prepared using different methods, resulting in different numbers of oxygen groups attached to lateral flake sizes ranging from submicron to 10s of microns, ~ 1 nm in thickness.

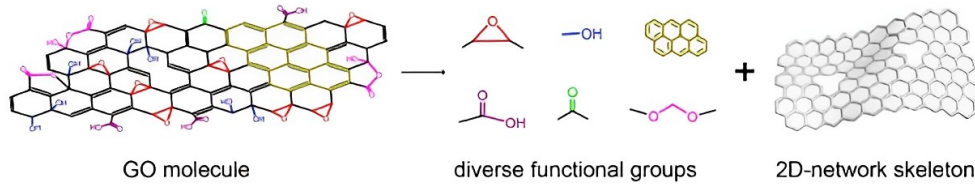


Figure 2.1: Diagram of GO structure, illustrating that the complex structure can be described by the combination of diverse functional groups and the 2D hexagonal lattice. Figure adapted from Du *et al.* (2020) [15].

GO is most commonly produced using procedures based on the Hummer's method [17]. This method involves chemically exfoliating graphite using Sodium nitrate (NaNO_3), potassium permanganate (KMnO_4) and sulphuric acid (H_2SO_4), and the resulting GO is then washed. Modified versions of this method are also prevalent in the literature [18]. Alternative methods, such as the Staudenmaier method [19] and Brodie method [14], also exist for GO synthesis, each offering variations in the degree of oxidation and the types of functional groups introduced [20].

While GO does not maintain the conductive or thermal properties of graphene,

it can be chemically reduced to rGO to recover some thermal and electrical properties [21]. GO is amphiphilic in nature, which results in its excellent abilities as a dispersing agent [22]. It can be readily dispersed in water due to the hydrophilic -COOH groups on its edges.

The stability of aqueous GO dispersions is a critical aspect influencing its applicability across various fields. The electrostatic repulsion between negatively charged GO sheets plays a vital role in stabilizing the dispersion [23]. The resulting colloidal stability prevents the agglomeration of GO sheets, ensuring a homogeneous distribution within the solution. However, achieving and maintaining stability is contingent on factors such as pH, ionic strength, and the concentration of GO, with a neutral pH shown to enhance stability [24, 25].

2.3 Sample Preparation

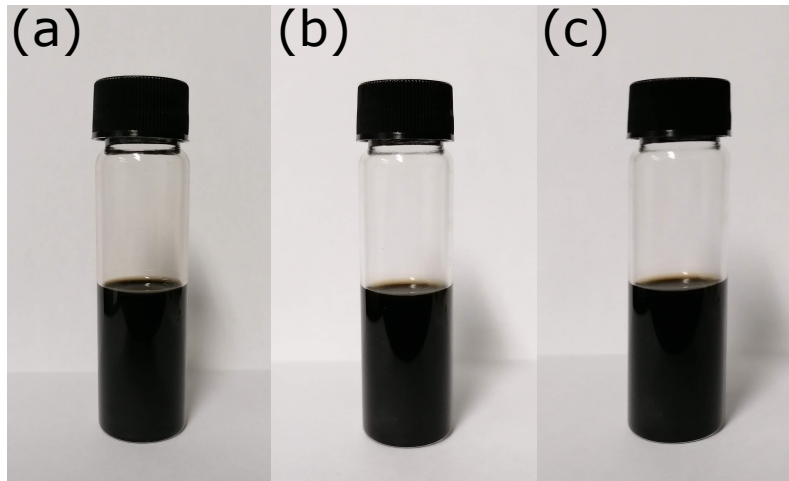


Figure 2.2: Stability of 5g/l GO in 50% v/v ethanol-water over time. Sample imaged at (a) 0 hours, (b) 20 hours and (c) 44 hours after sample preparation and shear mixing. Aggregation in such samples can be observed by a phase separation due to settling of the aggregates, which is not seen here.

GO samples were prepared by the dilution of a highly concentrated 2.5wt% stock of GO in water, commercially supplied by Graphenea, USA. The stock has a mean lateral flake size of 17 μ m, verified by SEM imaging. Samples were diluted

with ethanol and water to produce dispersions in a 50%v/v ethanol-water mixture. Ethanol was included in addition to water to lower the surface tension of the resulting dispersion from approximately 72 mN/m to around 30 mN/m, in order to promote splashing at lower impact velocities for drop impact experiments. The pH of each sample was adjusted to 7 by the addition of 0.5M NaOH. After dilution, all samples were shear mixed at 6000rpm for 30 minutes using a Silverson L5M-A laboratory mixer to ensure the GO is well dispersed. Samples were prepared in a range of concentrations from 0.5-6 g/l GO in 50%v/v ethanol-water, with stability tests carried out to show the samples remained stable over several days. All measurements were carried out within 3 hours of sample preparation. This lies well within the timescale for which the suspensions remain well dispersed, as illustrated in figure 2.2.

2.4 Surface Tension

Surface tension measurements were carried out using a Dataphysics OCA 25 tensiometer using the pendant drop method. This technique involves fitting the Young-Laplace equation to the drop profile of a droplet suspended from a capillary at equilibrium - the pendant drop. The Young-Laplace equation is given by

$$\gamma = \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta P = \Delta P_0 - \Delta \rho g z, \quad (2.1)$$

where R_1 and R_2 are the principle radii or curvature and ΔP is the Laplace pressure across the interface. The Laplace pressure can be written in terms of a reference pressure, ΔP_0 at the bottom of the droplet ($z = 0$, see figure 2.3), and a hydrostatic pressure $\Delta \rho g z$, where $\Delta \rho$ is the pressure difference between the fluid and the surrounding gas, and g is the acceleration due to gravity. The surface tension is obtained by numerically fitting an image of the droplet shape to the three

parametric equations

$$\frac{d\Phi}{ds} = -\frac{\sin \Phi}{x} + \frac{2}{R} \quad (2.2)$$

$$\frac{dx}{ds} = \cos \Phi \quad (2.3)$$

$$\frac{dz}{ds} = \sin \Phi, \quad (2.4)$$

where $\frac{2}{R} = (\frac{1}{R_1} + \frac{1}{R_2})$.

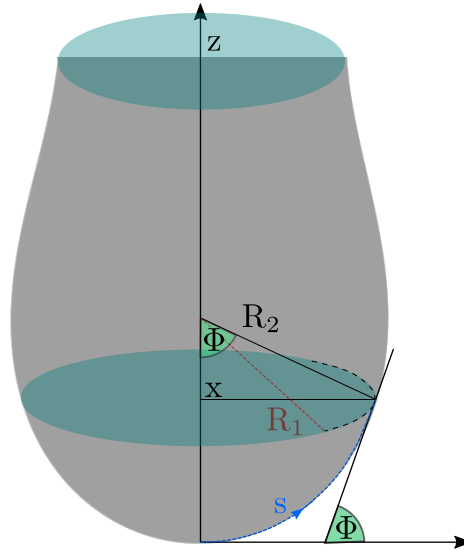


Figure 2.3: Pendant drop geometry.

Pendant drops were suspended from 2.08 mm outer diameter nozzles. Larger droplet volumes such as this allow the droplet to elongate and deviate from a spherical shape, reducing error in the measurement [26]. The accompanying Dataphysics software was used to analyse the drop shape and carry out fitting to determine the surface tension.

Surface tension measurements were carried out on samples of varying GO concentrations dispersed in a 50%v/v ethanol-water mixture with the results shown in figure 2.4. Each reported value represents 5 individual measurements. As the GO concentration is increased there is no significant effect on the surface tension

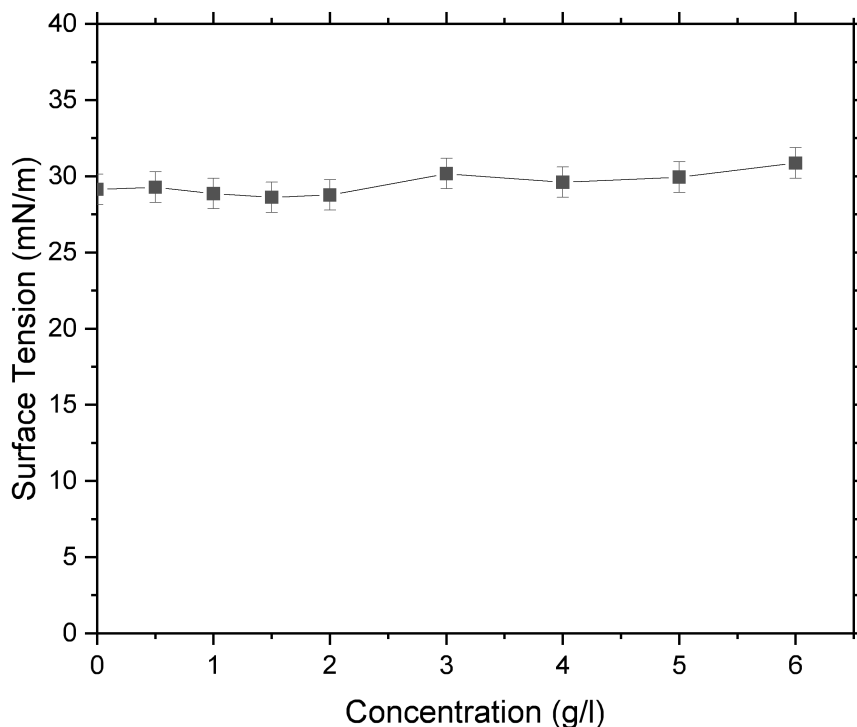


Figure 2.4: Surface tension as a function of GO concentration in 50%v/v ethanol-water.

observed for these samples. While no studies thus far have examined GO in water-ethanol mixtures, conflicting results have been seen in the literature for surface tension studies of GO suspensions in water. A 2019 study by Corker *et al.* [18] reported a 64% decrease in the surface tension over a similar concentration range, which was also observed to a lesser degree by Cabaleiro *et al.* (2018) [27]. In contrast, Zheng *et al.* (2014) [28] reported a small increase in surface tension with increasing GO concentration.

GO is reported to be amphiphilic, with its hydrophilic structural elements allowing it to disperse well in aqueous media while the basal plane is hydrophobic. This suggests GO colloids are surface active and will reduce the surface tension of the suspension [22]. The amphiphilicity of GO is dependent on the size of the nanosheets, which has been demonstrated by Kim *et al.* (2010) [22]. A decrease in the size of GO sheets results in an increase in the edge to area ratio, which implies the sheets would become more hydrophilic due to the edge groups dominating. This

results in larger sheets becoming more surface active. The mean lateral flake size of the GO used in the study by Corker *et al.* was 64 μm , which is consistent with the stronger surface activity observed in their study in comparison to the smaller 17 μm flakes studied here. In addition to flake size, both the pH of the suspension and the degree of oxidation of the GO can influence its amphiphilicity [29, 30], which suggests that GO from different sources will have varying surface activity.

2.5 Rheology

2.5.1 Viscosity

Comparing droplet impacts of non-Newtonian drops with Newtonian studies in the literature presents a challenge as the various proposed mechanisms and models for splashing, spreading and jetting assume that the viscosity remains constant throughout the impact. The shear rate varies considerably during the impact of a drop, changing several orders of magnitude over the course of a single impact. Should a drop's viscosity have a dependence on this shear rate, the viscosity can change considerably over the course of the impact. Studies concerning drop impacts of non-Newtonian drops often adopt a "characteristic viscosity" used to approximate the viscosity as a constant value for a given impact, dependant on the given impact velocity [31, 32].

GO suspensions are complex fluids, with their viscosity dependant on shear rate. Aqueous GO is a shear-thinning fluid, with its viscosity decreasing with increasing shear rates, as demonstrated in the literature [18][33][27], with the shear viscosities increasing with concentration at a given shear rate.

Rheological measurements were carried out using an Anton Paar MCR 302e with a 50 mm cross-hatched plate-plate geometry at a gap size of 1 mm. Shear controlled flow ramps were carried out with shear rates from 0.2 to 400 s^{-1} , measuring the

apparent viscosity. At high shear rates, centrifugal forces induce a secondary flow that leads to additional dissipation and an incorrect viscosity measurement, and as such shear rates were limited to 400 s^{-1} .

Figure 2.5 shows the shear rate curves for varying concentrations of GO in 50%v/v ethanol-water. The shear thinning behaviour of the suspensions can be clearly observed from the plot, with the low shear viscosity increasing with GO concentration. Below 1.5 g/l the suspension is Newtonian with no appreciable shear rate dependence and above, it exhibits shear thinning behaviour. As the shear rate is increased, the viscosity of higher concentration samples will tend to the solvent viscosity.

The viscosity data was fit to the Herschel-Bulkley model for non-Newtonian fluids,

$$\eta = \frac{\tau_{HB}}{\dot{\gamma}}; \quad \tau_{HB} = \tau_0 + m\dot{\gamma}^n, \quad (2.5)$$

where η , τ_{HB} , τ_0 , m , n and $\dot{\gamma}$ are the apparent viscosity, shear stress, yield stress, consistency index, flow index and shear rate respectively. These fits are represented in figure 2.5 by the solid lines, with the fit parameters detailed in table 2.1.

Table 2.1: Herschel-Bulkley parameters for samples of GO in 50%v/v ethanol-water, solvent viscosity $\eta = 2.90 \text{ mPa s}$.

GO concentration (g/l)	HB parameters		
	$\tau_0(Pa)$	$m(Pas^n)$	n
0.5	0.000 ± 0.001	0.003 ± 0.001	0.99 ± 0.02
1	0.000 ± 0.001	0.004 ± 0.001	0.97 ± 0.02
1.5	0.0002 ± 0.001	0.005 ± 0.001	0.95 ± 0.02
2	0.001 ± 0.001	0.006 ± 0.001	0.96 ± 0.02
3	0.003 ± 0.001	0.013 ± 0.001	0.91 ± 0.02
4	0.013 ± 0.001	0.033 ± 0.001	0.82 ± 0.02
5	0.070 ± 0.001	0.073 ± 0.001	0.77 ± 0.02
6	0.290 ± 0.001	0.137 ± 0.001	0.76 ± 0.02

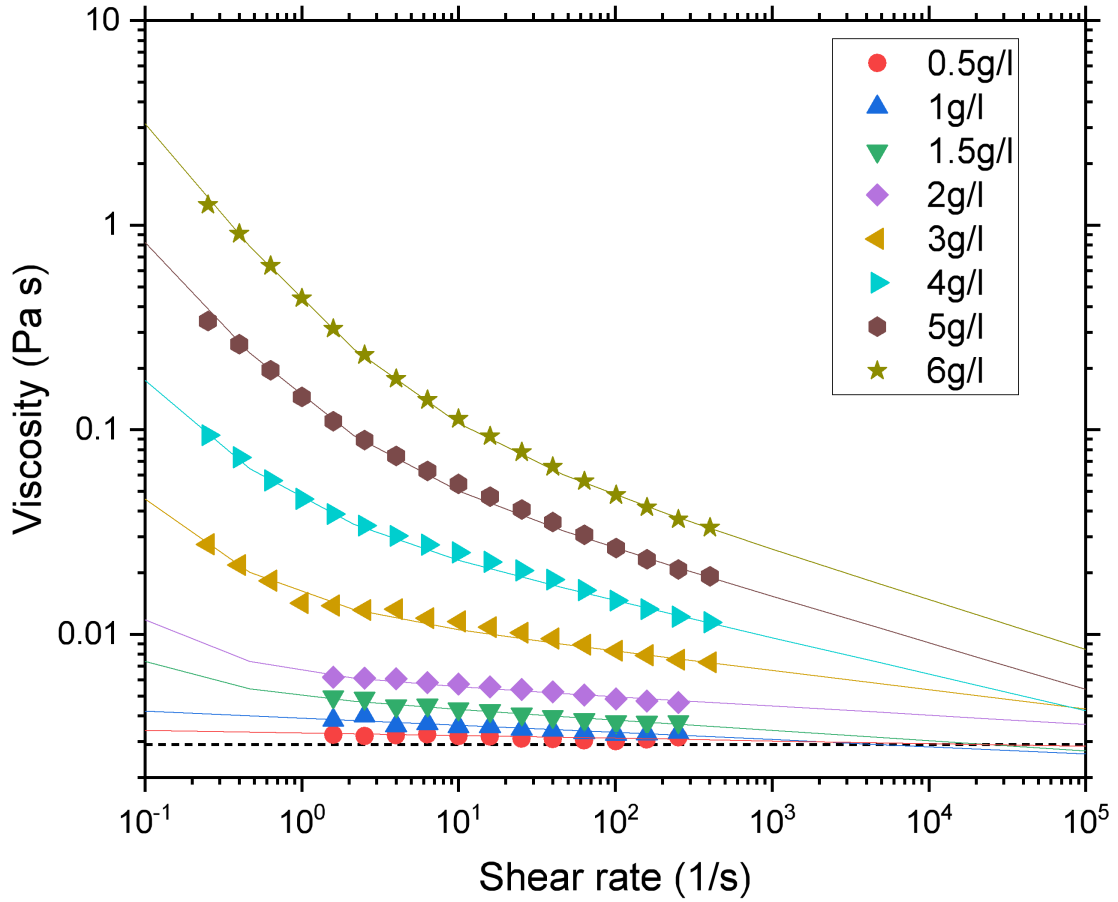


Figure 2.5: Viscosity as a function of shear rate for varying concentrations of GO in 50%v/v ethanol-water. Herschel-Bulkley fits to the data are indicated by the solid lines which are extended to estimated maximum shear rates present in the droplet impact experiments. The black dashed line indicates the solvent viscosity, 2.90 mPa s.

2.5.2 Gelation

Oscillatory rheological measurements were also carried out on the GO suspensions. These measurements involve applying sinusoidal deformation to the material and studying its response over a range of frequencies. This helps characterize the viscoelastic properties, including storage modulus, G' , (elastic behavior) and loss modulus G'' (viscous behavior). The storage modulus characterises the solid-like component of a material's response to stress or strain, and is defined as the component of the response that is in phase with the input. The loss modulus characterises the liquid-like response, and is defined as the component of the response that is out

phase with the input.

Above a certain critical particle concentration, GO flakes touch and form a stress bearing microstructure - a gel. A gel is a state of matter with properties intermediate between those of liquids and solids. In rheological terms, gelation is associated with a significant increase in the material's viscosity and the development of a three-dimensional network structure that resists flow and gives it a more solid-like behavior. When this occurs, we observe in the oscillatory rheology that $G' > G''$.

Figure 2.6a shows a frequency sweep for 4, 5 and 6 g/l samples of GO in 50%v/v ethanol-water. We can estimate the gelation point, or critical concentration, from this figure. If we examine the relationship between the storage and loss moduli of each sample at low frequencies, we can see that beyond 5g/l, the storage modulus is greater than the loss modulus. This indicates that the gel transition lies somewhere around 5g/l. In order to determine the gelation point more precisely, a concentration series that extends well beyond the critical concentration would be required, while the highest concentration investigated here is the only sample above the gelation point [34]. A study carried out on GO dispersed in water, prepared using the same source of high concentration GO stock, found the gelation point to lie at ≈ 4 g/l [35].

2.5.3 Yield Stress

Beyond the gelation point the suspensions develop a yield stress, τ_0 . Yield stress refers to the minimum stress required to initiate flow or deformation in a material. It is a critical rheological parameter for materials that exhibit a solid-like behavior at low stresses but transition to a more fluid-like behavior once a certain stress threshold, known as the yield stress, is exceeded. There are various methods of defining and measuring yield stress, each with its advantages and limitations.

Flow curve extrapolation: This method involves fitting a rheological model (e.g.,

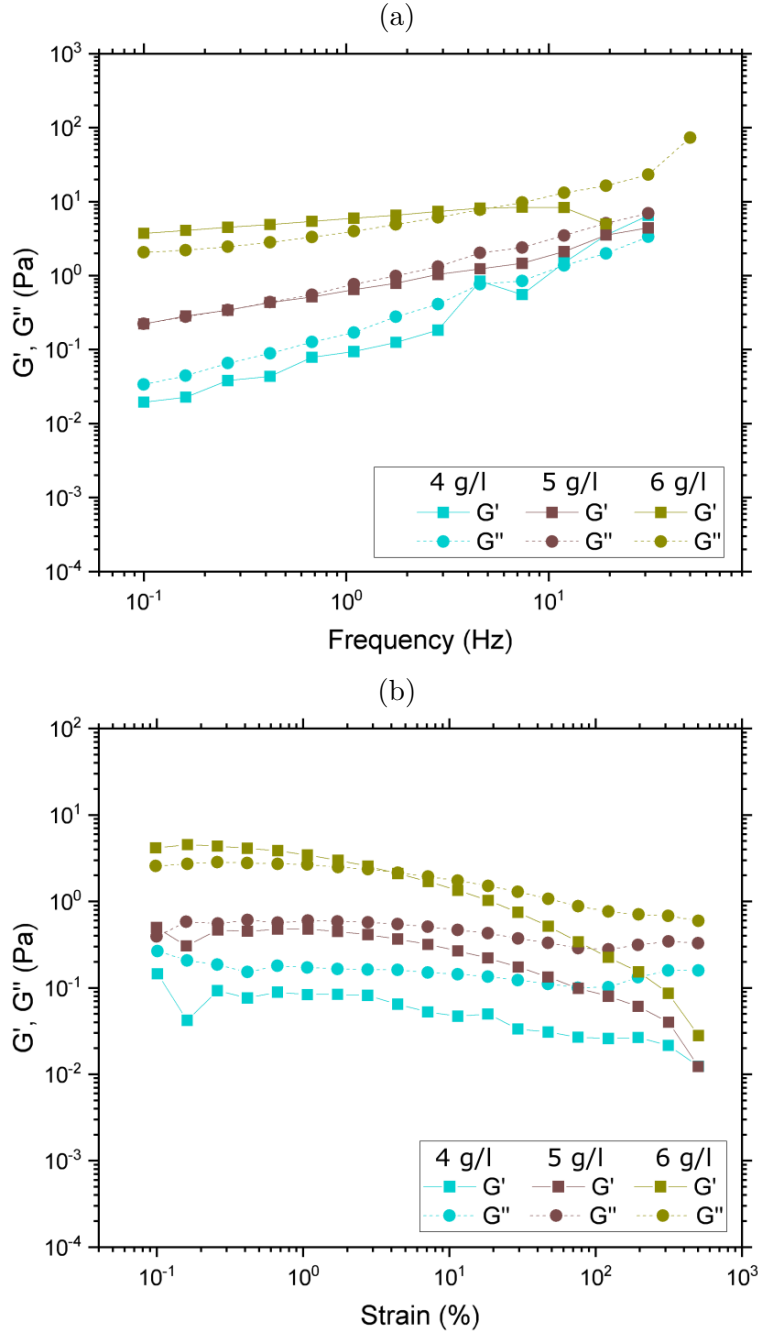


Figure 2.6: (a) Frequency sweep of 4-6 g/l GO in 50%v/v ethanol-water at 1% strain, (b) Strain amplitude sweep 4-6 g/l GO in 50%v/v ethanol-water at a frequency of 1 Hz.

the Herschel-Bulkley model) to steady-state flow data and extrapolating to determine yield stress. This indirect method depends on the accuracy of the model fit. Figure 2.7a shows the Herschel-Bulkley fits for 4-6 g/l GO samples, with the fit parameters given in table 2.1.

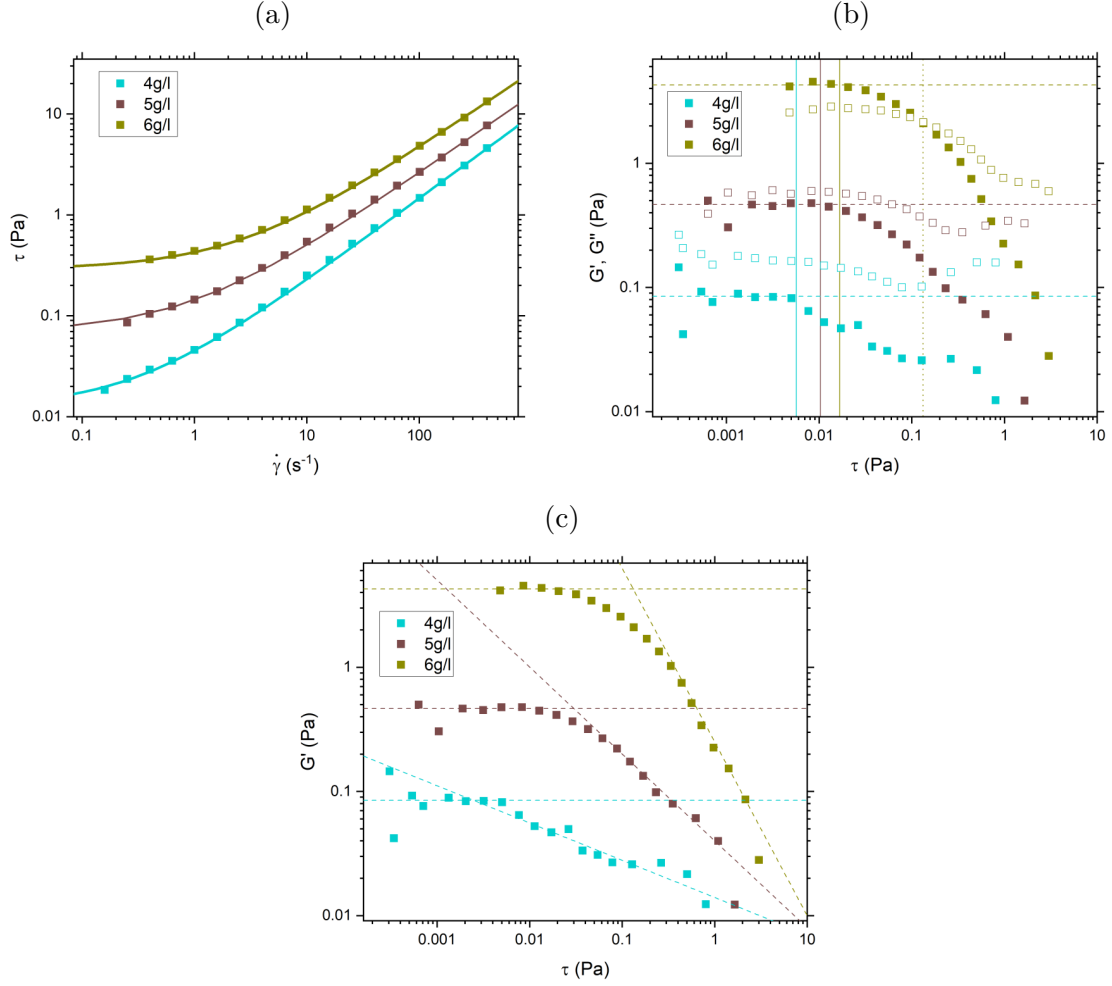


Figure 2.7: (a) Fit of Herschel-Bulkley model to 4-6 g/l GO samples, (b) oscillatory data for 4-6g/l GO samples, the dashed line indicated the estimated LVE plateau and the solid line indicated the point of deviation of G' from the plateau. The dotted vertical line indicates the crossover point of G' and G'' . (c) Storage modulus from oscillatory amplitude sweeps with lines of fit to plateau and power-law region to determine the yield stress by intersection.

Stress ramp test: This consists of gradually increasing the applied stress and identifying the stress at which the material begins to flow. This method directly measures yield stress but can be sensitive to experimental conditions and sample history. There are multiple definitions of the point of yield stress using this method, which include the highest τ at which the response is still elastic, the maximum τ or the stress at which a steady state is achieved. This method is highly dependant on the imposed strain rate [36].

Creep test: This method consists of a series of measurements of the strain response of a material under a constant applied stress over time where the stress value is varied. Yield stress is inferred from the stress value where the strain rate begins to accelerate. This method can be time consuming, and is vulnerable to structural changes over the extended duration of the test [36].

Oscillatory shear test: This method uses an oscillatory shear amplitude sweep to determine the yield stress by observing the transition from elastic to viscous behaviour. Figures 2.7b and 2.7c show the results of an amplitude sweep plotted as a function of stress for 4-6 g/l GO samples. With this measurement there are, however, multiple definitions of the yield stress, all of which are based on the departure from the linear viscoelastic (LVE) regime, described in section 1.4. The first of these methods defines the yield stress as the point at which $G' = G''$, known as the characteristic modulus [37–39], indicated by the dotted line in figure 2.7b for the 6g/l GO sample. Another definition is that the yield stress is the point at which G' begins to deviate from the LVE plateau value, illustrated by the intersection of the solid and dashed lines in figure 2.7b. Tangent analysis is also used to define the yield stress, where the intersection of the line of fit to the LVE plateau to a power-law fit above the LVE region is taken as the yield point [40]. Figure 2.7c illustrates this method for 4-6 g/l GO data.

We carried out both flow curve extrapolation and oscillatory shear tests to determine the yield stress of our samples. A comparison of the results for the two methods and different yield stress definitions is shown in figure 2.8. We chose the oscillatory testing in addition to the Herschel-Bulkley fitting as it is suited to a wide range of viscosities [41]. The Herschel-Bulkley fits give the largest range of yield stress values. As we have estimated the gelation point to lie at approximately 5g/l, we would not expect a yield stress to be present in the 4g/l sample. Below the gelation point, samples generally do not have a yield stress as they lack the

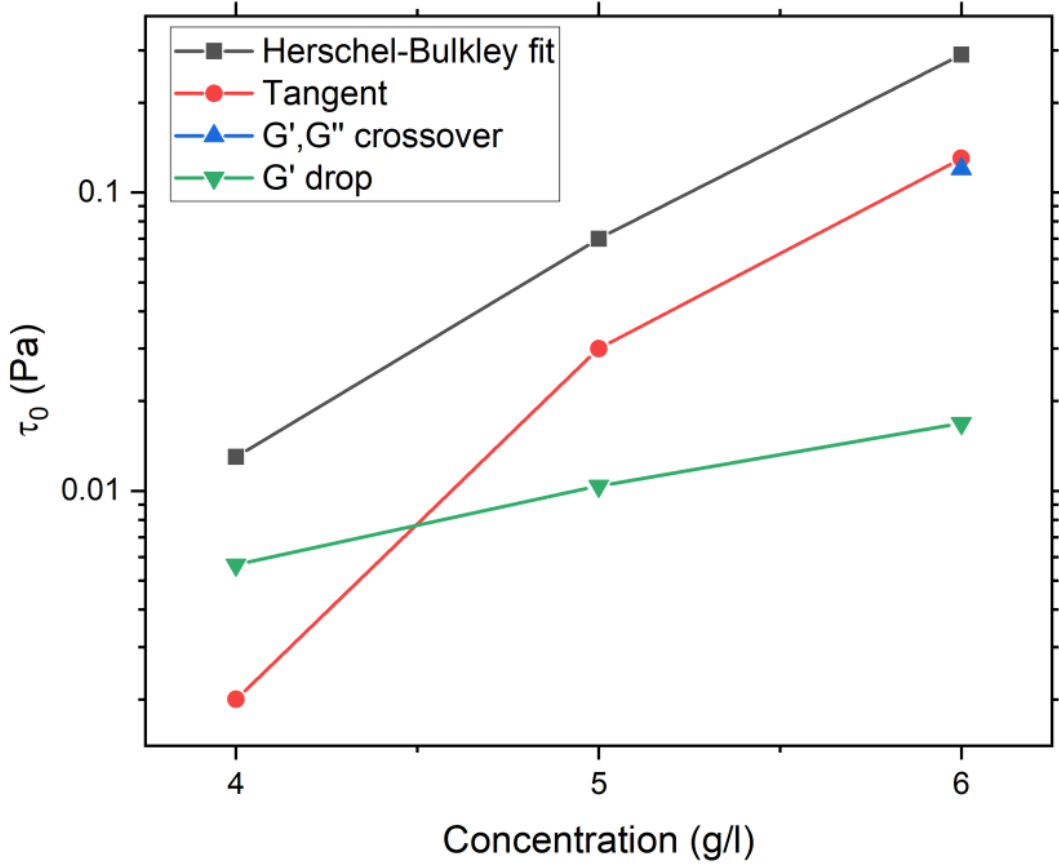


Figure 2.8: Comparison between methods of determining the yield stress, τ_0 , for 4-6 g/l GO samples.

structural network necessary to resist deformation up to a specific stress threshold. While fits have been made to the 4g/l oscillatory data to determine a yield stress by the three definitions given above, it is clear from the data that the occurrence of a LVE regime is not robust in the dataset, and the loss modulus is consistently higher than the storage modulus. While fits have been attempted here using the tangent method and the determination of the drop in the G' plateau, the data is not sufficient to have a satisfactory fit. With this in mind, we note that the G', G'' intersection definition results in no yield stress for the 4g/l sample, suggesting this definition is most accurate. However, we also do not see an intersection for the 5g/l dataset within the range of strain amplitudes implemented, which lies at the approximate gel transition. The tangent method results in the lowest value of yield

stress for the 4g/l sample, while still capturing a yield stress for the 5g/l sample, suggesting this definition is most representative of our samples. The LVE regime is, however characterized by $G' > G''$, which is only true for the 6g/l at the range of amplitudes shown here [36].

2.6 Conclusions

In this chapter, we have explored the fundamental properties of aqueous GO suspensions and the methodologies essential for their characterization.

For our experimental investigations, we prepared GO suspensions using a dilution method and adjusted the pH to ensure stability. Surface tension measurements revealed no significant dependence on GO concentration in 50%v/v ethanol-water mixtures, contrary to some literature findings. Rheological studies demonstrated the shear-thinning behavior of GO suspensions, with viscosity decreasing as shear rate increases. Additionally, oscillatory rheology revealed gelation behavior, with a critical concentration around 5 g/l. Above this concentration, suspensions exhibited yield stress behavior, transitioning from solid-like to fluid-like behavior.

In summary, over the concentration range examined here we see that GO suspensions vary from Newtonian to a yield stress fluid. This comprehensive characterisation provides a solid foundation for further exploration of GO suspension behavior in the complex dynamic processes of droplet impacts and pinch-off, which we will investigate in the following chapters.

Chapter 3

Spreading of Aqueous GO Suspensions

3.1 Introduction

The precise control of droplet impacts on solid surfaces plays an important role in many industrial applications, from inkjet printing to rapid spray cooling [4]. As a liquid droplet impacts on a solid surface, it spreads to a maximum diameter that depends on the impact velocity, viscosity, surface tension, initial diameter and density of the drop, along with the surface roughness and wettability [42]. Considerable work has been carried out to understand and predict the maximum spreading diameter for Newtonian fluids. Two regimes governing the spreading process have been distinguished. A viscous regime, where viscous dissipation of the kinetic energy dominates, and a capillary regime, where a balance between capillary and inertial forces arises.

The rapidly evolving area of nano-suspensions presents further potential applications in printing. Predicting the maximum spreading diameter of these droplets is essential to optimizing the resolution of printed patterns.

The outcome of a droplet impact depends heavily on the fluid parameters, such as viscosity and surface tension. Aqueous GO suspensions are non-Newtonian, exhibiting shear thinning behavior with increasing nanoparticle concentration [18]. With shear rates rapidly changing over the course of a single droplet impact we need to ascertain how a changing viscosity affects the maximum spreading diameter. While more studies have emerged in recent years addressing this question [31, 32, 43–48], no studies thus far have examined the spreading behaviour of 2D nanoparticle suspensions.

In this chapter, we investigate the spreading behavior of GO in ethanol-water suspensions using high speed photography. The experimentally determined maximum spreading diameter is compared to Newtonian models for GO samples with varying concentration using a characteristic viscosity for a given impact. A new energy balance model is presented that captures the behaviour in existing Newtonian literature data, along with GO samples analysed using a characteristic viscosity.

3.2 Theory

When a drop impacts on a solid substrate, the drop flattens and spreads tangentially across the substrate until it reaches some maximum spreading diameter. For a sufficiently high impact velocity, droplets can be ejected from the spreading drop resulting in what is known as splashing. The tangential spreading is inertia driven with capillary and viscous forces opposing the motion and non-dimensional numbers are typically used to describe the balance between these forces. The Weber number, $We = \frac{\rho D_0 U_0^2}{\sigma}$, describes the ratio of inertial to capillary forces and the Reynolds number, $Re = \frac{\rho D_0 U_0}{\mu}$, describes the ratio of inertial to viscous forces, where ρ , D_0 , U_0 , σ , and μ are the density, initial droplet diameter, impact velocity, surface tension and viscosity respectively. An important parameter in droplet impact experiments is the spreading ratio, $\beta_{max} = \frac{D_{max}}{D_0}$, the ratio of the maximum diameter of the

spreading droplet, D_{max} , to the initial diameter of the droplet upon impact, D_0 , which is useful in comparing spreading dynamics between fluids.

There are numerous Newtonian models that predict the spreading ratio with empirical [49], semi-empirical [50–56], and numerical [57] models proposed. A good tabulated summary of the majority of models can be found in the paper from Aksoy *et al.* [58]. There are two main methods by which spreading models have been derived - empirical ones, such as those by Scheller & Bousfield [49], Clanet *et al.* [59], and Laan *et al.* [60], and those derived by means of an energy balance approach, for example the models by Wildeman *et al.* [61], Ukiwe & Kwok [54] and Aksoy *et al.* [58].

Studies on Newtonian liquids to predict β_{max} typically distinguish between the viscous and capillary regimes. Chandra *et al.* (1991) have shown by volume conservation that the spreading ratio scales with Re in the viscous regime, $\beta_{max} \sim Re^{1/5}$ [62]. This relation has been supported by several experimental studies [50, 56, 59, 63]. Other viscous power law scalings with Re have been reported in the literature [50, 51, 64, 65].

In the capillary regime, there are two dominant scalings. The first is derived from energy conservation between kinetic energy and surface energy [51, 66] and scales with the Weber number $\beta_{max} \sim We^{1/2}$. The second is the result of momentum and mass conservation where the spreading ratio scales as $We^{1/4}$ [59].

A universal model that interpolates between both capillary and viscous regimes was proposed by Laan *et al.* (2014) [60]. This model uses a Padé approximant to estimate a scaling function, $f_{EC}(P_L = WeRe^{-2/5})$, derived from capillary and viscous regimes $We^{1/2}$, $Re^{1/5}$ by Eggers in 2010 [66], given by

$$\beta_{max} Re^{-1/5} = \frac{P_L^{1/2}}{A + P_L^{1/2}}, \quad (3.1)$$

where A is a fitting parameter. Laan found that their data collapsed to a universal curve using this model, however when a capillary scaling of $We^{1/4}$ was used, the data did not collapse.

Lee *et al.* (2016) adapted this model to account for the non-zero spreading ratio in the limit of zero impact velocity [67], with the limiting value β_0 obtained by fitting the experimental data to the function

$$\beta_{max} = \beta_0 = A \frac{U_0^C}{B + U_0^C}, \quad (3.2)$$

where β_0 , A , B , C are all fitting parameters. Using a similar method to Laan *et al.* they arrive at a relation between an adjusted spreading ratio and the two scaling regimes, given by

$$\left(\beta_{max}^2 - \beta_0^2\right)^{1/2} Re^{-1/5} = \frac{We^{1/2}}{A + We^{1/2}}. \quad (3.3)$$

An example of energy balance models from the literature is that of Wildeman *et al.* (2016) [61], given by the expression

$$\frac{3(\cos\theta)}{We} \beta_{max}^2 + \frac{\alpha_w}{\sqrt{Re}} \beta_{max}^2 \sqrt{\beta_{max} - 1} = \frac{12}{We} + \frac{1}{2} \quad (3.4)$$

for fitting parameter α_w and contact angle θ .

They show their model agrees well with experimental data from Laan *et al.* [60] with their suggested universal values for α_w and θ of 0.7 and 180° respectively.

Impacts for non-Newtonian drops present a challenge due to the shear rate dependence of the drop viscosity. When a drop impacts on a solid surface, the shear rate changes by several orders of magnitude over a small timescale (ms) as the spreading slows and the kinetic energy is dissipated by capillary and/or viscous forces. This results in a changing viscosity which is not accounted for in Newtonian models. In recent years more studies have emerged concerning the spreading of non-Newtonian

liquids. By estimating a characteristic viscosity, some non-Newtonian fluids have been shown to be well approximated by existing Newtonian models [31, 32, 43–46], while others present discrepancies [47, 48].

3.3 Experimental Methods

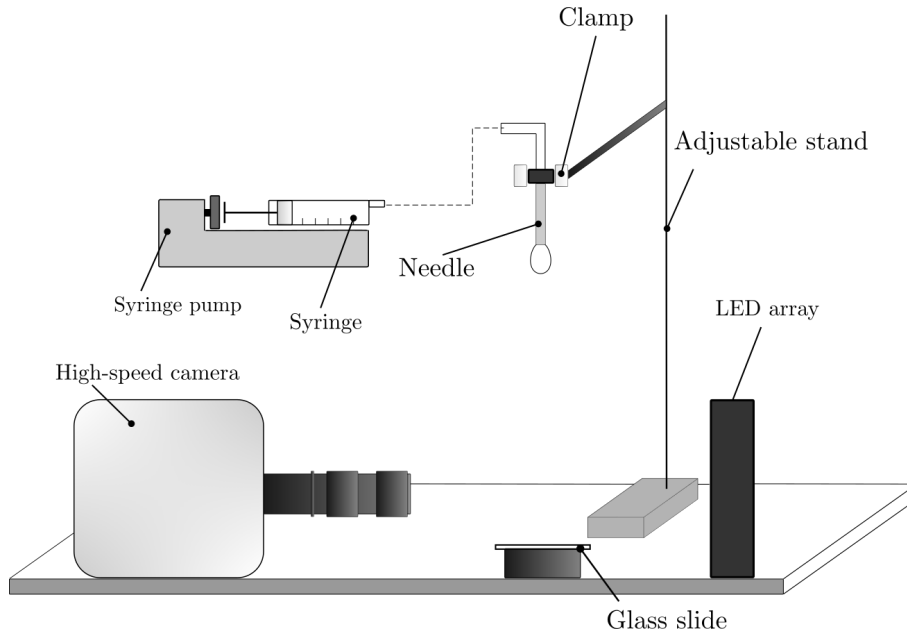


Figure 3.1: Experimental apparatus for imaging droplet impacts.

Drops were ejected from a 0.8 mm outer diameter blunt tip stainless steel needle using a syringe pump, with the experimental set up shown in figure 3.1. The drops impacted on a clean glass slide, with the fall height adjusted to vary the impact velocity of the impinging drop. Figure 3.2 shows the impact velocity as a function of fall height experimentally observed for 1.3mm radius drops of 50%v/v ethanol-water. This is compared to the predicted relation between impact velocity and fall height for such a drop assuming turbulent drag, the derivation of which can be found in appendix D. Discrepancies can be observed between the two, with the drag coefficient, C_d the likely culprit. The drag coefficient is in fact a function of the drop velocity, as evident in the figure in appendix B (figure B.1), where C_d is shown to vary with the Reynolds number, Re . Additionally, this prediction assumes the drop

has a spherical shape, while in reality, a drop will oscillate after detachment from a nozzle [68]. As such, impact velocity is verified for each droplet impact by direct measurement.

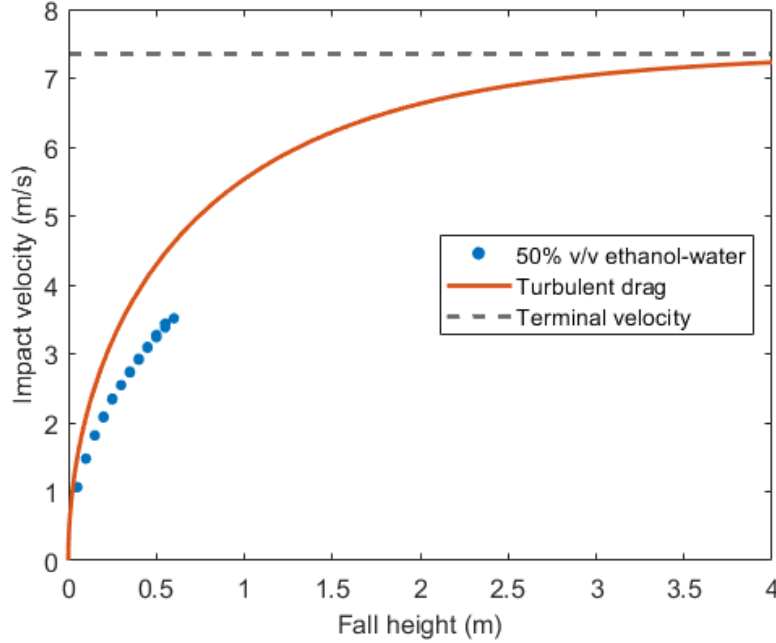


Figure 3.2: Observed impact velocity as a function of fall height for a 1.3 mm radius spherical drop of 50%v/v ethanol-water. Turbulent drag prediction, assuming a drag coefficient $C_d = 0.5$ compared, with terminal velocity indicated. For derivation, see appendix D.

Impact velocities ranged from 0.3-3 m/s with impacts below the splashing transition only considered. Impacts were backlit with a Phylox HSC LED array and captured using a Phantom v2010 high-speed camera at a frame rate of 40,000 frames per second. A custom MATLAB script was created to measure the droplet diameter and impact velocity of each drop. Spreading diameters were tracked up to 30 ms after the droplet impact for non-splashing droplets using a custom MATLAB routine. Figure 3.3 shows that impact velocities and radii of impacting drops were very reproducible, with minimal deviation from the mean.

In order to compare our results for non-Newtonian GO suspensions to spreading predictions from the literature, we adapt the method used by Balzan *et al.* (2021)

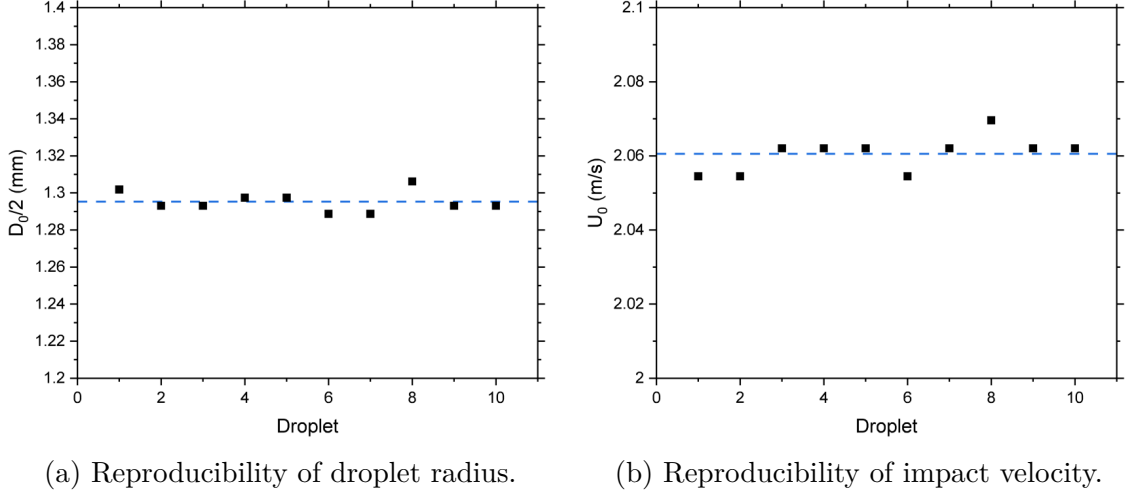


Figure 3.3: Reproducibility of drop impact experiments with 0g/l GO in 50%v/v ethanol-water at a fall height of 19.2cm. Data for 10 repeated measurements shown, with the mean indicated by the blue dashed line.

to calculate a characteristic viscosity during the spreading process [32]. Using an approximation for the shear rate during spreading [62],

$$\dot{\gamma} \sim \frac{U_0}{h}, \quad (3.5)$$

and an approximation for the lamella thickness at maximum spread from volume conservation of a cylindrical disc [69],

$$h = \frac{2D_0^3}{3D_{max}^2}, \quad (3.6)$$

where U_0 and h are the impact velocity and lamella thickness at maximum spread respectively. In a similar method to Balzan *et al.*, we deduce an expression for a characteristic viscosity based on a Herschel-Bulkley model using equations 2.5, 3.5 and 3.6,

$$\mu_{HB} = \tau_0 \left(\frac{2D_0^3}{3U_0 D_{max}^2} \right) + m \left(\frac{3U_0 D_{max}^2}{2D_0^3} \right)^{n-1}. \quad (3.7)$$

Figure 3.4a shows the characteristic viscosity calculated for each GO sample as a

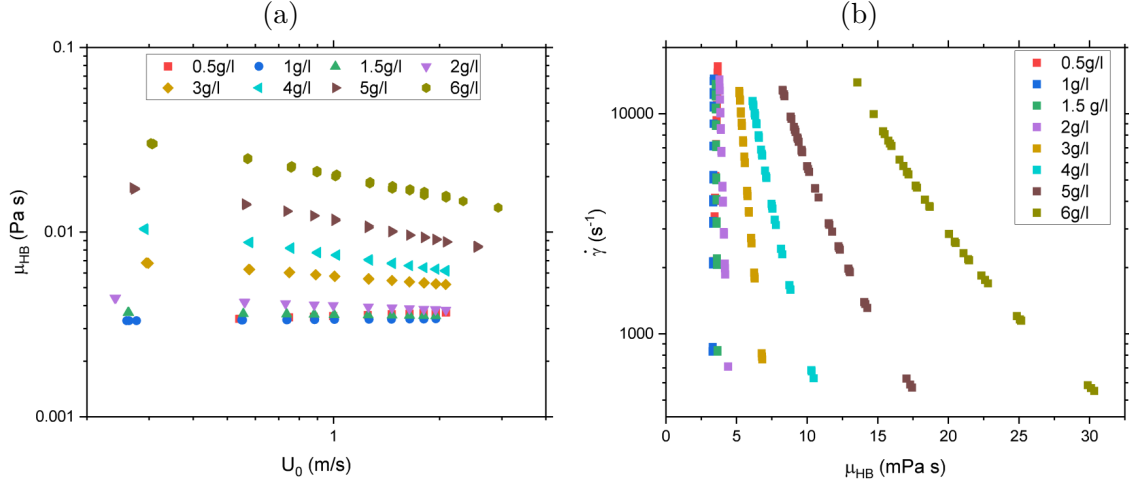


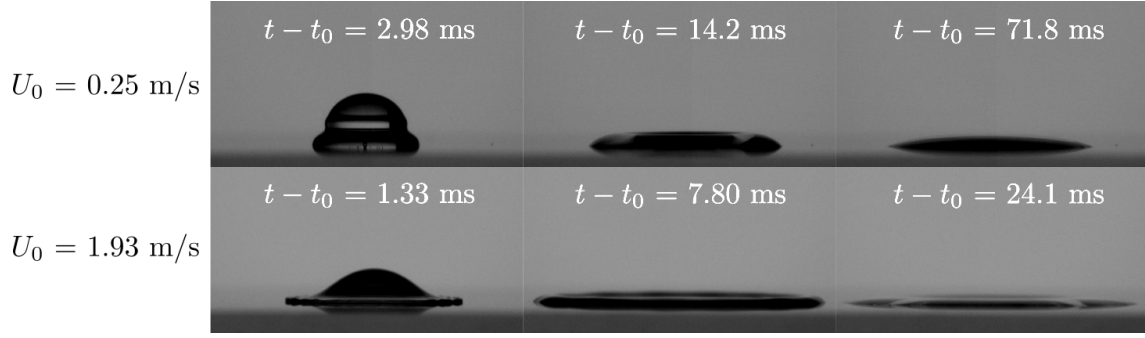
Figure 3.4: (a) Characteristic viscosity as a function of impact velocity for samples of varying GO concentration in 50%v/v ethanol-water, (b) equivalent shear rate, $\dot{\gamma}$, for μ_{HB} calculated using equation 3.7.

function of impact velocity for the dataset taken. As μ_{HB} is dependant on velocity it must be calculated for each impact. Higher concentration GO samples show a greater variation in μ_{HB} over the range of impact velocities investigated here which is expected as these samples display a higher degree of shear thinning behaviour. Figure 3.4b shows the equivalent shear rates for each calculated value of μ_{HB} .

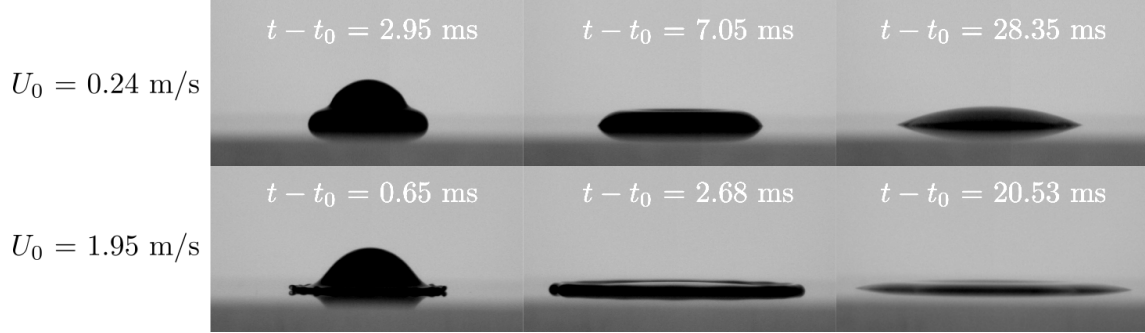
3.4 Results

Figure 3.5 shows the shape evolution of impacting drops GO suspension drops at two different impact velocities. The strong influence of impact velocity on spreading radius, droplet shape and contact angle can be clearly observed.

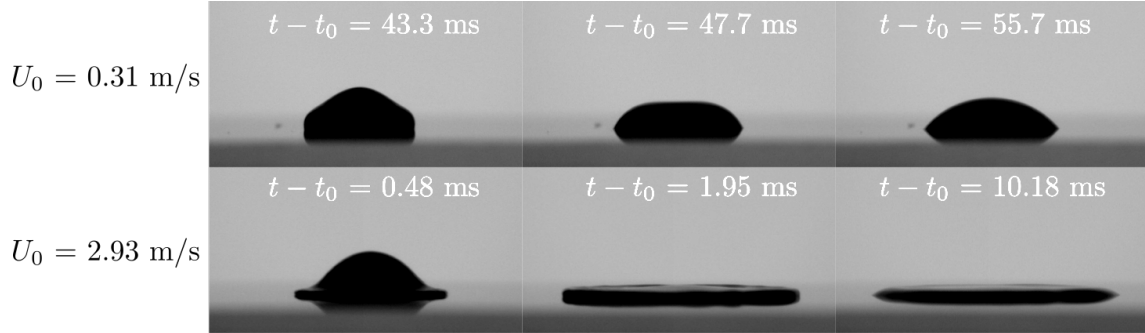
Experiments observing the maximum spreading diameter were carried out up to velocities below the splashing threshold for samples of varying GO concentration. The spreading ratio, $\beta_{max} = \frac{D_{max}}{D_0}$, of these measurements as a function of impact velocity is shown in figure 3.6. As the GO concentration is increased there is a clear decrease in the spreading ratio across all impact velocities particularly for samples above 2g/l. Measurements of droplet impacts at lowest impact velocities resulted in



(a) 0g/l GO in 50%v/v ethanol-water.



(b) 2g/l GO in 50%v/v ethanol-water.



(c) 6g/l GO in 50%v/v ethanol-water.

Figure 3.5: Shape evolution of impacting drops of (a) 0g/l, (b) 2g/l, and (c) 6g/l GO in 50%v/v ethanol-water below the splashing threshold. The impact velocity is indicated by U_0 , and the time after impact is indicated by $t - t_0$.

some drops not reaching an equilibrium maximum spread droplet within the experimental timescale (~ 60 ms), with an increasing amount of droplets affected with increasing GO concentration. These impacts are nonetheless within approximately 5% of their final extrapolated spreading diameter, and as such are included in figure 3.6 as open symbols.

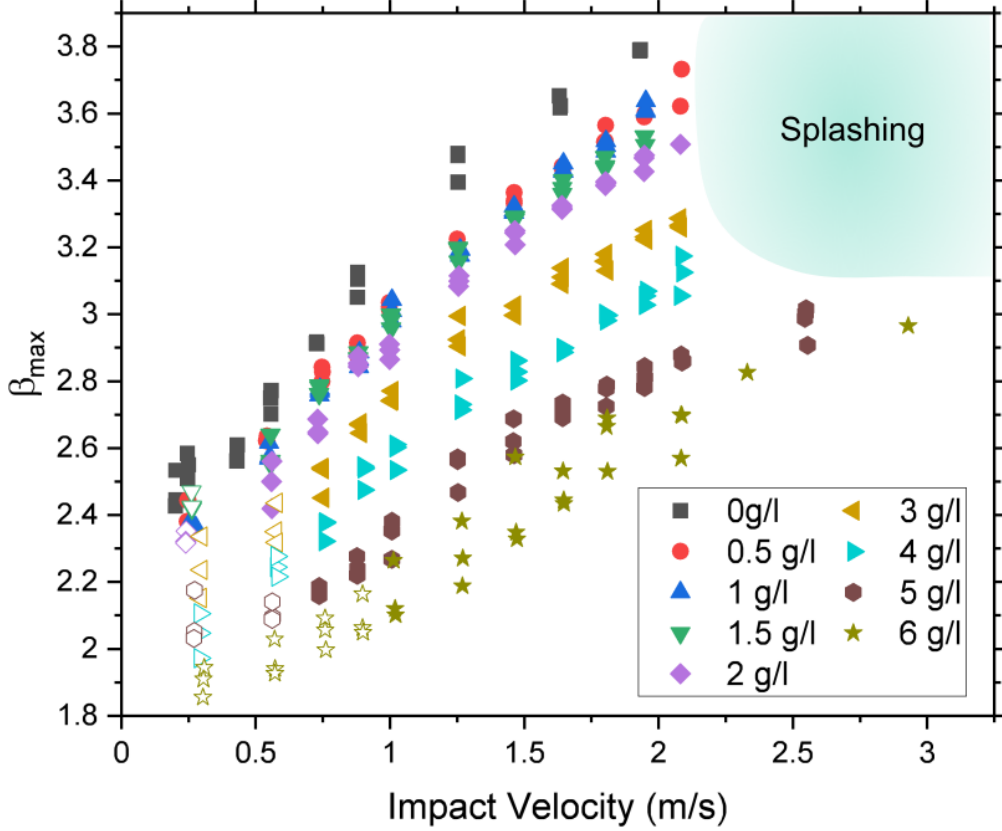


Figure 3.6: Spreading ratio as a function of impact velocity for varying GO concentration in 50%v/v ethanol-water. The open symbols denote drops that have not reached an equilibrium maximum spread within the experimental timescale.

3.4.1 Diameter Evolution

A recent study by Gorin *et al.* proposed a universal spreading curve that captures time dependent spreading for both Newtonian and non-Newtonian fluids [70]. By rescaling data for the diameter evolution over time for water, hexadecane, aqueous polymer (PEO) solutions and aqueous Carbopol solutions, they observed a collapse of data on to a universal curve. The curve can be approximated by a polynomial function,

$$f(t/\tau_r) = a(t/\tau_r)^{1/2} + b(t/\tau_r) + c(t/\tau_r)^{3/2}, \quad (3.8)$$

where time, t , is rescaled by $\tau_r = \frac{D_{max}}{U_0}$, the observation time, and the constants

take the values $a = 1.401 \pm 0.002$, $b = 0.903 \pm 0.008$, and $c = -1.379 \pm 0.007$.

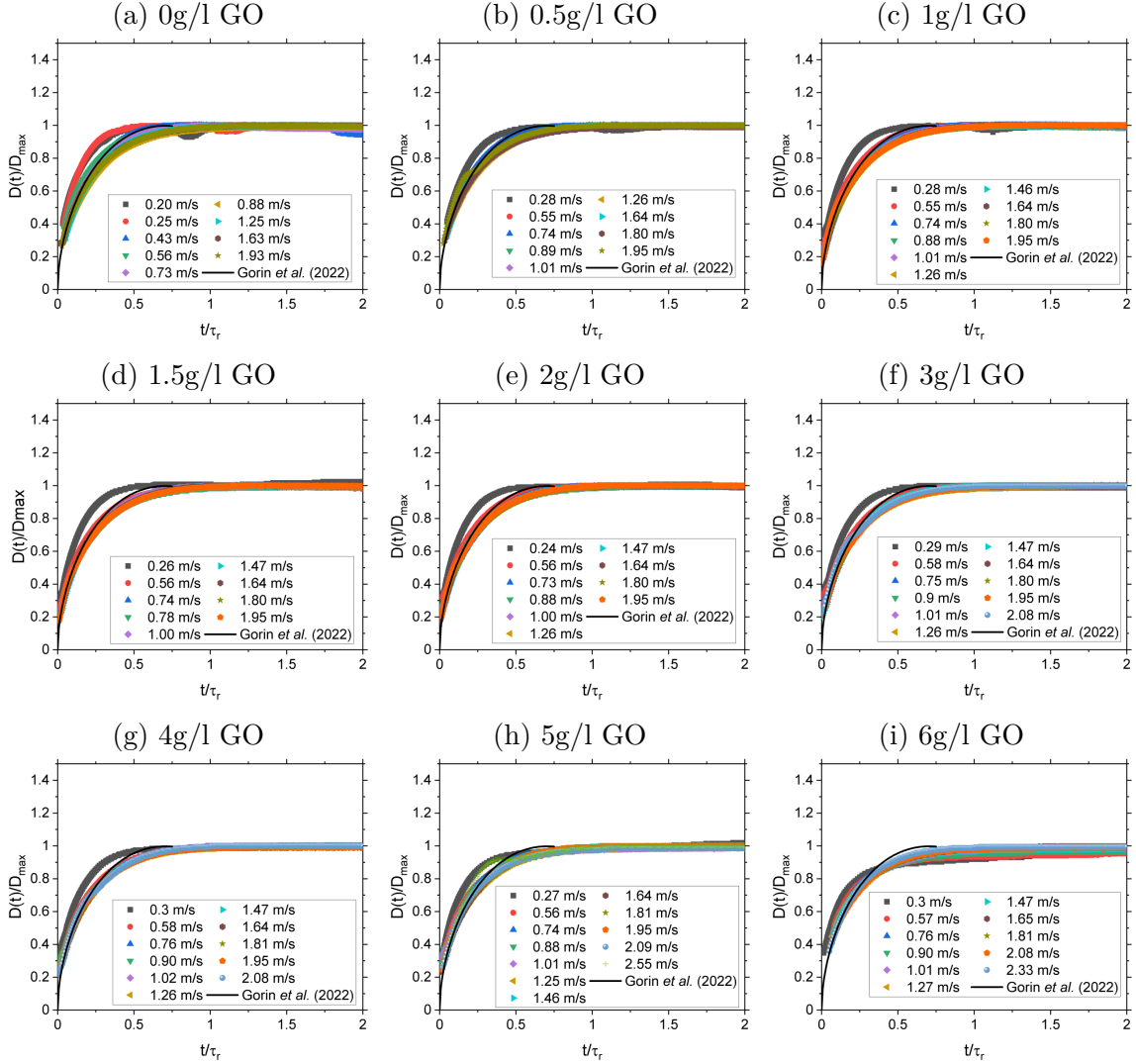


Figure 3.7: Dimensionless evolution of droplet diameter over time for (a)-(i) 0-6g/l GO in 50%v/v ethanol-water at different impact velocities.

Figure 3.7 shows diameter evolution data for varying concentrations of GO in 50%v/v ethanol-water rescaled using the method described by Gorin, in which the diameter is rescaled by the diameter at maximum spread, and the time is rescaled by τ_r [70]. The GO data does not collapse as well as the data shown in Gorin *et al.*. Notably, the lowest impact velocity datasets, $U_0 \leq 0.3$ m/s deviate significantly from the both the predicted curve and the higher impact velocity datasets. This trend is seen across all concentrations of GO examined here with the exception of the 6g/l sample, in which there is more of a spread across all velocities.

3.4.2 GO Experiment Comparison with Newtonian Models

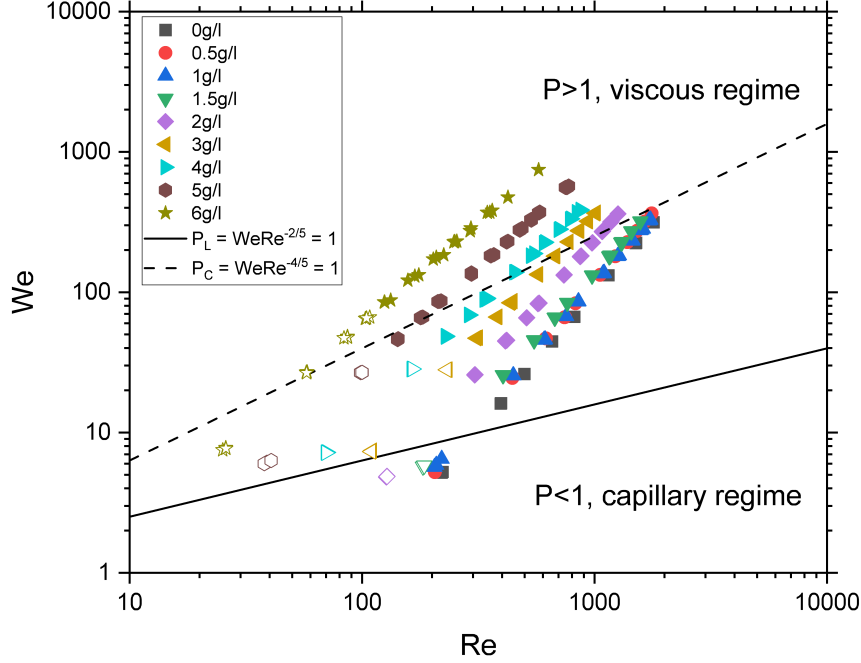


Figure 3.8: Phase diagram of impact regimes defined by impact parameters $P_C \equiv WeRe^{-4/5}$ [59], and $P_L \equiv WeRe^{-2/5}$ for $Re = Re^*$ [60]. Open symbols denote droplets that have not reached maximum spread within the experimental timescale.

As there is an abundance of different Newtonian spreading models in the literature, we first determine if our data falls into one of the two major regimes – the capillary or viscous regime, or if it transitions across both. Clanet *et al.* (2004) proposed an impact parameter

$$P_C \equiv WeRe^{-4/5}, \quad (3.9)$$

where for $P_C < 1$ the impact is in the capillary regime ($\beta_{max} \sim We^{1/4}$) and for $P_C > 1$ the impact is in the viscous regime ($\beta_{max} \sim Re^{1/5}$) [59]. A phase diagram of the two regimes can be seen in figure 3.8, with Re calculated using the viscosity obtained in equation 3.7,

$$Re^* = \frac{\rho D_0 U_0}{\mu_{HB}}. \quad (3.10)$$

Samples with a GO concentration below 2g/l lie in the capillary regime with higher concentrations crossing into the viscous regime.

An impact parameter defined by the energy-conservation capillary scaling, $We^{1/2}$, used in the universal Laan model [60] based on the scaling function proposed in Eggers (2010) [66],

$$P_L \equiv WeRe^{-2/5}, \quad (3.11)$$

results in almost all experimental data for GO suspensions, including most of the 0g/l data, falling in the viscous regime as shown in figure 3.8.

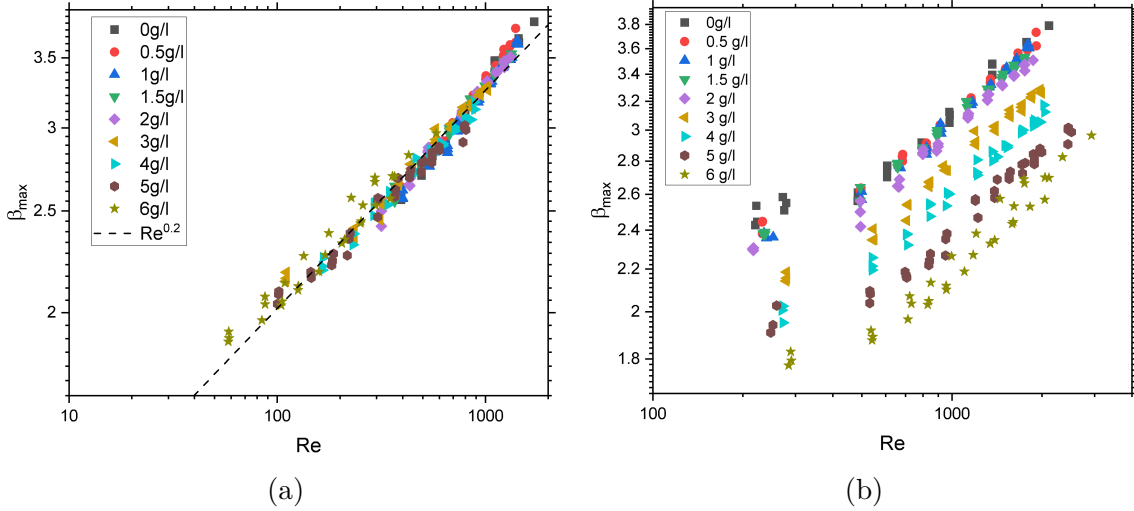


Figure 3.9: (a) β_{max} dependence on Re for all concentrations of GO in 50%v/v ethanol-water, $Re = Re^*$. The dotted line represents a scaling law $\propto Re^{0.2}$. (b) β_{max} dependence on Re for all concentrations of GO in 50%v/v ethanol-water for Re calculated using solvent viscosity, $\mu = 2.90\text{mPa s}$ ($Re = Re_s$).

A strong β_{max} power law dependence on Re was observed in figure 3.9a for all GO concentrations. For $Re = Re^*$, all concentrations collapse onto a single exponent of $Re^{0.2}$. This is consistent with the $Re^{1/5}$ scaling predicted for the viscous regime derived from volume-conservation [62] included in both impact parameter definitions, and the universal model by Laan [60]. Interestingly, recreating this plot of β_{max} vs. Re for Re calculated using the solvent viscosity of each sample rather than the characteristic viscosity, μ_{HB} ($Re = Re_s$), results in a failure of the data to collapse on to a single curve as shown in figure 3.9b.

A semi-empirical model proposed by Roisman in 2009 is derived from an energy balance that contains the $Re^{1/5}$ scaling, and as such it is prudent to examine how well this model can capture our experimental data. The final form of the model after a fit to Roisman's experimental data is expressed as

$$\beta_{max} = 0.87Re^{0.2} - 0.4 \frac{Re^{0.4}}{\sqrt{We}}. \quad (3.12)$$

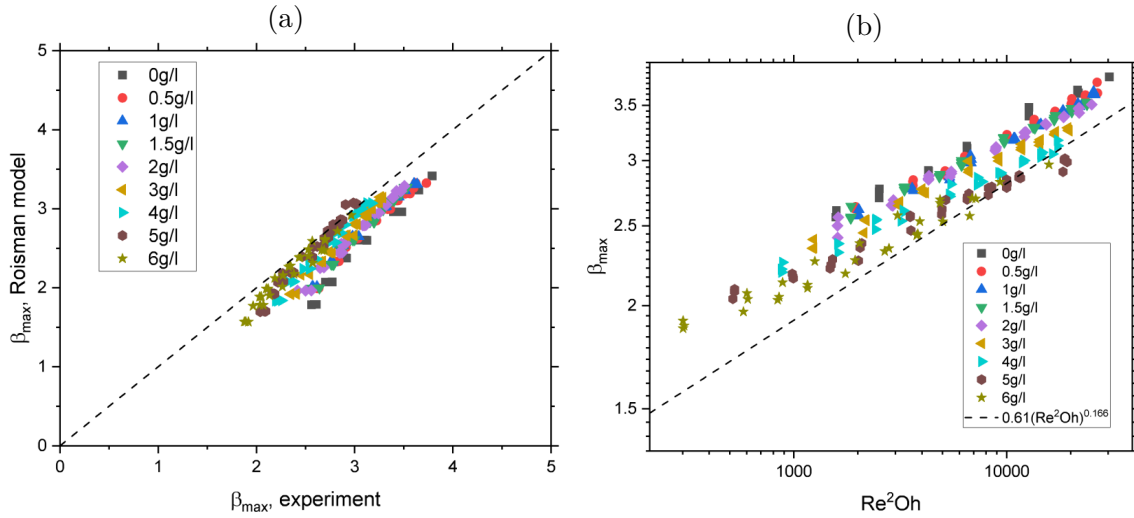


Figure 3.10: (a) Comparison of GO spreading data to Roismann spreading model (equation 3.12) for $Re = Re^*$ [56], (b) comparison of GO spreading data to Scheller *et al.* spreading model (equation 3.13) for $Re = Re^*$ [49].

Figure 3.10a shows a comparison between our results and the model calculated for $Re = Re^*$ where we can see the model overestimates the spreading ratio for all concentrations of GO, with the effect more pronounced for lower concentration samples.

A comparison has also been made to one of the earliest semi-empirical spreading models, that of Scheller *et al.* from 1995 [49] for our GO data, shown in figure 3.10b. The model is given by

$$\beta_{max} = 0.61 \left(Re^2 Oh \right)^{0.166}. \quad (3.13)$$

The experimentally determined spreading ratio is consistently larger than that pre-

dicted by the model, with the effect more pronounced at low concentrations and low impact velocities.

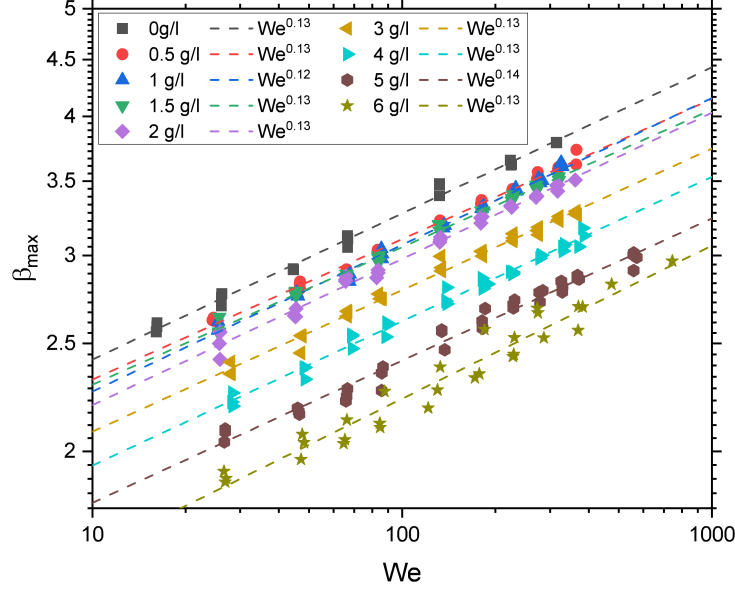


Figure 3.11: β_{max} dependence on We for all concentrations of GO in 50%v/v ethanol-water.

Examining the β_{max} dependence on We in figure 3.11 does not produce the same satisfying collapse of data on to a single curve, suggesting the data falls predominantly in the viscous regime. Assuming the energy-conservation-derived capillary scaling, P_L , the phase diagram in figure 3.8 agrees with this.

This universal model proposed by Laan [60], provided a poor fit to our experimental data, shown in figure 3.12a. Comparison of our experimental data to the Lee *et al.* model in figure 3.12b shows a better approximation than the Laan model, however some spread is observed from the fitted curve $A = 7.6$ obtained in Lee *et al.*, and a best fit is given by $A = 9.3$ [67]. The fits of the GO data to equation 3.2 in order to determine β_0 are given in figure 3.13, and the fit parameters are given in appendix A.

The Laan model was also examined by Balzan *et al.* in 2021 for non-Newtonian

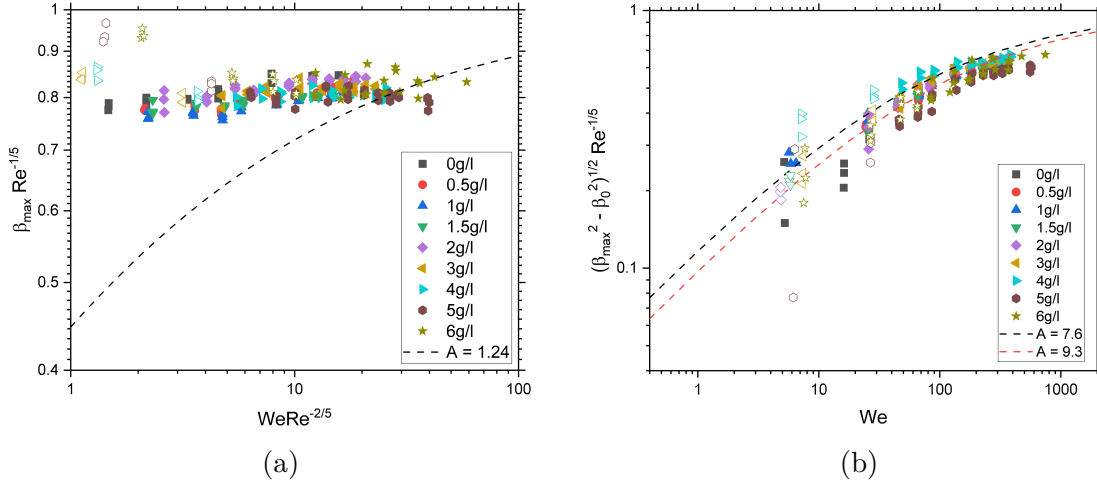


Figure 3.12: (a) Comparison of GO experimental data to universal model of Laan *et al.* (2014) (equation 3.1) for $Re = Re^*$ [60]. Our data does not collapse to the universal curve ($A = 1.24$). (b) Comparison of GO experimental data to universal model of Lee *et al.* (2016) (equation 3.3) for $Re = Re^*$ [67]. Our data does not fit well to the universal curve ($A = 7.6$). Open symbols in (a) and (b) denote droplets that have not reached maximum spread in the experimental timescale.

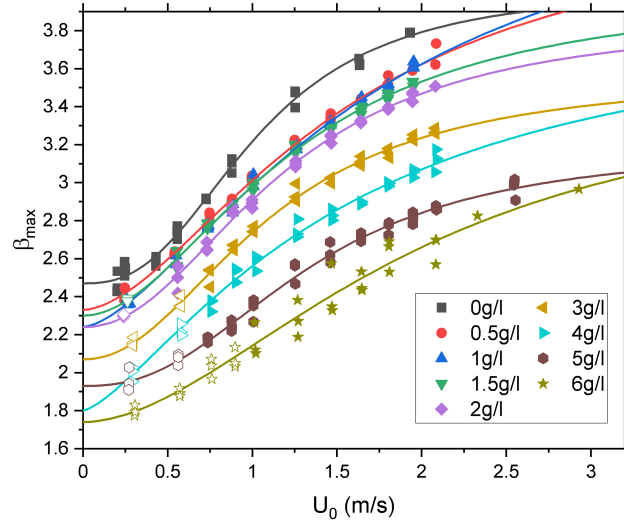


Figure 3.13: Fits of GO data to equation 3.2.

dairy based solutions, who, using a characteristic viscosity method, found a reasonable agreement in contrast to our findings for GO suspensions.

3.4.3 Energy Balance Model

We propose a new spreading model that takes an energy balance approach

$$E_{kin} = \Delta E_s + E_v, \quad (3.14)$$

where E_{kin} , E_s and E_v are the kinetic, surface and viscous energies. The kinetic energy is deduced from the kinetic energy of the impacting drop,

$$E_{kin} = \frac{2}{3} \rho \pi R_0^3 U_0^2, \quad (3.15)$$

where $R_0 = \frac{D_0}{2}$ is the radius of the impacting drop.

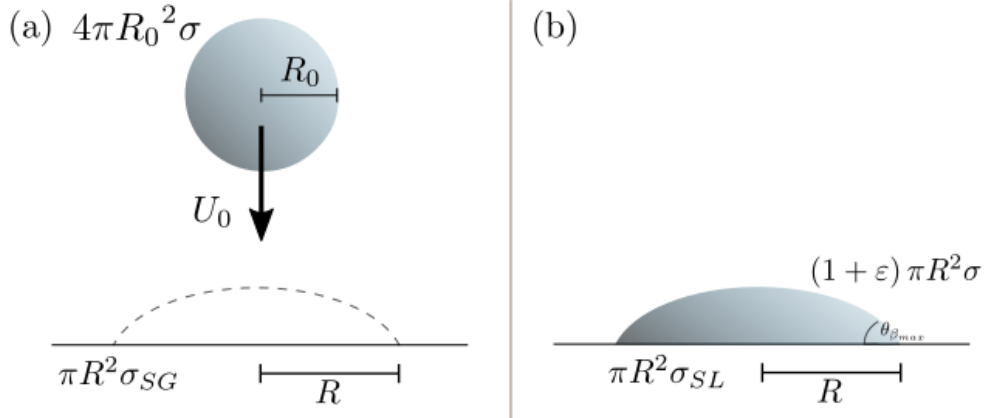


Figure 3.14: Surface energy contributions (a) before and (b) after impact of a spherical drop, assuming a spherical cap shape at maximum spread.

The surface energy has two contributions, firstly the energies of the surfaces before impact, namely the surface energy of the spherical drop and the energy between the substrate and the gas. The second contribution is the energies after spreading, the energy of the interface between the drop and the surrounding gas at maximum spread assuming a spherical cap shape and the energy between the substrate and the drop. The surface area of the liquid gas interface at maximum spread is given by $(1 + \varepsilon) \pi R^2$ in order to account for the range of shapes observed at maximum spread as noted by Wörner [71] and by Lee *et al.* [67], also illustrated in figure 3.15. For

high We (or high U_0) the shape at final spread can be approximated as a cylinder of negligible height, and so $\varepsilon = 0$. For a thin cylinder, using volume conservation we obtain $\varepsilon = \frac{8}{3\beta_{max}^3}$. At low We (or low U_0) if we assume the droplet shape is that of a spherical cap as illustrated in figure 3.14, $\varepsilon = 4\frac{\sin^2(\frac{\theta}{2})}{\sin^2(\theta)} - 1$. In figure 3.15, ε is given for each drop profile at maximum spread, calculated assuming a spherical cap shape from measurements of β_{max} and the thickness at the center of the drop.

The surface energy term is then given by

$$\Delta E_s = -\left(4\pi R_0^2\sigma + \pi R^2\sigma_{SG}\right) + \left(\pi R^2\sigma_{SL} + (1 + \varepsilon)\pi R^2\sigma\right), \quad (3.16)$$

where R is the radius of the drop at maximum spread, σ_{SG} is the interfacial tension between the substrate and the gas and σ_{SL} is the interfacial tension between the substrate and the drop.

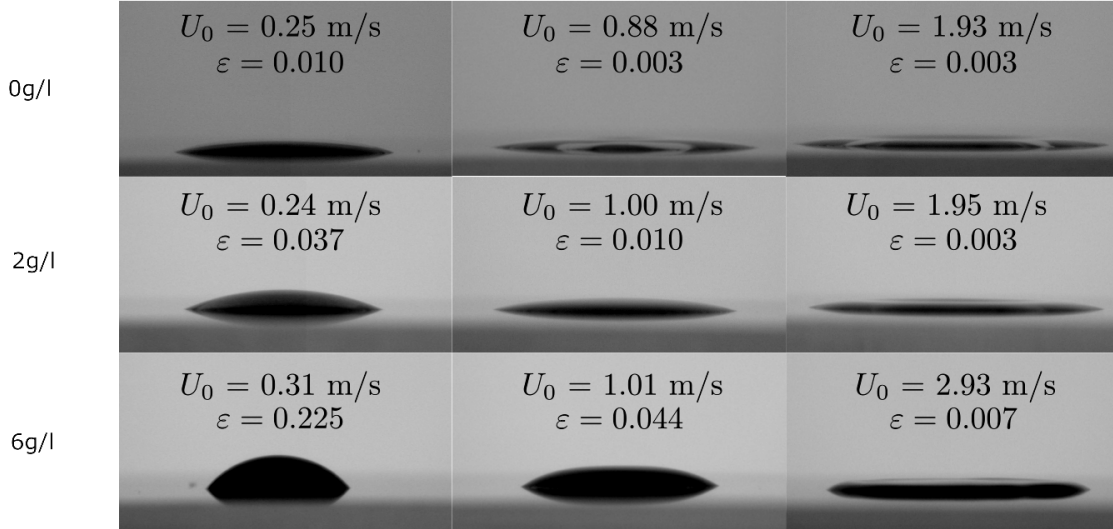


Figure 3.15: Droplet shape at maximum spreading radius at different impact velocities, U_0 . Three different GO concentrations are shown, 0g/l, 2g/l and 6g/l GO in 50%v/v ethanol-water from top to bottom.

Using the definition of the spreading coefficient [72],

$$S = \sigma_{SG} - \sigma_{SL} - \sigma = \sigma(\cos\theta - 1), \quad (3.17)$$

equation 3.16 can be simplified to

$$E_s = (\varepsilon + (1 - \cos \theta)) \pi R^2 \sigma - 4\pi R_0^2 \sigma. \quad (3.18)$$

There are various schools of thought in the literature as to which is the most appropriate choice of contact angle in the context of spreading models. For example, Chandra *et al.* suggest the advancing contact angle, θ_a , is most relevant [62], while Bennett *et al.* chose the equilibrium contact angle, θ_{eq} . According to Ukiwe *et al.*, neither is correct, with the preferred approach to take $\theta = \theta_{\beta_{max}}$, the hydrodynamic contact angle at β_{max} , which is angle we choose here.

The last term is the viscous dissipation energy, given by

$$E_v = \mu \dot{\gamma}^2 \tau_s V_d \quad (3.19)$$

for drop volume V_d and time to maximum spread τ_s , as described by Chandra *et al.* [62]. We approximate $\tau_s \sim \frac{R}{U_0}$ in an analogous fashion to the observation time defined in Gorin *et al.* [70] (see section 3.4.1). However, we use the droplet radius rather than the diameter used by Gorin, as we found this more accurately represents both GO and literature spreading data. Using this and the shear rate assumption from equation 3.5 with an estimate of the lamella thickness from volume conservation from a spherical droplet to a disc (equation 3.6), equation 3.19 becomes

$$E_v = \frac{4}{3} \pi \left(\frac{9}{16} \mu U_0 R_0^2 \beta_{max}^5 \right). \quad (3.20)$$

Combining 3.14, 3.15, 3.18 and 3.20,

$$\beta_{max}^5 + \left(\frac{4}{3} \frac{Re}{We} \alpha \right) \beta_{max}^2 = \frac{4}{9} Re + \frac{16}{3} \frac{Re}{We}, \quad (3.21)$$

we arrive at an equation relating the maximum spreading ratio to Re and We ,

where $\alpha = \varepsilon + (1 - \cos\theta)$, which we leave as a free parameter. Solutions to this quintic polynomial can be obtained numerically for a given α , which reflects both the wetting properties of the substrate and the shape of the droplet at maximum spread.

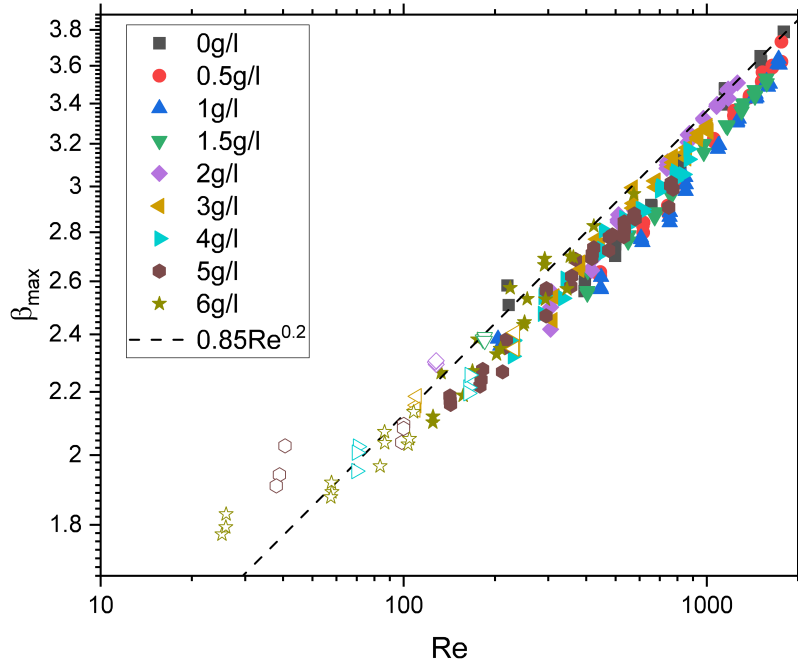


Figure 3.16: β_{max} dependence on Re for all concentrations of GO in 50%v/v ethanol-water. Dotted line represents the high viscosity, low surface tension limit of the new energy balance model, $\beta_{max} = 0.85Re^{1/5}$.

In the capillary limit where $\frac{Re}{We} \gg 1$, equation 3.21 reduces to $\beta_{max} \sim We^{1/2}$. In the limit of high viscosity and low surface tension, where $\frac{Re}{We} \rightarrow 0$, the expression simplifies to $\beta_{max} = 0.85Re^{1/5}$. Figure 3.16 shows this relation compared to the GO spreading data, and can be seen to give a good representation of the data. For a Newtonian fluid, equation 3.21 is analytically solvable as it can be written as a quadratic equation in U_0 ,

$$\frac{2}{3}\rho U_0^2 R_0 = \frac{3}{4}\mu U_0 \beta_{max}^5 + \sigma(\alpha \beta_{max}^2 - 4). \quad (3.22)$$

New Energy Balance Model

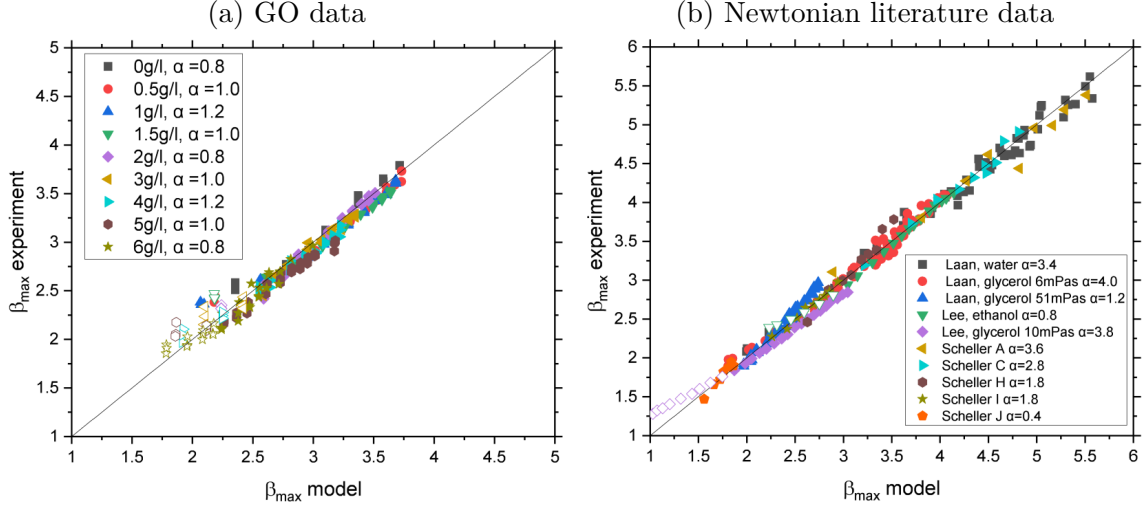


Figure 3.17: Comparison of GO and Newtonian literature data to the new energy balance model. (a) GO data for α fitted to the new energy balance model (0.8-1.2), open symbols represent GO data points in which a maximum spread was not achieved. (b) Newtonian literature data for α fitted to the new energy balance model (0.4-4), open symbols represent data points where $We < 30$.

Figure 3.17a shows a comparison of experimental data to model predictions for our energy balance model and GO suspensions, using α as a fitting parameter. The roots of equation 3.21 for each impact velocity were determined numerically in MATLAB. This was repeated for a range of α values, the residuals calculated in each case and the best fit value was determined by means of the least squares method. Model predictions in figure 3.17a are calculated with $Re = Re^*$ for each data point (equation 3.10). α here varied between 0.8-1.2. Interestingly, despite ε changing considerably with U_0 particularly for higher concentration samples (see figure 3.15, figure 3.22b), all data for a given concentration of GO can be fit to the model using a single value of α while velocities range from 0.2-2.9 m/s.

For $\theta < 90^\circ$, $\varepsilon < 2$ and thus $\alpha < 3$ assuming a spherical cap shape. As $\theta \rightarrow 0$, $\alpha \rightarrow 1$, and the fit parameters we see for the GO samples all lie close to this value, with some falling below. This would suggest a drop shape that is closer to a flattened disc than a true spherical cap. Examining figure 3.15 we observe this to be true,

particularly for higher velocity impacts.

Figure 3.17b shows a model and literature data comparison for data from Lee *et al.* (2016) [67], Scheller *et al.* (1995) [49] and Laan *et al.* (2014) [60], with α ranging from 0.4-4. This suggests a large range of drop shapes, including cases where, from the fitted α , we would expect $\theta > 90^\circ$. While contact angles are not available from all of the literature data, We can see that the glycerol-water sample from Lee *et al.* shows this to be true, as $\alpha = 3.8$ for a dynamic contact angle $\theta_D = 121^\circ$. The spreading regime phase diagram for this data is shown in figure 3.18, and the fluid properties of the literature samples are given in appendix C.

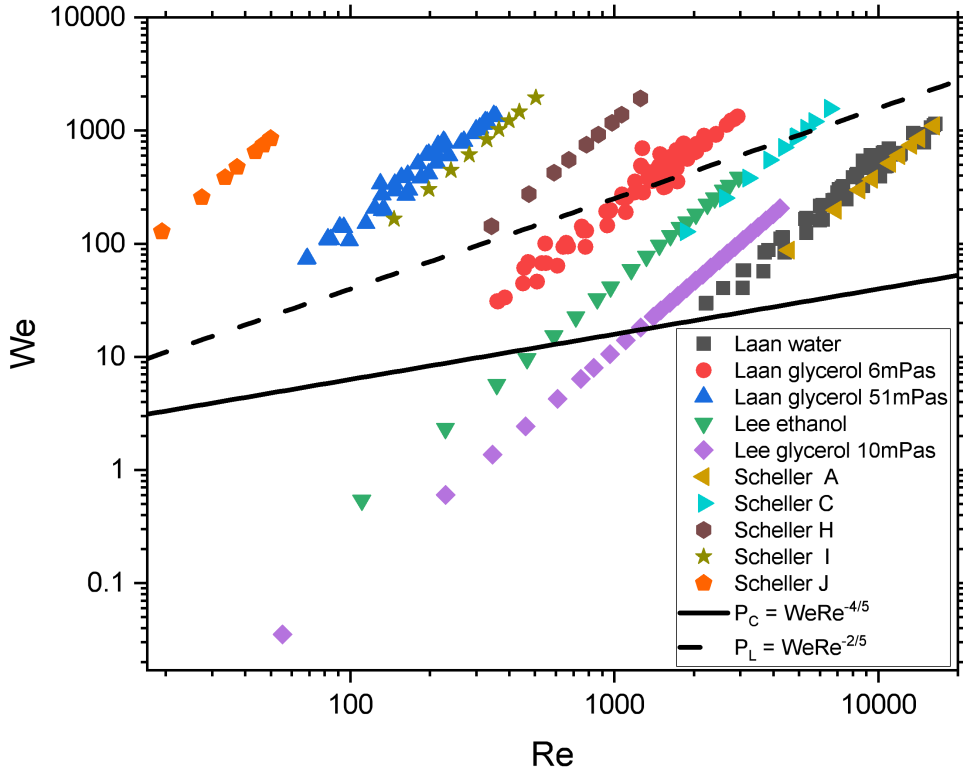


Figure 3.18: Spreading regime phase diagram for Newtonian literature data.

We also compare data from the study of Balzan *et al.* (2021) which examined spreading for non-Newtonian dairy based solutions with varying total solids content. This study implemented the method of characteristic viscosity to estimate the relevant viscosity for impacts. Figure 3.19 shows that this non-Newtonian data agrees

well with the model for fit parameters given in appendix C.

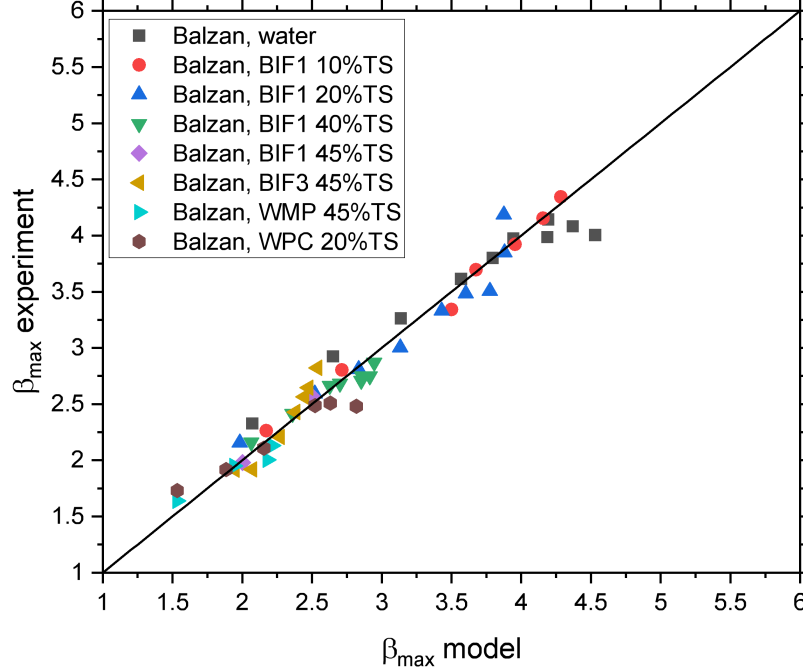


Figure 3.19: Comparison of non-Newtonian data from Balzan *et al.* (2021) [32] to energy balance model.

Figure 3.20 shows a comparison between the model experimental results and predicted values using the energy balance model in the case where $\sigma = 0$, for GO samples. The model prediction is independent of α in this case, and the model predictions can be seen to overestimate the spreading ratio for all concentrations of GO. While the deviation is minor, a better fit is given when the surface tension is accounted for (see figure 3.17a), indicating that the surface energy has a non-negligible contribution to the energy balance.

As discussed in section 3.2 there are other energy balance models presented in the literature, such as that from Wildeman *et al.* given in equation 3.4 [61]. Their model is of similar form to what has been presented here. There are, however, a few fundamental differences between these two models. The Wildeman model includes different surface energy terms. In addition to this, a different estimate of the lamella

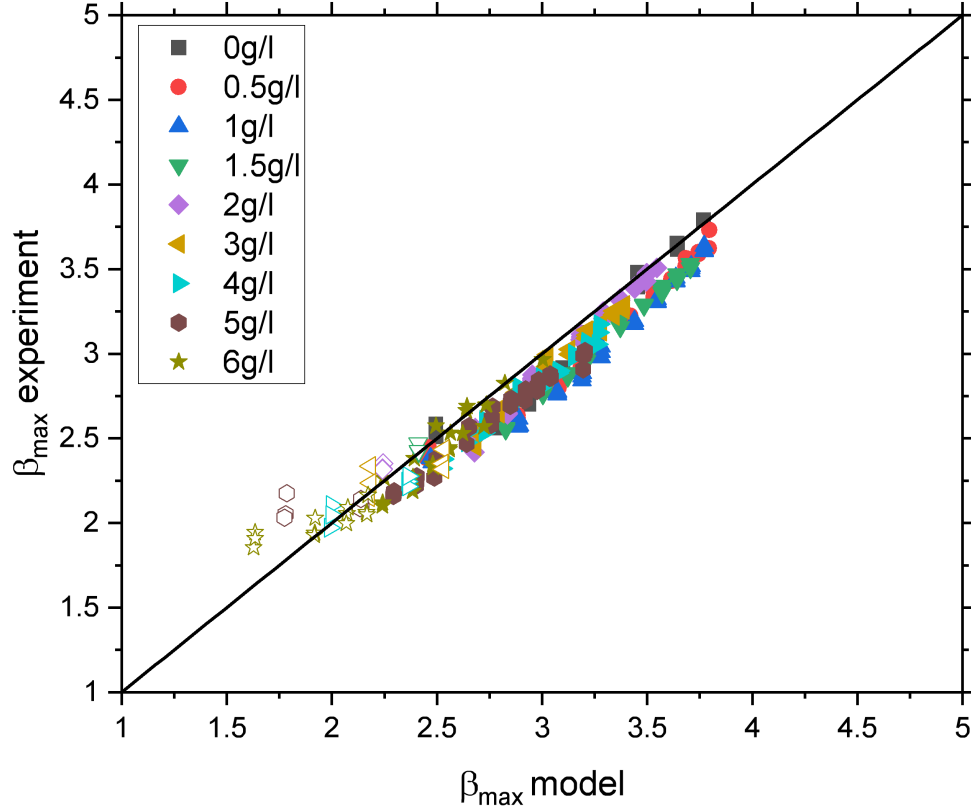


Figure 3.20: Spreading ratio from experiment compared to energy balance model prediction for GO data for $\sigma = 0$.

thickness is used. The Wildeman model uses the expression $h \sim \sqrt{\tau_s / Re}$ derived by Eggers *et al.* (2010) [66] for the case of high-velocity impacts (large We and Re), in which wetting is negligible and contact angles are 180° . The assumption of the time to maximum spread τ_s also differs between the two models, where Wildeman use $\tau_s = (D_{max} - 1)$ based on their simulation data. The Wildeman model also includes a term for head loss $E_v^H \approx E_k/2$.

The fit parameter α_w is proposed to have a universal value of 0.7. However, assuming this value and the fixed contact angle of 180° , we obtain a poor fit to our experimental data, shown in figure 3.21a. This poor agreement however is not exclusive to our non-Newtonian GO samples, as figure 3.21b shows that for data from Lee *et al.* for ethanol [67], the Wildeman model does not agree well.

An advantage of the new energy balance model is that it has only one free

Wildeman (2016) model

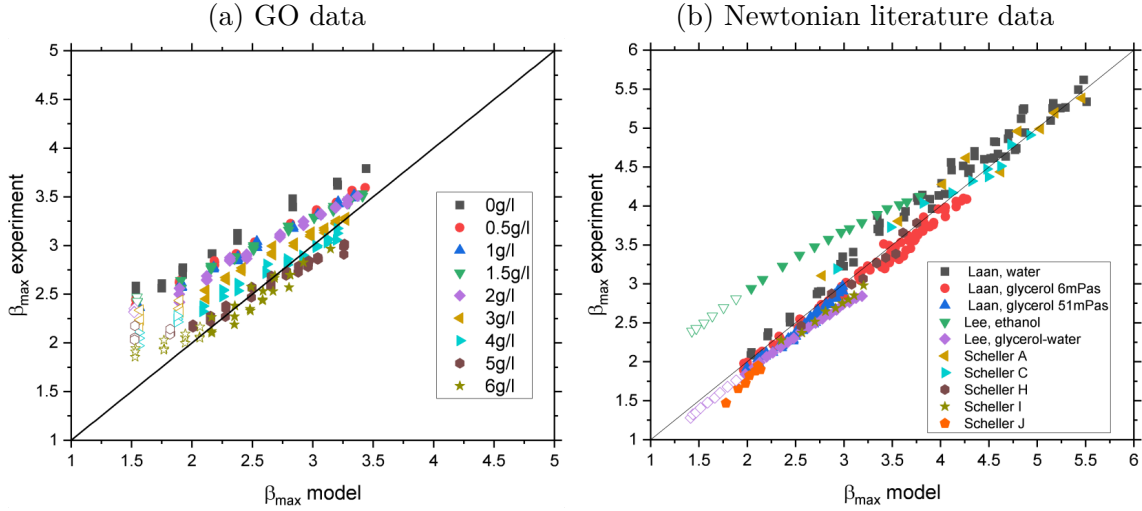


Figure 3.21: Comparison of GO and Newtonian literature data to the Wildeman (2016) model. (a) GO data compared to the Wildeman model for fixed α_w and θ as proposed by the authors, open symbols represent GO data points in which a maximum spread was not achieved. (b) Newtonian literature data compared to the Wildeman model for fixed α_w and θ as proposed by the authors, open symbols represent data points where $We < 30$.

parameter, α that is a function of the contact angle and droplet shape, as opposed to two terms, α_w and θ , in the Wildeman model. In addition to this, the universal contact angle and fit parameter proposed in the Wildeman model result in the model not capturing behaviour recorded in our GO data and Newtonian literature data, as per figures 3.21a and 3.21b.

It remains, however, to relate α to the contact angle of the advancing lamella. The contact angle of the lamella changes considerably over the spreading process, and it is clear from figure 3.22a that it also varies with impact velocity. The comparison of the Wildeman model to more literature data shows that the simplification that a contact angle of 180° can be universally used is not accurate. Figure 3.22c shows the extremely large range of contact angles exhibited over time by a drop of 6g/l GO in 50%v/v ethanol-water. It is also clear that the drop shapes observed during spreading vary considerably with impact velocity.

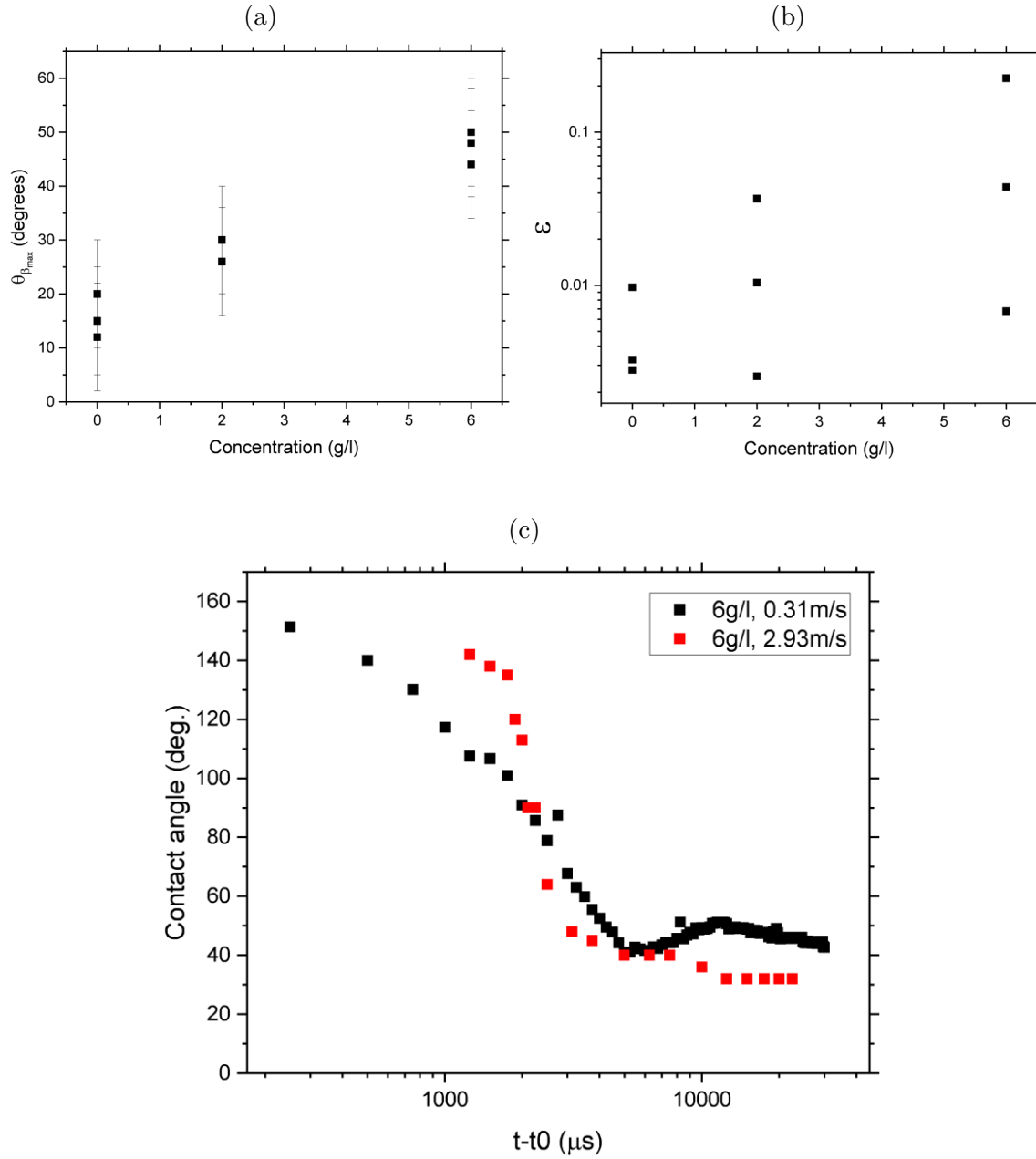


Figure 3.22: (a) Contact angle at maximum spread, $\theta_{\beta_{max}}$, for drops shown in figure 3.15, (b) ε calculated for spherical cap shape for drops in figure 3.15. (c) Contact angle over time for 6g/l GO in 50%v/v ethanol-water at two different impact velocities.

The new energy balance model has the advantage of being adaptable for different droplet shapes at maximum spread by equating $(1 + \varepsilon)$ to different formulae for the drop surface area, such as that of a flat disc, a thin cylinder and a spherical cap. Lee *et al.* clearly demonstrate that the spherical cap model often over estimates

the drop volume when the shape is closer to a truncated spherical cap, where the top of the drop is flattened, similar to that shown in figure 3.15 for a 6g/l GO drop at $U_0 = 1.01$ m/s [67]. This becomes further apparent when we calculate α using a spherical cap shape for the literature data from Lee *et al.* for a glycerol-water sample impacting on steel. Using the dynamic contact angle they provide of 121° , we would expect a value of $\alpha = 5.6$ which is significantly higher than the fitted value of $\alpha = 3.8$. However, the drop is observed to have a disc-like shape at maximum spread [67].

3.5 Conclusions

Despite the complication of a rapidly changing viscosity on droplet spreading, the method of using a characteristic viscosity in the analysis of non-Newtonian liquid drops proves exceedingly effective. While the viscosity may change over several orders of magnitude, the spreading behaviour can still be captured with a Newtonian model with only small variations in the fit parameter, α , for impacts on a glass substrate. The fitted α is also constant across the entire range of velocities captured for each GO concentration, ranging from 0.2-2.9 m/s.

In addition, the implementation of the new energy balance model presented here proves effective for existing Newtonian and non-Newtonian literature data and experimental data from this study, with the added benefit over other models of a single fit parameter required that is adaptable to a wide range of drop shapes at maximum spread. It remains however, to obtain a more thorough understanding of the relationship between this fit parameter and the drop shape at maximum impact velocity. It is important to note that in general, all spreading models are approximations, with various assumptions made in their derivations. These assumptions are necessary for tractability but may introduce limitations in capturing the full complexity of real-world spreading phenomena.

Chapter 4

Splashing of Aqueous GO Suspensions

4.1 Introduction

To further refine resolution control in droplet deposition, the case of splashing needs to be well understood, with prediction of its occurrence vital.

The topic of splashing in droplet impacts has been widely explored in the case of Newtonian liquids, however a complete picture of the process and dynamics is yet to be developed, with a wide range of models to predict splashing behavior existing in the literature. When considering then the splashing of nanoparticle suspensions, ideal materials for applications in printed electronics such as graphene-based suspensions are often non-Newtonian, presenting another obstacle in predicting their splashing on impact. In this case, the changing shear rates during droplet impact and resulting variable viscosity further complicate predicting the occurrence of splashing.

In this chapter, we investigate the splashing transition for non-Newtonian graphene-oxide (GO) nanosheet suspensions at a range of particle concentrations on glass

substrates. The observed splashing behaviour of GO suspensions is compared with experiments for Newtonian water-ethanol-glycerol (W-E-G) mixtures that were prepared to have approximately the same surface tension values as the GO samples, over a range of viscosities. Using a characteristic viscosity for each GO sample, we investigated if the splashing behavior can be predicted using several Newtonian models for the splashing threshold. We find that the splashing threshold for sample concentrations approaching the gelation point of the suspension display an inhibition of splashing when compared to a Newtonian fluid, that cannot be captured using a Newtonian model. The complete suppression of splashing is also noted in both W-E-G and GO samples above a threshold viscosity within the experimental limits, and that this threshold viscosity is much higher for GO suspensions than for Newtonian W-E-G mixtures.

4.2 Theory

When a Newtonian droplet impacts on a solid surface, it will either splash or spread across the substrate in a process called forced wetting. In the latter case, the droplet flattens on impact and a thin liquid sheet – the lamella - spreads tangentially along the substrate. In the former, splashing can take place by different mechanisms, such as prompt splash, where droplets are ejected from the tip of the lamella as it advances along the substrate [73] or corona splash, in which the lamella first dewets the substrate as it spreads and breaks up into droplets in a “fingering” pattern similar to that seen in impacts on liquid substrates. The occurrence of a prompt or corona splash is dependent on the surface roughness, with corona splash occurring only on smooth surfaces [74]. The transition from splashing to spreading has been shown to have dependencies on several fluid properties, namely the density, surface tension, droplet radius and viscosity, along with the impact velocity [42].

Much of the work carried out thus far in the literature concerning the splashing-

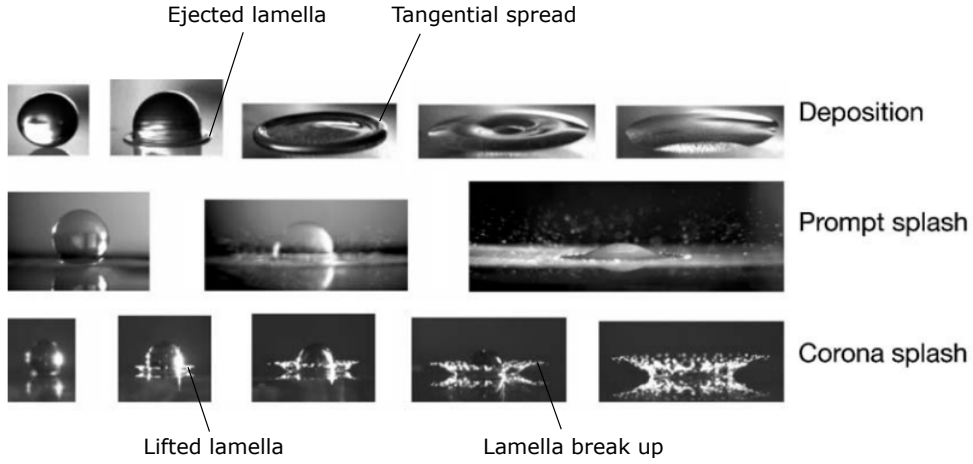


Figure 4.1: Illustration of deposition, prompt and corona splash, adapted from Riboo *et al.* (2001) [73]

spreading transition in droplet impacts focuses on understanding the case of Newtonian droplets. Several splashing criteria have been proposed, often using some ratio of dimensionless numbers such as the Reynolds and Weber numbers defined in the previous chapter. The Ohnesorge number is also commonly used in the context of splashing $Oh = \frac{\mu}{\sqrt{\rho\sigma l}}$, where ρ, σ, μ and D_0 are the density, surface tension, viscosity and initial droplet diameter respectively [74, 75].

Mundo *et al.* (1995) [74] showed an empirical relation that marked a threshold for deposition or splashing on a smooth or rough surface,

$$K = Oh \cdot Re^{1.25}, \quad (4.1)$$

where a value of K above 57.7 results in splashing.

Palacios *et al.* (2011) [75], characterised impact outcome regimes for ranges of the Reynolds and Weber numbers, where

$$We = (Oh \cdot Re)^2 = \frac{\rho v^2 R}{\sigma}, \quad (4.2)$$

and using a variety of liquids showed a transition region from splashing to de-

position at $Re \gtrsim 1000$, suggesting that viscosity, while promoting splashing at low and high Reynolds numbers, promotes lamella thickness in this transitory regime, inhibiting splashing.

These dimensionless numbers alone, however, cannot account for surface roughness and air pressure, which have been shown to influence the onset of splashing [76]. Wetting properties also have an impact on when splashing occurs for superhydrophobic and superhydrophilic smooth surfaces [77].

The surrounding gas in which a droplet impact occurs has a significant affect on the splashing outcome. Xu *et al.* in 2005 provided a crucial insight into the mechanism of splashing [76] by revealing that reducing the pressure of the ambient gas will completely suppress splashing.

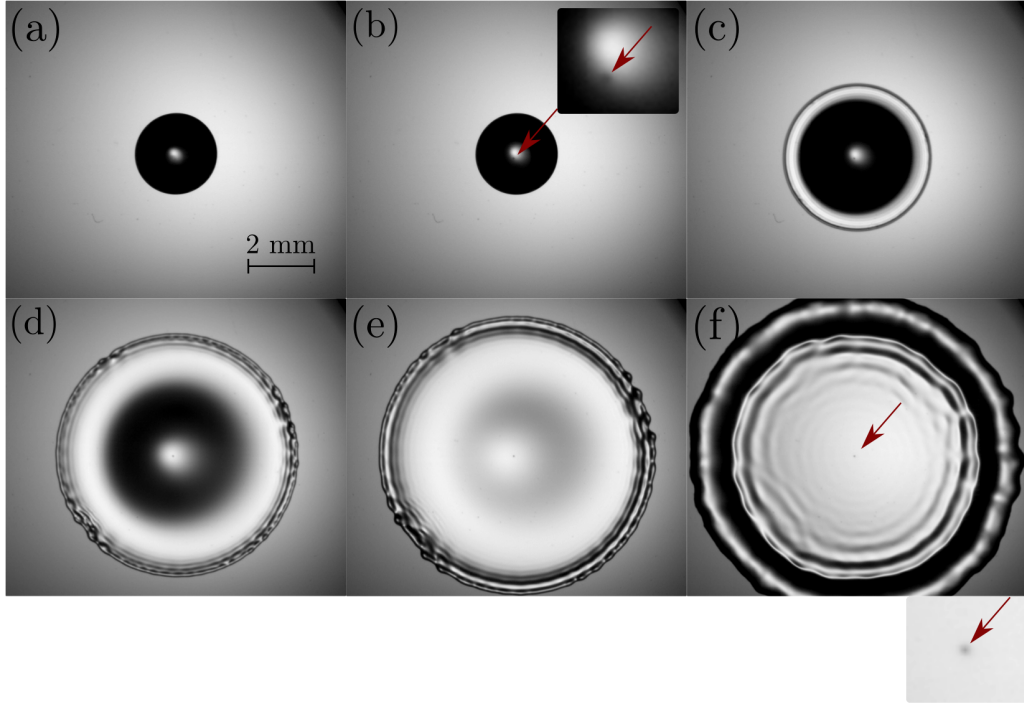


Figure 4.2: Spreading evolution of water on a glass substrate shown at (a) 0.02, (b) 0.05, (c) 0.58, (d) 1.53, (e) 2.13 and (f) 6.81 ms after impact. The entrapped central bubble can be first observed in (b).

Driscoll *et al.* in 2010 observed for their viscous silicone oil samples that the thin sheet ejection that resulted in splashing outcomes had a threshold pressure above

which it occurs [78]. A centrally trapped air bubble upon impact has been observed in several studies, first by Chandra [62], with the mechanism by which it occurs outlined by Thoroddsen [79]. Figure 4.2 shows the impact of a drop of water on a glass slide imaged from below using a 45 degree mirror. The entrapped bubble can be observed from as early as 50 μs after impact, shown in figure 4.2 (b). The formation of such an entrapped bubble is shown in figure 4.3 for a drop of 50%v/v ethanol-water.

Driscoll also showed that this bubble entrapment persists at pressures below that necessary for the thin sheet formation. They went on to show, in a 2011 paper by means of interferometry, that despite the presence of this bubble, no further air layer is formed until the time that splashing occurs [80].

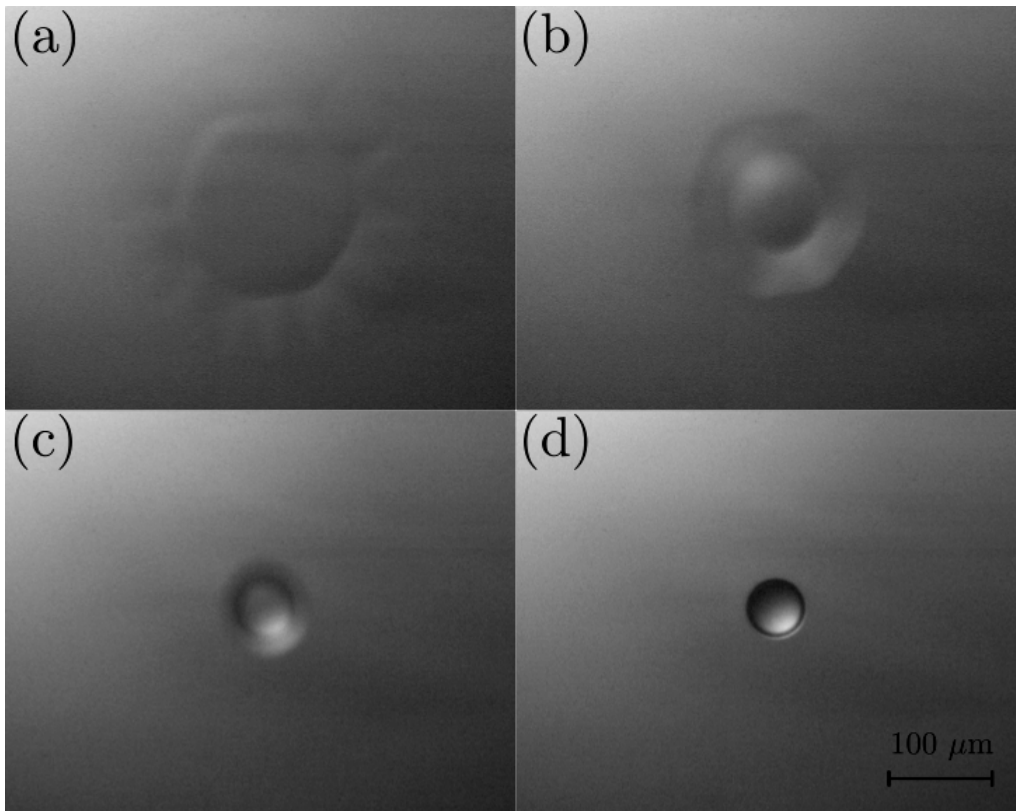


Figure 4.3: Bubble entrapment for impact of a drop of 50%v/v ethanol-water at (a) 33, (b) 67, (c) 100 and (d) 133 μs after impact.

The effects of the surrounding gas have since been implemented in a model by Riboux & Gordillo (2014) (R&G model, hereafter) [81]. This Newtonian splashing

model predicts the critical impact velocity at which a drop of a given Newtonian fluid will transition from spreading to corona splashing. They propose two criteria for splashing to occur. Firstly the ejection of the lamella which can only occur if the tip of the lamella is advances faster than the circular wetted region, derived from momentum balance,

$$\frac{\sqrt{3}}{2}Re^{-1}t_e^{-1/2} + Re^{-2}Oh^{-2} = 1.21t_e^{3/2}, \quad (4.3)$$

where t_e is the ejection time of the lamella. Secondly, they propose a splashing criterion, β_c that outlines the magnitude of the combination of forces on the lamella required to overcome surface tension in order for droplets to be ejected. The forces are comprised of a vertical lift force on the lamella tip by the surrounding gas, ℓ ,

$$\beta_c = \left(\frac{\ell}{2\sigma} \right)^{1/2}. \quad (4.4)$$

The lift force ℓ is made up of two contributions, the lubrication force at the wedge, $K_l\mu_g V_t$, and the suction force at the top of the lamella, $K_u\rho_g V_t^2 H_t$. V_t and H_t are the velocity and thickness of the edge of the lamella respectively, given in equations 4.7 and 4.8 respectively (see figure 4.5),

$$\ell = K_l\mu_g V_t + K_u\rho_g V_t^2 H_t. \quad (4.5)$$

These forces depend on K_l and K_u . K_l is given in equation 4.6 where α_{RG} is the wedge angle and λ is the mean free path of the gas. $K_u = 0.3$, μ_g is the viscosity of the surrounding gas, ρ_g is the density of the gas, U_0 is the impact velocity of the droplet, and R is the droplet radius. A summary of all the terms used in the model is shown in table 4.1.

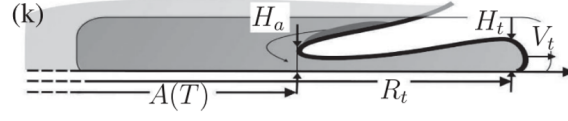


Figure 4.4: Illustration of the variables used to describe the R&G splashing model. Figure adapted from Riboux *et al.* (2014) [81]

$$K_l = -\frac{6}{\tan^2 \alpha_{RG}} \left[\ln \left(19.2 \frac{\lambda}{H_t} \right) - \ln \left(1 + 19.2 \frac{\lambda}{H_t} \right) \right], \quad (4.6)$$

$$V_t = \frac{1}{2} \sqrt{3} U_0 t_e^{-1/2}, \quad (4.7)$$

$$H_t = \frac{\sqrt{12}}{\pi} R t_e^{3/2}. \quad (4.8)$$

Symbol	Description
t_e	Lamella ejection time
β_c	Splashing criterion, constant for all liquids at 0.14
σ	Surface tension of the liquid
K_l	Suction constant, calculated using equation 4.6
K_u	Lubrication constant, ≈ 0.3
ρ_g	Density of the surrounding gas, 1.2 kgm^{-3} at 20°C
μ_g	Viscosity of the surrounding gas, $1.8 \times 10^{-5} \text{ Pa} \cdot \text{s}$ at 20°C
V_t	Velocity of thin liquid sheet, see equation 4.7
H_t	Thickness of thin liquid sheet, see equation 4.8
ℓ	Vertical lift force on edge of liquid sheet, see equation 4.5
λ	Mean free path of gas, 65 nm at 20°C
U_0	Impact velocity of the droplet
R	Radius of the droplet
α_{RG}	Wedge angle, 60°

Table 4.1: Description of symbols used in the Riboux splashing model [81]

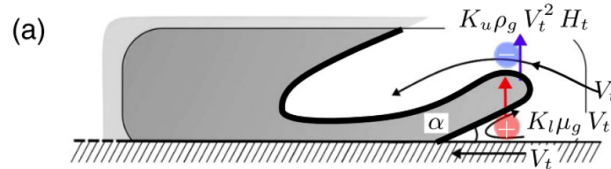


Figure 4.5: Contribution of lubrication and suction forces as described in the Riboux splashing model. Figure adapted from Riboux *et al.* (2014) [81].

The R&G model must be solved numerically to determine the critical splash

velocity for a given fluid. In order to do this, equation 4.3 is rearranged to form an expression for the splashing velocity,

$$v_{sp} = \frac{\frac{\sqrt{3}}{2} \frac{\mu}{\rho R} t_e^{-1/2} + \sqrt{\frac{3}{4} \left(\frac{\mu}{\rho R}\right)^2 t_e^{-1} + 4.84 \frac{\mu}{\rho R} t_e^{3/2}}}{2.42 t_e^{3/2}}, \quad (4.9)$$

and equation 4.4 is rearranged to obtain

$$K_l \mu_g V_t + K_u \rho_g V_t^2 H_t - 2\sigma \beta_c^2 = 0. \quad (4.10)$$

Then equation 4.10 can be evaluated using equations 4.9 and 4.6-4.8 to obtain an expression for t_e , the roots of which must be determined numerically.

Riboux *et al.* also included an approximation for the splashing velocity for the case of low Ohnesorge number, $Oh \ll 1$ [81], and was verified as accurate using β_c as a fit parameter by de Goede *et al.* [82]. At low Oh , K_l is approximately a constant and the suction force is negligible compared to the lubrication force. The ejection condition can also be simplified resulting in an approximation for the splashing velocity, given by

$$v_{sp} = \left(\frac{\sigma^{2/3} \beta_c \tan(\alpha_{RG})}{2.22 \sqrt{\mu_g} (\rho R)^{1/6}} \right)^{6/5}. \quad (4.11)$$

This approximation was developed for Newtonian fluids, i.e. fluids with a constant viscosity. It omits the liquid viscosity as a parameter, which is consistent with assuming a small Ohnesorge number. Notably it still contains the gas viscosity, maintaining the dependence novel to the full model. The approximation is valid for water droplets with radii $R > 0.1mm$ ($Oh = 1 \times 10^{-2}$), and as such is not valid for very small droplets, such as those used in inkjet printing.

A growing number of studies in the literature investigate droplet impacts of complex fluids, but a majority of these have focused on the spreading dynamics, rather than splashing outcomes [31, 32, 48]. Studies investigating splashing in nanoparticle

suspensions primarily focus on Newtonian suspensions, suspensions that are close to Newtonian, or polymer suspensions [82–88]. A study by de Goede *et al.* in 2018 probed the splashing behavior of blood, a non-Newtonian liquid that is weakly shear thinning. They showed that a low-Ohnesorge number approximation derived from the R&G model (equation 4.11) captured their experimental results well [82][81].

4.3 Experimental methods

4.3.1 Newtonian Sample Preparation

Newtonian samples used in this study are comprised of mixtures of water, ethanol and glycerol at different mass ratios, detailed in table 4.2. The ratios of each liquid were adjusted to produce samples that varied in viscosity but retained consistent surface tension values (± 3 mN/m), accordant with the surface tension values measured for GO samples detailed in chapter 2. This was accomplished through iterative experimentation, employing a methodical trial-and-error approach adjusting the concentrations of each component within the mixtures. The addition of glycerol served to vary the viscosity of the mixture, while the amount of ethanol added was adjusted in order to maintain the surface tension at around 30 mN/m. Surface tension measurements and rheological studies were carried out as detailed in chapter 2.6, with the results for GO samples described in sections 2.4 and 2.5 respectively.

4.3.2 Droplet Impacts

Droplet impacts were monitored by means of high speed video using a Phantom v2010 camera at frame rates of 40,000 frames per second, back-lit by an LED array. Samples were delivered to a nozzle using a syringe pump until their size exceeded an equilibrium at which time the drop was allowed to detach under gravity. The drops of ~ 2.5 mm diameter impacted on clean glass microscope slides. The experimental set up is identical to that described in chapter 3 (see figure 3.1), as both experiments

were run consecutively on the same sample set. To determine the critical splash velocity of the samples, the fall height was varied with millimeter precision until the splashing threshold could be determined. Figure 4.6 shows an example of how the critical splash velocity was determined for the 5g/l GO sample. The fall height was varied in 5cm intervals until splashing was observed on impact. At this point, the fall height was varied in increasingly smaller intervals until a fall height was found below which no splashing was observed.

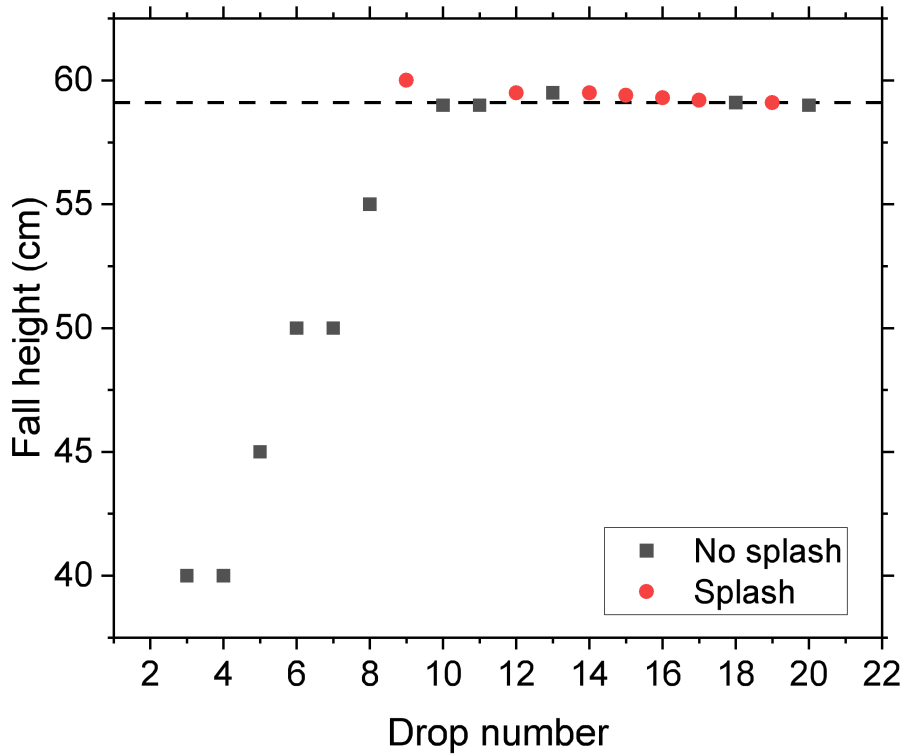


Figure 4.6: Experimental data to determine the splashing transition for 5 g/l GO in 50%v/v ethanol-water. The transition fall height was determined as the height below which no splashing was observed, 59.1 cm here.

Defining the transition between splashing and spreading is surprisingly not a trivial matter, and it is clear from figure 4.6 that the transition is not as sharp as one would expect. We see here for the 5g/l GO sample that beyond a certain fall height, and as such, impact velocity, we begin to see splashing events occurring, however there are occasional impacts beyond this threshold that we see no splashing. It then becomes non-trivial to determine a critical splash velocity for a given sample.

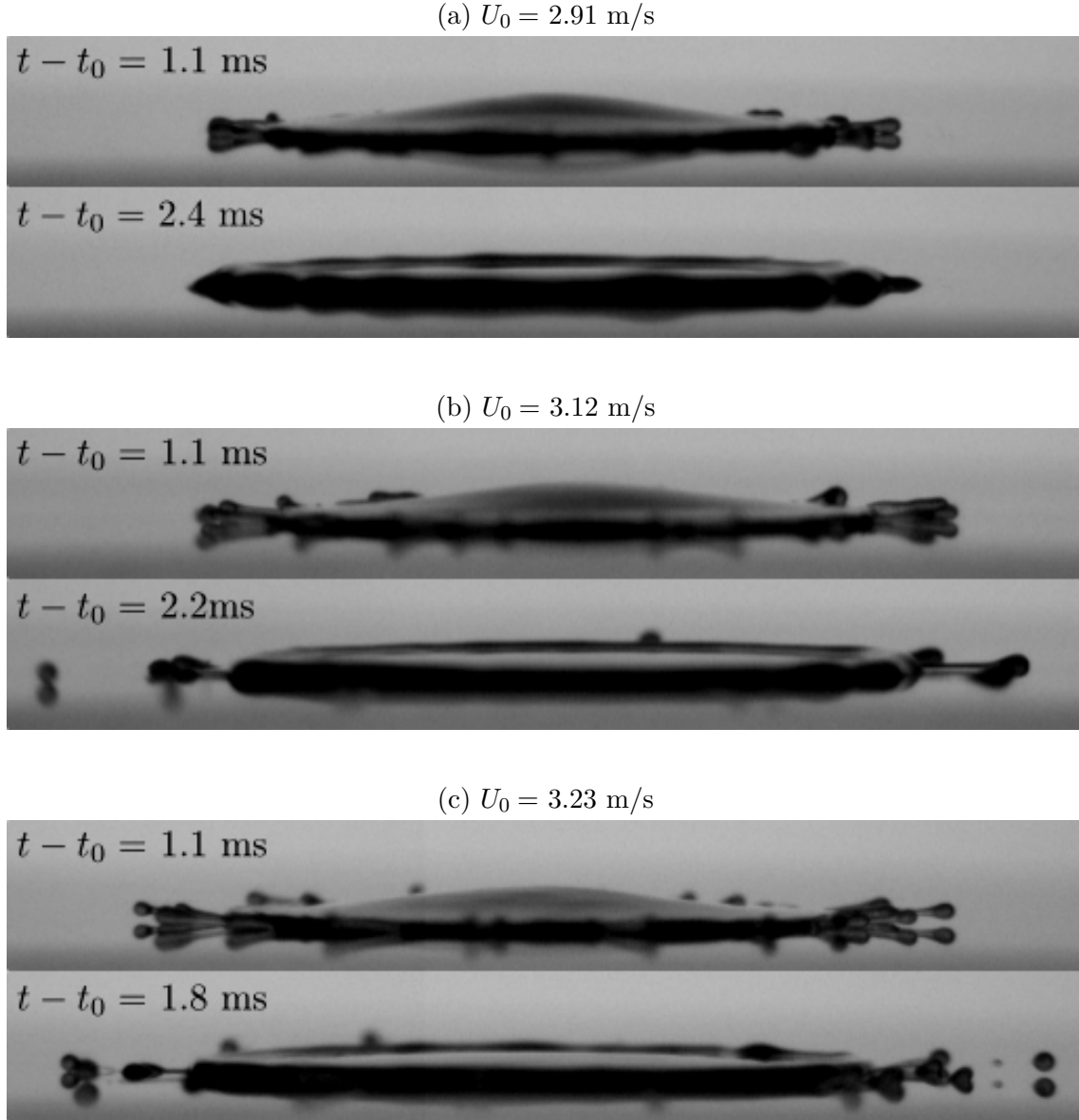


Figure 4.7: Impact of 4g/l GO in 50%v/v ethanol-water with time after impact, $t - t_0$, indicated for (a) $U_0 = 2.91$ m/s with no splashing event, (b) an impact close to the critical splash velocity, $U_0 = 3.12$ m/s, and (c) $U_0 = 3.23$ m/s with a splashing event.

An example of the images captured for the impact of 4g/l GO droplets are shown in figure 4.7. In 4.7c we see in the upper image that fingering of the spreading lamella occurs with the outer edges of these fingers lifted from the substrate. It is these fingers that possess sufficient momentum to detach from the lamella and eject outwards at a later time, shown in the lower image. At a lower impact velocity, as

shown in 4.7a, fingering still occurs but the fingers do not sufficiently lift nor have sufficient momentum to detach. No splashing can be observed at later times, as shown in the lower image. An interesting case is shown in figure 4.7b, a droplet impact at an impact velocity intermediate to that of the impacts discussed prior. Here we observe fingering in the upper image, but at a later time in the lower image, we can see that drops to the left of the image have detached while drops on the right of the image remain attached to the main drop body by means of a long filament. We have chosen to define the outcome of splashing as the ejection of any droplets from the lamella after impact, and as such the impact shown in figure 4.7b is described as having a splashing event occur. In the proposed application of inkjet printing with nanoparticle suspensions, the ejection of even a single droplet from the lamella can affect printing resolution, and it was with this in mind that we chose this definition. It is important to note that while figure 4.7 shows impacts for a single concentration sample of GO, the transition from spreading to splashing was qualitatively the same for all samples examined here.

It is clear from this figure that the occurrence of splashing may not always be symmetric. As such, it is possible for a single impact that a droplet may be ejected from the lamella in the direction perpendicular to the plane of view and be obscured by the body of the impacting drop. In order to compensate for this, we chose to define the transition using the fall height below which no splashing is observed for 3 repeated impacts.

4.4 Results

In this experiment a characteristic viscosity, μ_{HB} , is calculated (equation 3.7) using the method described in section 3.3. Figure 4.8 shows μ_{HB} calculated for GO droplets in 50%v/v ethanol-water at the threshold splashing velocity for varying GO concentration.

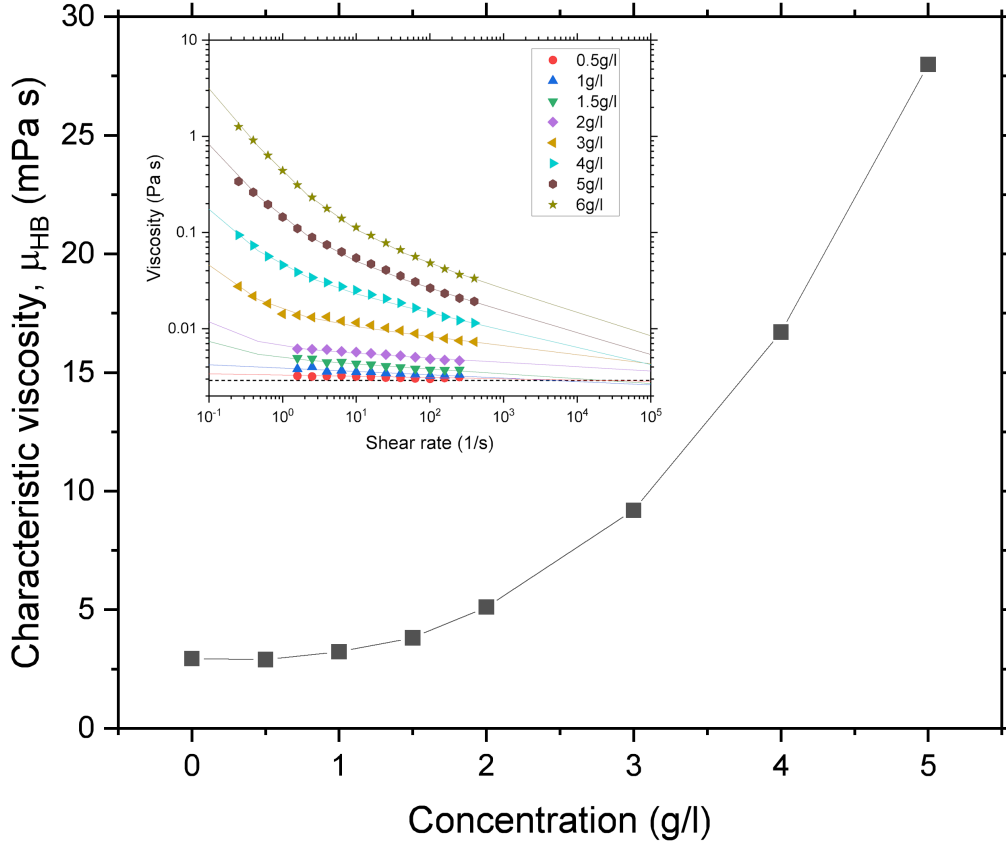


Figure 4.8: Characteristic viscosity μ_{HB} as a function of GO concentration in 50%v/v ethanol-water for droplets at the splashing threshold velocity. Inset: Herschel-Bulkley fits to apparent viscosity as a function of shear rate for GO samples (figure 2.5, included for reference).

Experiments examining the critical splashing velocity of GO suspensions in 50%v/v ethanol-water show an increase in the threshold with increasing GO concentration for higher concentration samples. Figure 4.9 shows that for lower concentration samples, up to 1.5g/l there is very little change in the critical splashing velocity, but above this concentration a significant increase in the threshold is observed, up to a maximum of 73%. This increase coincides with the presentation of shear thinning behavior observed in the rheological measurements for increasing GO concentration. For samples with a GO concentration above 5 g/l, we saw a suppression of splashing, with no splashing occurring for these samples up to our experimental limit, an impact velocity of 5 m/s.

Table 4.2: Properties of water-ethanol-glycerol samples. No splashing was observed for samples F and G up to the experimental limit of 5 m/s.

Sample	W-E-G ratio	Viscosity (mPa s)	Surface tension (mN/m)	Density (kg/m ³)	v_{sp} (m/s)
A	40:31:10	2.29 $\pm$ 0.05	30.10 $\pm$ 1.00	979 $\pm$ 5	2.00 $\pm$ 0.05
B	20:23:12	3.65 $\pm$ 0.05	28.56 1.00	963 $\pm$ 5	2.09 $\pm$ 0.05
C	4:7:5	8.19 $\pm$ 0.05	29.52 1.00	1036 $\pm$ 5	2.14 $\pm$ 0.05
D	4:7:6	9.84 $\pm$ 0.05	29.92 1.00	1056 $\pm$ 5	2.28 $\pm$ 0.05
E	4:7:7	11.81 $\pm$ 0.05	31.03 1.00	1067 $\pm$ 5	2.37 $\pm$ 0.05
F	1:2:2	12.45 $\pm$ 0.05	29.91 1.00	1071 $\pm$ 5	>5
G	1:4:6	28.71 $\pm$ 0.05	30.46 1.00	1093 $\pm$ 5	>5

Table 4.3: Properties of GO in 50%v/v ethanol-water samples

GO Concentration (g/l)	Characteristic viscosity, μ_{HB} (mPa s)	Surface tension (mN/m)	v_{sp} (m/s)
0	2.29	29.14 $\pm$ 1.00	2.00 $\pm$ 0.05
0.5	2.89	29.28 $\pm$ 1.00	2.00 $\pm$ 0.05
1	3.23	28.86 $\pm$ 1.00	2.02 $\pm$ 0.05
1.5	3.82	28.62 $\pm$ 1.00	2.02 $\pm$ 0.05
2	5.11	28.77 $\pm$ 1.00	2.08 $\pm$ 0.05
3	9.19	30.17 $\pm$ 1.00	2.33 $\pm$ 0.05
4	16.7	29.61 $\pm$ 1.00	3.12 $\pm$ 0.05
5	27.98	29.94 $\pm$ 1.00	3.46 $\pm$ 0.05
6	N/A	30.87 $\pm$ 1.00	>5

4.4.1 Comparison with Newtonian Splashing Models

We compared these findings to the predictions produced by the R&G model. The Newton-Raphson method was implemented in MATLAB in order to determine the roots of Equation 4.9. This method finds the roots of an equation using an iterative process. An initial guess is input and another guess is then generated and checked if it is a better approximation of the root, using

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}. \quad (4.12)$$

The MATLAB code utilized for the numerical solution of the equation can be found in appendix G.

The R&G model predictions for samples of GO in 50%v/v ethanol-water calcu-

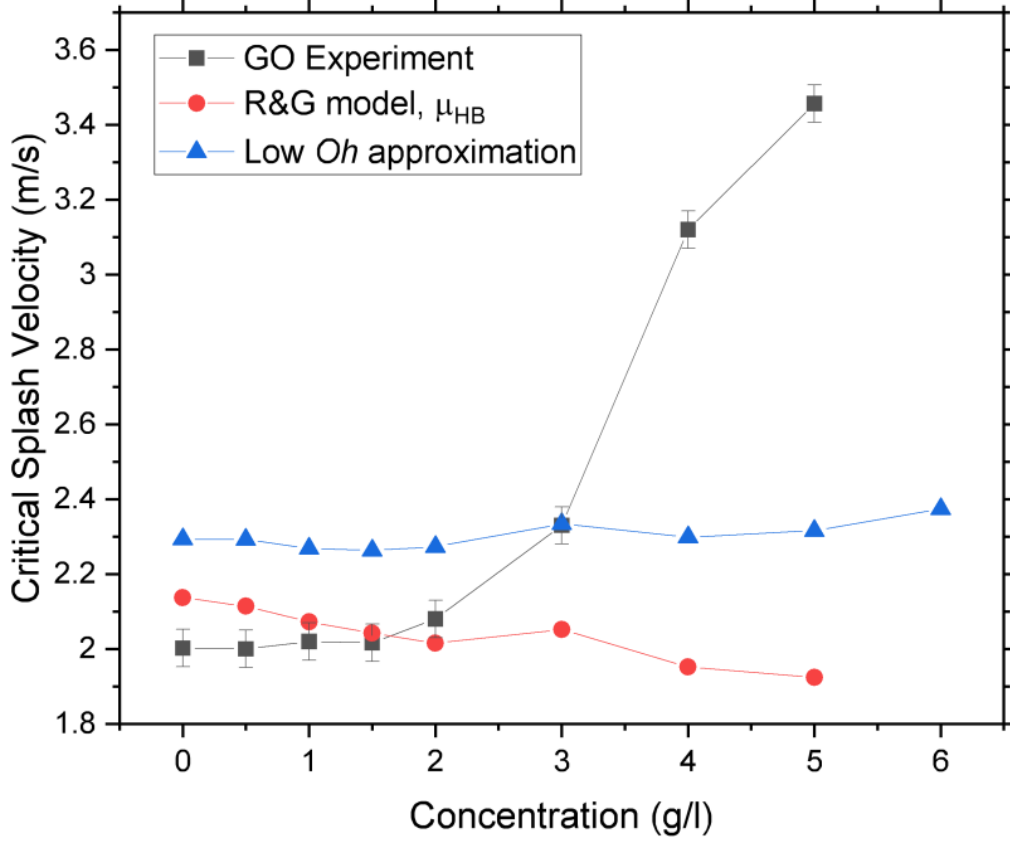


Figure 4.9: Critical splash velocity as a function of GO concentration in 50% v/v ethanol-water for experimental data and Riboux model prediction calculated at the characteristic viscosity, μ_{HB} , for each GO concentration. The 6g/l sample is not shown here as no splashing was observed withing the experimental range of 5 m/s and the R&G prediction is not shown as a velocity is required to calculate μ_{HB} .

lated using μ_{HB} are shown in figure 4.9 as a function of concentration, and again in figure 4.10 (a) as a function of viscosity. Fluctuations in the predicted values are a result of small fluctuations in the measured fluid parameters. This Newtonian model does not capture the jump in critical splash velocity we observed with increasing GO concentration. In addition to this, the R&G model predicts a decrease in the critical splash velocity with an increase in sample viscosity. As this model is derived from potential flow theory and assumes the limit of low viscosity, this effect is unsurprising as the model is not optimized to deal with more viscous fluids. The prediction from the low Oh approximation is shown in figure 4.9 for the 6g/l sample in which splashing was not observed. This was possible due to the lack of a viscosity dependence in the approximation. The full R&G model prediction could

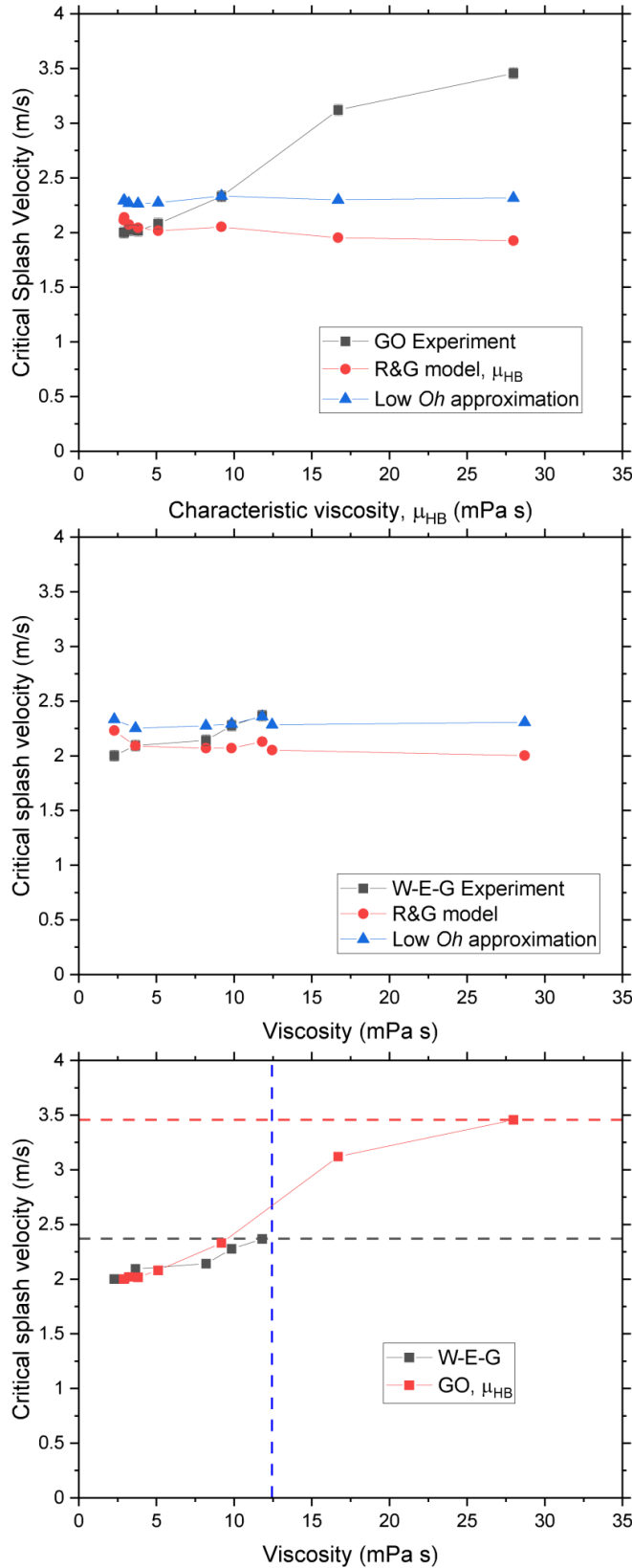


Figure 4.10: (a) Comparison between measured critical splash velocity and Riboux *et al.* splashing model [81] for GO samples as a function of characteristic viscosity, μ_{HB} . No splashing was observed for the 6g/l sample. (b) Comparison between measured critical splash velocity and Riboux *et al.* splashing model [81] for W-E-G samples as a function of viscosity. Splashing was not observed for samples F and G. (c) Critical splash velocity as a function of viscosity for GO and water-ethanol-glycerol samples. No splashing is observed above a viscosity of 12.45 mPa s for the W-E-G samples within the experimental limit indicated on the plot with a blue dashed line. The maximum critical splash velocity observed for W-E-G and GO samples are indicated by the grey and red dashed line respectively. Also shown in (a) and (b) is the low Oh approximation given in equation 4.11. Error bars for the experimental data are concealed by the data points.

not be calculated for this sample, as the characteristic viscosity requires an impact velocity in its calculation (equation 3.7), taken as v_{sp} in the case of these splashing experiments.

A comparison between the experimentally determined splashing threshold of Newtonian W-E-G mixtures and the R&G model is shown in figure 4.10 (b). Here a deviation is seen from the prediction for higher viscosity samples. Also shown is the low Oh approximation calculated for this dataset, which consistently overestimates the threshold predicted by the R&G model. Neither predictions capture the increase in the critical splash velocity with increasing viscosity. No experimental data is shown in this figure for samples F and G as no splashing was observed for these samples up to the experimental limit of 5m/s.

Figure 4.10c illustrates a comparison between the experimentally determined critical splash velocity for GO and W-E-G samples as a function of viscosity, calculated as μ_{HB} in the case of the GO samples. While only a small increase in the critical splash velocity of the different water-ethanol-glycerol (W-E-G) mixtures was observed, we also noted the suppression of splashing of these mixtures above some critical viscosity, ~ 12 mPa s, up to our experimental limit of $U_0 = 5$ m/s. The GO sample data is plotted for μ_{HB} for comparison. The highest observed GO characteristic viscosity producing a splashing outcome in the experimental range is 27.98 mPa s while the maximum splashing viscosity observed for W-E-G samples is 11.81 mPa s. The vertical blue dashed line indicates the viscosity beyond which no splashing was observed for W-E-G samples up to the experimental limit of 5 m/s. The grey and red dashed lines mark the maximum critical splash velocity determined for W-E-G and GO samples respectively.

4.4.2 Viscosity Dependence

Pierzyna *et al.* (2021) have proposed a machine learning model based on the theory of the R&G model [89]. This model estimates the splashing parameter (equation 4.4) while robustly accounting for uncertainties in the relevant parameters. This model predicts that the splashing threshold decreases with increasing viscosity up to around 3 mPa s, beyond which point the threshold remains constant. The non-monotonic relation between viscosity and the threshold for splashing has been reported in the literature, and it has been shown that at low viscosities splashing is promoted as viscosity increases, but studies have also shown that in the higher viscosity regime, splashing is inhibited with increasing viscosity [75, 77, 90, 91]. The Newtonian W-E-G samples investigated here are in agreement, as can be seen in figure 4.10 (b), where an 18% increase in v_{sp} can be seen over a viscosity range of 2.3-11.8 mPa s. Here, the higher viscosity samples examined show an increased inhibition of splash. Notably, in the study by Zhang *et al.*, both the promotion at lower viscosity and suppression at higher can be clearly seen, [91].

Zhang *et al.* also proposed a semi-empirical splashing criterion based on a modified version of the Riboux model that aims to better account for viscous liquids, incorporating a second criterion for higher Ohnesorge cases in which viscous forces must also be overcome. The criteria for the two regimes are given by

$$\left. \begin{aligned} Re \cdot Oh^{1.3} &= 3.8, & Oh < 0.007 \\ (Re - 5.03Re^{0.67}) \cdot Oh^{1.3}, & & Oh > 0.007 \end{aligned} \right\}. \quad (4.13)$$

Figure 4.11 shows a comparison between this new criterion and our experimental data for both GO and W-E-G samples, with data points representing the experimentally determined splashing threshold. The Newtonian data agrees well with this model, but higher viscosity samples deviate more from the prediction. This effect

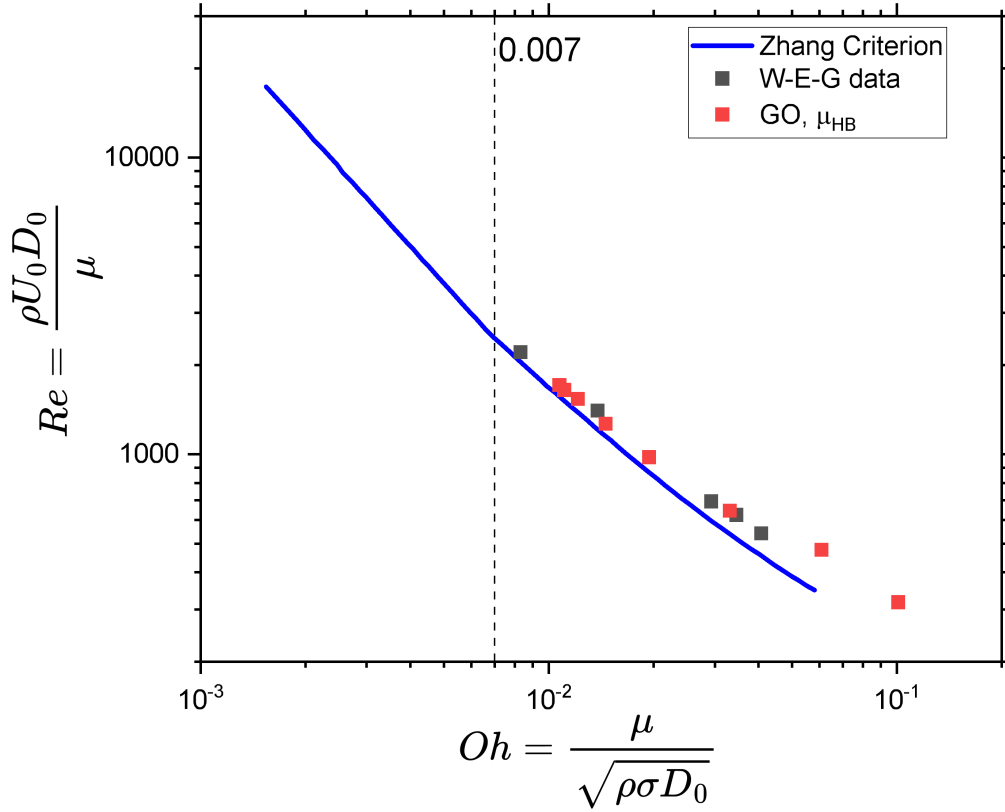


Figure 4.11: Comparison of experimental data for 0-5 g/l GO samples and W-E-G samples A-E to Zhang *et al.* splashing criterion (equation 4.13) [91]. The vertical dashed line at $Oh = 0.007$ indicates the transition between the low and high Oh criteria.

is seen more strongly in the GO samples, with lower concentration and hence lower viscosity samples lying close to the model predictions, while higher concentration data points deviate from the curve.

Almohammadi *et al.* (2019) took a different approach to predicting the splash transition, instead basing their model on the previously used empirical method of combining all relevant forces in droplet impact which can be captured by a relation of the form $WeRe^{\alpha_s} = K$ [74, 77, 92–95]. Various values of K and α_s have been suggested in the literature. In order to capture the non-monotonic role of drop viscosity, their model consists of equations for two different transition boundaries, given by

$$We = K_1 Re^{\beta_1} + K_2 Re^{\beta_2}, \quad (4.14a)$$

$$We = K_3 Re^{\beta_3}, \quad (4.14b)$$

where β_1 , β_2 and β_3 are 1, $-\frac{1}{2}$ and 1 respectively, and K_1 , K_2 and K_3 are fit parameters. Figure 4.12 shows equation 4.14a fit to the splash transitions of W-E-G samples, with the fit parameters given in table 4.4. The GO splash transitions also included here fit well with the model for lower concentration samples (high Re), while higher concentrations of 4 and 5g/l (low Re) deviate considerably. This plot exhibits the difference in behaviour for the higher concentration non-Newtonian suspensions of GO very clearly. Splashing is inhibited for these higher concentration drops, resulting in a higher splashing threshold than expected. Some studies have been carried out on the drop impacts of viscoelastic fluids and suspensions, with Crooks *et al.* (2000) showing that the critical Weber number for splashing is increased by adding polymers [87]. This, along with inhibition of droplet rebound is suggested to be a result of stretching of the polymer molecules in the lamella during impact resulting in energy dissipation, described well by Bertola *et al.* (2013) [96].

Table 4.4: Fit parameters for equation 4.14a

Source	K_1	K_2
Almohammadi <i>et al.</i> [77]	0.06	6762
W-E-G fit	0.054	10551

A recent paper by Aksoy *et al.* (2022) investigated the splash transition of Newtonian nanofluids and showed that for low Re , splashing is promoted by the addition of nanoparticles by an unquantified amount, contrary to our results for GO [85].

4.4.3 Suppression of Splash

The suppression of splashing at higher viscosity noted here is not a new phenomenon. It was observed by Zhang *et al.* (2021) in their study of the splashing of viscous liquids using water-glycerol mixtures at a similar viscosity, above 12 mPa s [91], along with the Almohammadi study [77]. Despite splash suppression observed in

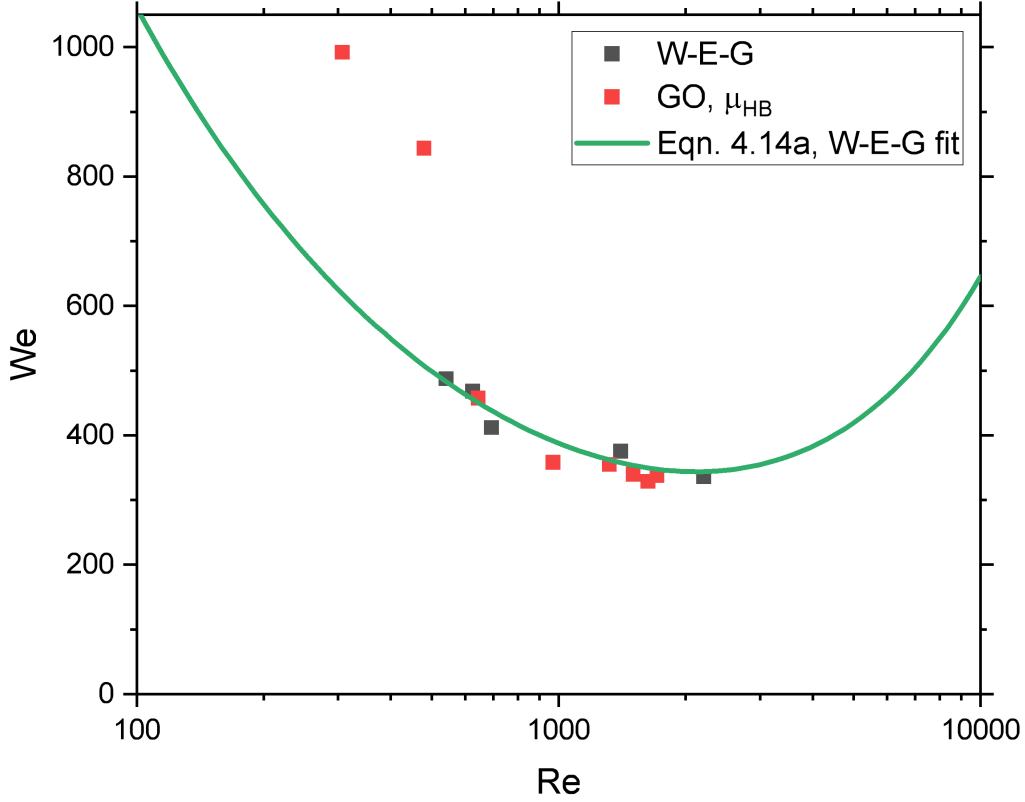


Figure 4.12: W-E-G and GO data compared with Almohammadi model [77]. Equation 4.14a is fit to the W-E-G data here with $\beta_1 = 1$, $\beta_2 = -\frac{1}{2}$, $K_1 = 0.054$ and $K_2 = 10551$ (see table 4.4 for comparison to ref. [77]).

the experiments of Zhang *et al.*, their model does not capture the suppression in its predictions. In both our study and that by Zhang, suppression of splashing was noted upon increasing the sample viscosity up to the same velocity limit of 5m/s. Figure 4.13 shows that the threshold splashing velocity predicted by the Zhang model is much lower than 5m/s. As splashing was not observed at this velocity, further increasing the velocity past the current experimental limit until the true splashing velocity is reached would result in an even greater deviation from the model predictions.

The Almohammadi model accounts for suppression by the introduction of the second splashing-spreading boundary given by equation 4.14b, which they determined empirically. Figure 4.14 shows the fit to this equation for the W-E-G data (see Appendix E for details). In order to capture the behaviour of the W-E-G data,

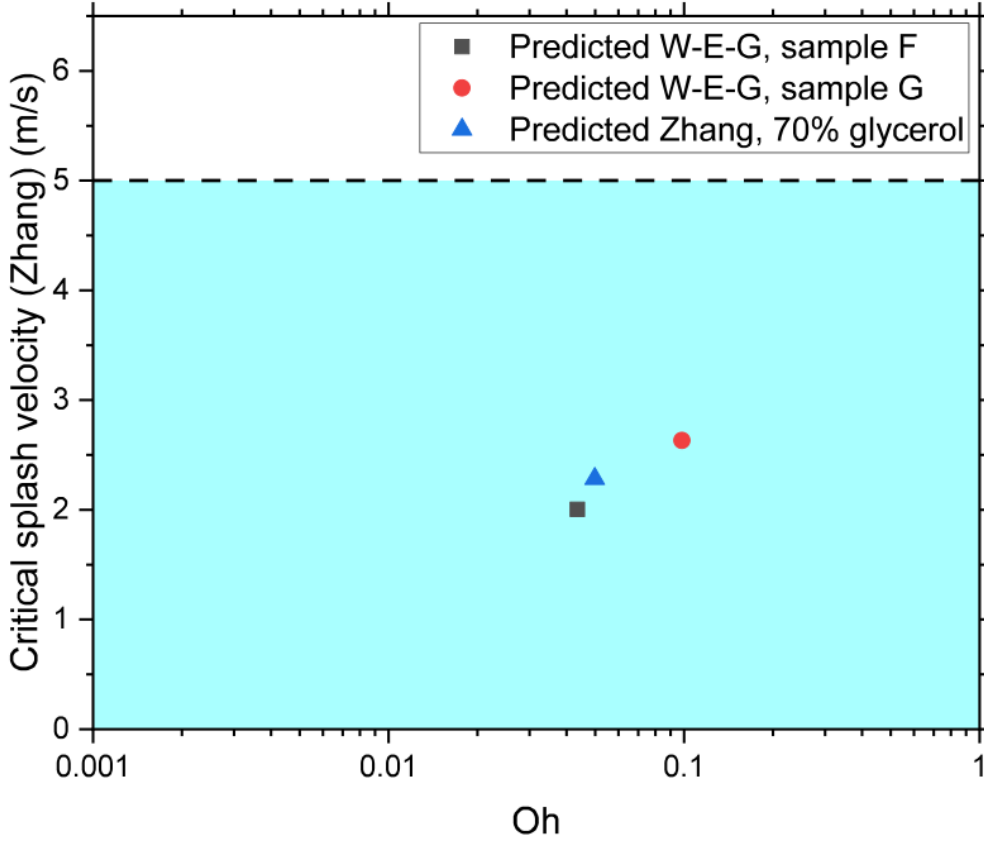


Figure 4.13: Critical splash velocity predicted by Zhang criterion for drops with suppressed splashing below impact velocity of 5m/s [91]. No splashing was observed for these droplets in the shaded region despite the predicted values lying within it.

we did not constrain β_3 in the fit, resulting in a significantly different value of 2 compared to 1 reported by Almohammadi [77]. A comparison between the two fits and the data recorded by Almohammadi is shown in Appendix E, in which it can be seen that the W-E-G fit with $\beta_3 = 2$ also represents their data well.

Table 4.5: Fit parameters for equation 4.14b

Source	K_3	β_3
Almohammadi <i>et al.</i> [77]	1.6	1
W-E-G fit	0.00167	2

Despite the Almohammadi model capturing the suppression of splash well in the Newtonian case, the GO deviates from this behaviour, continuing to splash at lower Re compared to W-E-G samples. Higher threshold velocities are also reached before suppression of GO when compared to W-E-G, evident in figure 4.10c. The

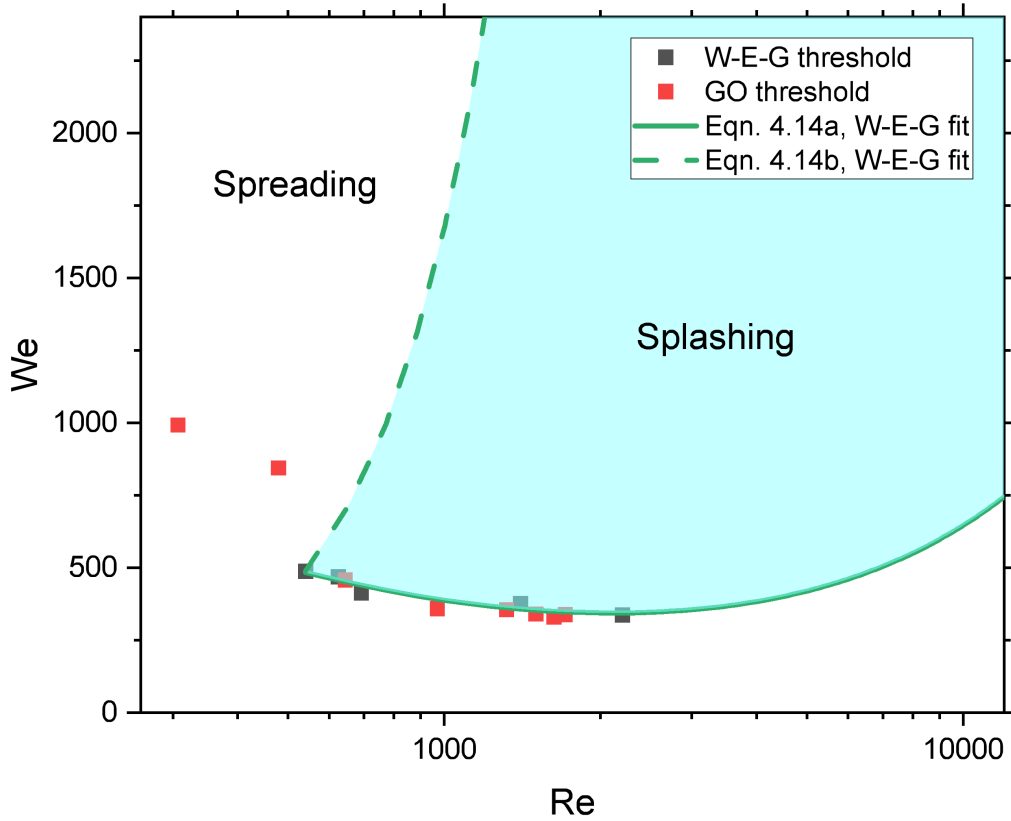


Figure 4.14: W-E-G fits to equations 4.14a and 4.14b compared to splashing threshold of W-E-G and GO samples, with fit parameters $\beta_1 = 1$, $\beta_2 = -\frac{1}{2}$, $\beta_3 = 2$, $K_1 = 0.054$, $K_2 = 10551$ and $K_3 = 0.00167$. For GO samples $Re = Re^*$ (equation 3.10).

underlying cause of this deviation in behaviour is unclear. It is possible that this is simply an artefact that arises as a result of implementing a characteristic viscosity, assuming a single characteristic shear rate can represent an impact in which the shear rate varies over several orders of magnitude, despite the technique working well for modelling spreading behaviour.

4.5 Conclusions

The case of splashing for GO suspensions, unlike spreading examined in chapter 3, presents a more complex behaviour. While their spreading behaviour can be captured by a Newtonian model by implementing a characteristic viscosity for a given impact, this is not true for their splashing behaviour. Low concentrations

behave similarly to equivalent Newtonian fluids but as the concentration of GO increases there is a growing inhibition of splashing, resulting in higher critical splash velocities than predicted by Newtonian models.

When compared to a set of Newtonian samples at a similar range of viscosities, complete suppression of splash within the experimental parameters here occurs after higher threshold impact velocities, or higher We , than are achieved in the Newtonian samples. This is illustrated by comparison of the two horizontal dashed lines that indicate that maximum v_{sp} for each dataset in figure 4.10c. The GO samples also continue to splash at a characteristic viscosity, μ_{HB} , where the Newtonian W-E-G samples do not at an equivalent viscosity, μ .

The model presented by Almohammadi *et al.* successfully captures the suppression of splashing observed experimentally for Newtonian W-E-G mixtures. This is not the case for samples of GO in 50%v/v ethanol-water when using a characteristic viscosity for concentrations above 3g/l.

Chapter 5

Pinch-off of Fluid Filaments in Magnetic Fields

5.1 Introduction

When a droplet falls from an orifice, as the droplet first begins to move away under gravity, a column-like neck is formed between the orifice and drop. The neck thins to a fluid filament of some minimum diameter at which it breaks, and the droplet detaches, as shown in figure 5.1. This process involves a balance between inertial and surface tension forces, causing the droplet to move and the neck to thin. This process is an integral part of DoD inkjet printing, and understanding and controlling this aspect of jetting would provide another method of tuning printing systems.

MagrowTec, a company that has developed crop irrigation equipment, has implemented magnetic fields in their technology that has been shown to reduce drift of sprays by up to 70% and influence droplet adhesion [97]. The suppression of smaller droplets in the sprays would reduce drift, with a change in surface tension of the sprayed water a likely culprit of this effect, as the drop volume median diameter in a spray is related to the surface tension by $D_{50} \propto \sigma^{1/3}$, as shown by Kooij *et al.* in

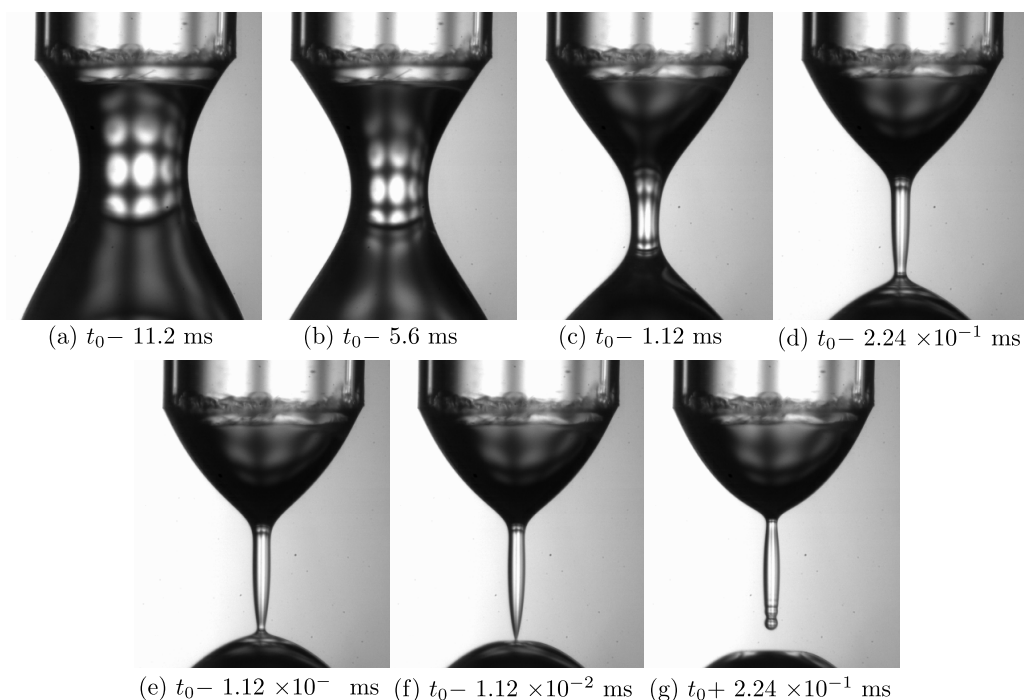


Figure 5.1: (a)-(f): Image sequence of water filament pinch-off from a 3.02 mm OD quartz tube, under no magnetic field, with time to pinch-off shown. Circular pattern seen at larger filament diameters is a reflection of the LED backlight array.

2018 [12]. If magnetic fields have an influence on surface tension, this would provide a useful method of tuning jetting in inkjet printing.

In this chapter, an investigation of the effect of magnetic fields on the pinch-off of Newtonian liquid drops in air is reviewed (see [98] for published text). Section 5.2 outlines current theory surrounding the pinch-off process and magnetic field effects on water. The experimental method for the investigation is outlined in section 5.3, and the results are presented and discussed in section 5.4.

5.2 Theory

5.2.1 Pinch-off of Fluid Filaments

Self-similar behaviour is exhibited in the fluid filament formed during the pinch-off process [99] and the thinning close to pinch-off does not depend on the initial conditions of the experiment, but is universal [100]. For inviscid liquids, potential

flow theory describes the thinning dynamics [101], and Keller (1983) [99] developed a universal scaling law that governs the thinning of the fluid filament prior to breaking in the limit of low viscosity,

$$D_{min} = A \left(\frac{\sigma}{\rho} \right)^{1/3} \tau_c^{2/3}, \quad (5.1)$$

where D_{min} is the minimum diameter of the filament, and ρ and σ are the density and surface tension of the fluid respectively, with A a dimensionless prefactor (see appendix F.1 for derivation). τ_c is the characteristic time scale, given by $(t_0 - t)$, the time to drop detachment, which occurs at $t = t_0$. This expression is independent of gravity as the typical length scale in the necking process is much smaller than the capillary length, $\kappa^{-1} = \sqrt{\frac{\sigma}{\rho g}}$, a measure of the length scale below which gravity is negligible compared to surface tension forces, 2.72 mm for water.

This scaling law was predicted to hold for minimum filament radius values, R_{min} , much higher than the viscous length scale $l_v = \frac{\mu^2}{\sigma \rho}$, where μ is the dynamic viscosity [102]. As the filament thins past this point ($l_v = 14$ nm for water), the dynamics transitions to the inertial-viscous regime in which viscosity contributes [103]. There is considerable variation in the literature on values obtained for the universal prefactor in equation 5.1, of the range 0.2-1.46 from both numerical and experimental studies [101, 104–107].

Hauner (2017) [108], showed that by measuring D_{min} close to pinch-off, a dynamic surface tension can be inferred using equation 5.1 for low viscosity liquids. Dynamic surface tension is a term most used in the context of surfactant solutions. When a new surfactant interface is formed, its initial surface tension value will decrease as surfactant molecules are transported to the interface until the equilibrium surface tension is reached [109]. In the pinch-off of a pure liquid, the dynamic surface tension inferred is the value at an interface that is in the process of forming -

the fluid filament - which happens on a millisecond timescale. For pure liquids, no discrepancy between the static and dynamic surface tension is expected. However, Hauner's results [108] suggested a higher dynamic value for water, ~ 90 mN/m compared to the static value of 72.8 mN/m, calculated using a prefactor of 0.9, which they determined experimentally by fitting equation 5.1 to data for several liquids using the prefactor as a fit parameter. They hypothesised that the dielectric relaxation, typically at a scale of $\sim$ ps, may be longer at the surface, with the time scale of relaxation during pinch-off of an order of ~ 1 ms.

It has since been shown that the prefactor in equation 5.1, assumed to be constant for all liquids, varies due to the influence of viscosity for minimum filament radii $R_{min} \gg l_v$ [110]. While the model may not be used to quantitatively infer an absolute value for the dynamic surface tension of the pinch-off system without further work, this study seeks to investigate any *relative differences* in surface tension for pinch-off in the presence of a magnetic field by examining the minimum filament diameter as a function of characteristic time, τ_c .

5.2.2 Magnetic Field Effects on the Surface Tension of Water

Studies on the effect of magnetic fields on water have shown varying results, with inconsistent effects often reported across the literature. Much experimental work has considered the effect of fields on evaporation in which there is a stronger consensus that evaporation is increased for magnetized water, although no mechanism has been universally accepted to explain the phenomena [111–113]. More recently, it has been proposed that it is the ratio of ortho and para isomers present above the evaporating liquid that are modified by a magnetic field, resulting in this observed difference [114].

There is particular ambiguity regarding the effect magnetic fields have on the

surface tension of water. Water presents a high equilibrium surface tension value of 72.8 mN/m at 20°C as a result of its polar nature and the presence of hydrogen bonds. Electrical field effects have been documented and resulting phenomena are reasonably well understood, for example the case of the Taylor cone [115].

Numerous studies have examined the static surface tension of water, a diamagnetic fluid, after magnetic treatment, and while some displayed a decrease in surface tension of 3% in a 0.5-0.65 T field [113], other experiments resulted in an increase in surface tension, with an increase of 1.8% reported by Fujimara *et al.* in a 10T field [116] and an increase of 4.5% reported in a 0.045-0.065 T field by Toledo *et al.* [117]. Other studies, namely that of Otsuka *et al.* reported no affect at all [118] for pure water with field strengths ranging upwards of 2 T. A 2019 paper from Hayakawa *et.al* [119], examined static surface tension in the presence of a magnetic field using the pendant drop method for moderate field strengths (up to 140 mT). They showed that any small apparent change in surface tension in a non-uniform field is due to body forces deforming the droplet shape which is not accounted for in the shape analysis of the droplet on which this measurement technique relies. These forces are the Maxwell stress and forces due to the field gradient.

While the previous studies in the literature deal with magnetic field effects on the static surface tension of water, our study is the first to examine the effect on the dynamic surface tension, which we carry out by investigating pinch-off behaviour in magnetic fields.

5.3 Experimental Methods

High-speed videos of the pinch-off of the fluid filaments were obtained using a Phantom v2010 camera with a Navitar 12x microscope lens, see figure 5.2 for the experimental set up. Videos were captured at 89,000 fps, with an exposure time of 10 μ s. Fluid was delivered to a nozzle using a syringe pump at a constant rate of 100 μ l/min

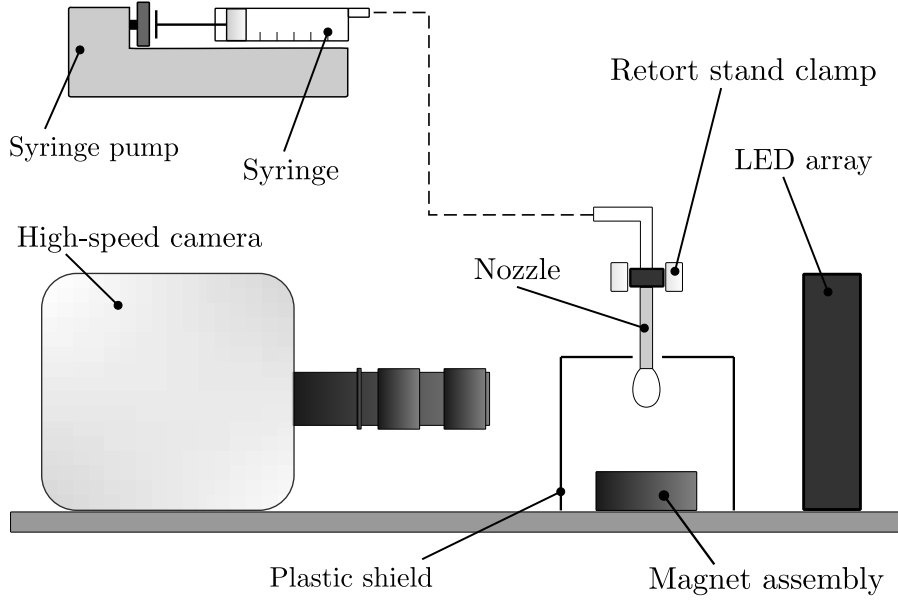


Figure 5.2: Experimental set up for the imaging of droplet pinch-off.

to form a pendant droplet on the nozzle tip. Additional fluid was then incrementally added to the pendant drop until the droplet reached a critical volume and continued to deform in the absence of flow. This allowed the droplets to detach under their own weight. Two nozzles were used in this investigation, a 0.91 mm outer diameter (OD) stainless steel dosing needle and a 3.02 mm OD quartz glass tube. The nozzles had inner diameters of 1.52 and 1.72 mm respectively. Typical drop diameters for each needle were ~ 4 mm and ~ 6 mm. Two different nozzles were used to negate any possible magnetic effects from the steel nozzle, as the quartz tube is completely non-magnetic. The resolution of the pinch-off videos were 3 and 12 μm for the steel and quartz needle respectively. The difference is due to lower magnification necessary in order to scale the videos with the larger needle size.

Measurements were taken in the absence of a magnetic field, and with four varying field configurations, shown in figure 5.3. An array of five 1 cm cube neodymium magnets was used in fields 1 and 2, as shown in figure 5.4a, which produces a field directed perpendicularly away from the centre of the array. The array is 3 cm in diameter. The array has a field strength of 0.8 T at the surface of the centre of the

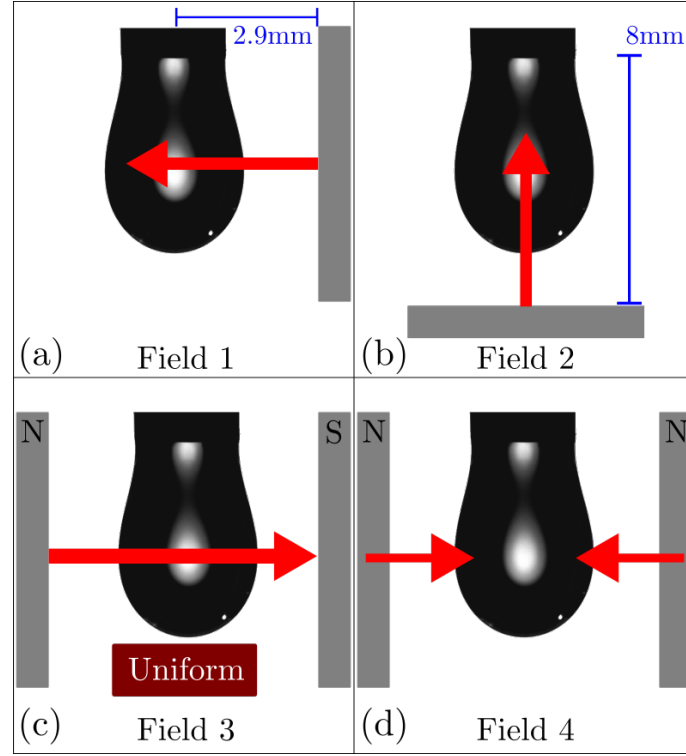
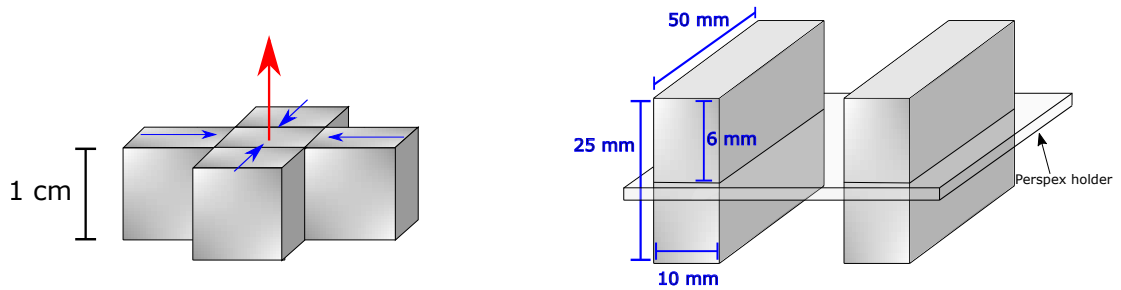


Figure 5.3: Field directions used in the experiment. Field direction 1 is shown in (a), where the centre of the 3 cm magnet array was vertically aligned with the centre of a stable pendant drop on the nozzle, (b) shows field direction 2, in which the centre of the nozzle was aligned over the centre of the magnet array. Field directions 3 and 4 are shown in (c) and (d) respectively. The end of the nozzle was aligned with the top of the magnets in these fields, with the centre of the nozzle positioned at the centre point between the two magnets. The field shown in (c) is the only uniform field.



(a) Magnet configuration fields 1 and 2. (b) Magnet configuration fields 3 and 4.

Figure 5.4: (a) Magnet configuration for fields 3 and 4, two identical parallel magnets in a perspex holder. The nozzle was aligned with centre of the mid line between the two magnets. (b) Magnet configuration for fields 1 and 2, five identical 1 cm cube magnets arranged to form a vertical gradient field from the centre of the array.

array, 419.5 mT 3 mm away from the array centre, and 162.3 mT 8 mm away. These distances, shown in figure 5.3, were the minimum magnet to nozzle distance possible without the droplet making contact with the magnet before pinch-off. Fields 3 and 4 were produced by two parallel identical neodymium magnets in a 3D printed perspex holder, see figure 5.4b. For field 3, the field strength at the nozzle tip aligned with the top of the magnets is 137 mT. The field strength at the nozzle tip for field 4 is approximately 0.3 mT. All field strengths were measured using a gauss meter. These fields were selected so that effects of a variety of gradient fields could be compared, with a strong field gradient produced with the 5-magnet array in fields 1 and 2, a weaker gradient field in 4 and a uniform field in 3. A clear plastic shield was placed around the nozzle and magnets for each measurement to shield the droplets from any draft which improves reproducibility significantly, as shown in figure 5.6.

Table 5.1: Magnetic susceptibilities of samples

	Water	0.11M DyCl ₃
Magnetic susceptibility	-9×10^{-6}	51.8×10^{-6}

The obtained videos were converted to images and the minimum diameter of the fluid filament was measured using a custom MATLAB script. Two different fluids were examined using this process – millipore water and 0.11M DyCl₃. Water is a diamagnetic fluid, and as such paramagnetic DyCl₃ was chosen to compare and contrast results. The magnetic susceptibilities are given in table 5.1. Images obtained for field direction 1 displayed tilt in the fluid filament due to the magnetic field for both fluids, which can be seen in figure 5.5. This was compensated for in the MATLAB routine by rotating the images so the filament was vertical for measurement.

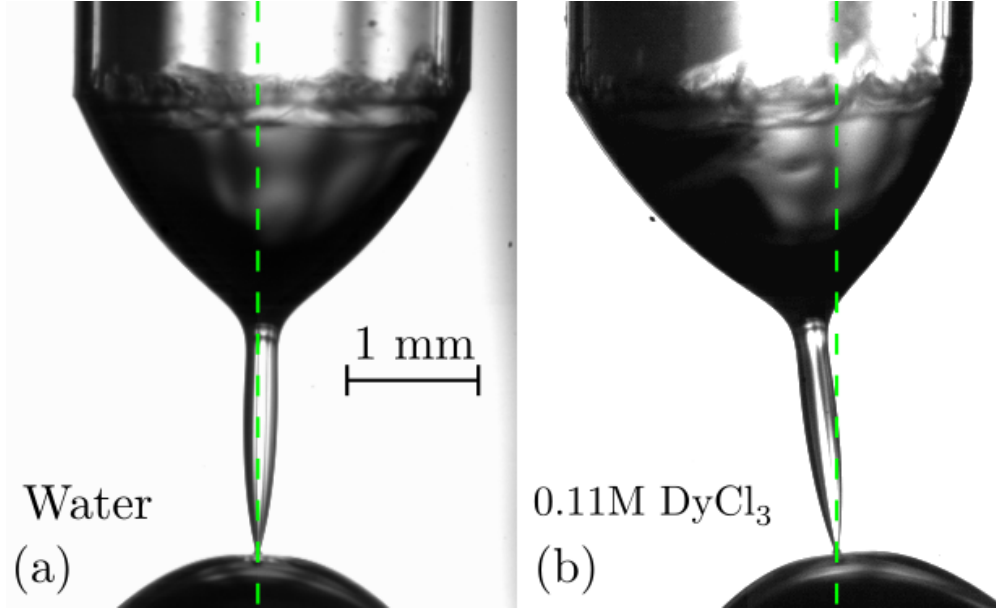


Figure 5.5: Fluid filament for (a) water and (b) 0.11M DyCl₃ at 45 μ s to pinch-off, 3.02 mm OD quartz nozzle, field direction 1. The magnet lies to the right of the filament in each image. Vertical line through the filament tip shown in green.

5.4 Results

5.4.1 Dynamic Surface Tension

To analyse the filament diameter data, t_0 was found for each of the 10 filaments measured per field. This is done by plotting $\log_{10} D_{min}$ as a function of $\log_{10} \tau_c$ for different values of t_0 , in the range where the data is linear i.e. obeys the scaling law for $\tau_c < 0.4$ ms. Equation 5.1 with a fixed slope of $2/3$ is fit to this data, and the value of t_0 that gives the best agreement with the fit is selected, illustrated in figure 5.6c for a single fluid filament of water in no field. $D_{min}^{2/3}$ can then then plotted against τ_c calculated using the determined t_0 for all 10 filaments, and the slope of a linear fit can be used to calculate the dynamic surface tension, using a rearrangement of equation 5.1,

$$\text{slope} = A^{3/2} (\sigma_{DST} / \rho)^{1/2}, \quad (5.2)$$

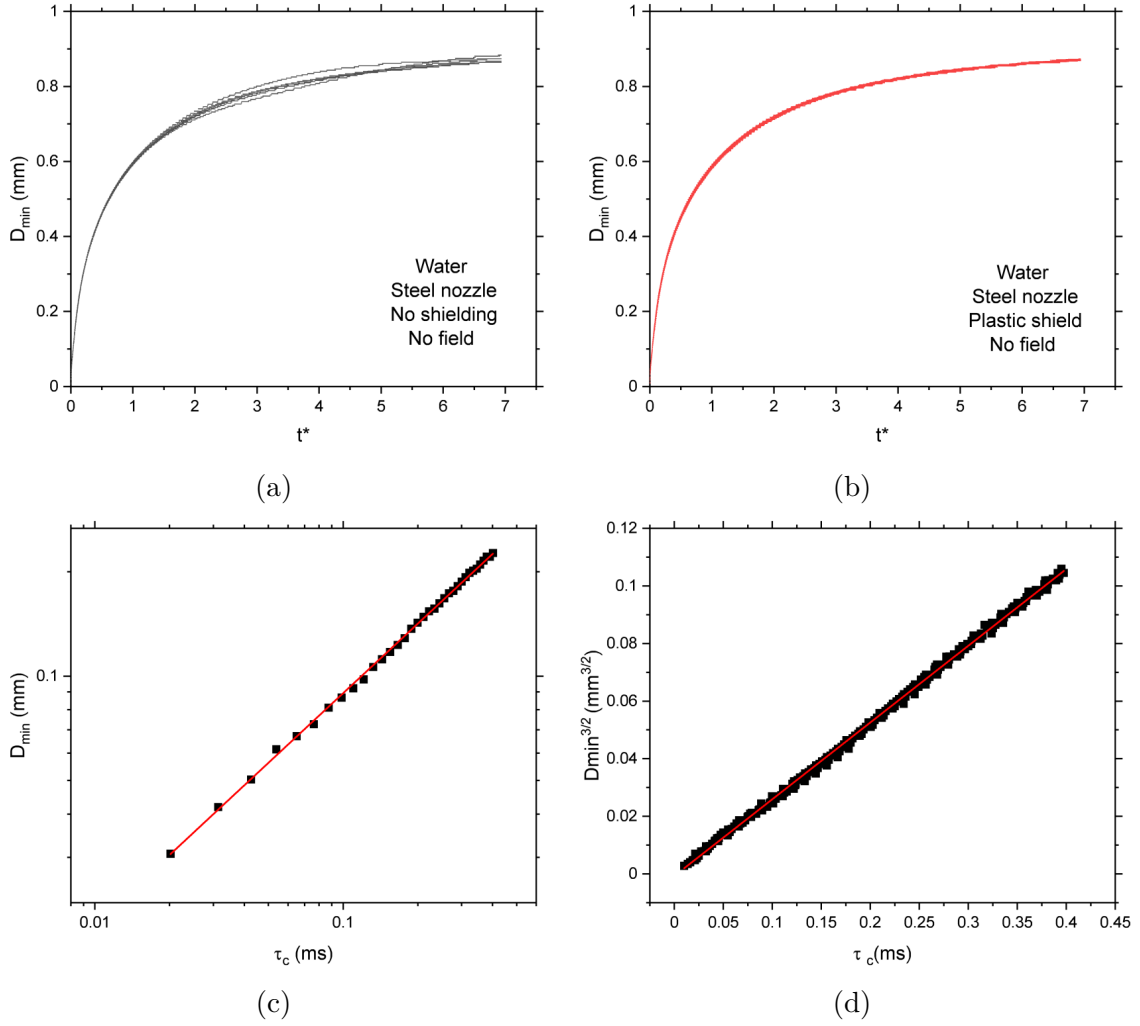


Figure 5.6: D_{min} as a function of t^* for water with a 0.91 mm OD steel nozzle (a) without plastic shield, and (b) with a plastic shield. (c) Log-log fit of equation 5.1 for a single fluid filament to find t_0 , and (d) linear fit over 10 droplets to determine dynamic surface tension using equation 5.1 for water with 0.91 mm OD nozzle, no field. (a), (b) and (d) contain datasets for 10 repeated measurements overplotted.

where σ_{DST} is the apparent dynamic surface tension, given the density of the fluid and some prefactor value A , which we know from Deblais *et al.* is not constant. As such, we are interested in the relative changes of the pinch-off dynamics in the presence of magnetic fields, rather than the calculated dynamic surface tension values. This plot is shown in figure 5.6d, and, assuming a constant prefactor of $A = 0.9$ as determined by Hauner [108], a dynamic surface tension of 97.3 ± 0.03 mN/m was obtained for water in no field. To compare measurements for different fields, the D_{min} data for the 10 droplets per field was averaged using built in statistical

analysis in Origin.

Figures 5.6a and 5.6b show the change in minimum filament radius D_{min} with the dimensionless time t^* , given by $t^* = \frac{\tau_c}{t_c}$, with $t_c = \sqrt{\frac{\rho D_0^3}{\sigma}}$ the capillary time, D_0 the nozzle OD and σ the static surface tension. They compare measurements taken in two different experimental set ups - one with a plastic shield surrounding the magnet and nozzle, 5.6b, and one without, 5.6a. A much wider spread of data can be seen in 5.6a, where no shield is used, while noise is reduced by shielding the droplet from any ambient airflow, improving the reproducibility of the experiment.

Figure 5.7a shows no variation in D_{min} for water in the different field configurations with the 0.91 mm OD nozzle for both length scales displayed in the figure. The data plotted for each field represents the average of 10 individual measurements. The plotted data for each field all lies upon the same curve, indicating that there is no change in the dynamic surface tension of water in these different fields. Figure 5.8a shows similar results for water with the 3.02 mm OD quartz nozzle, the small deviation for field 4 seen at small D_{min} lies within the error (shaded regions, standard deviation of averaged data, ranging from 3×10^{-4} to 2×10^{-3} mm). Once again, this plot shows that there is no variation in dynamic surface tension under the influence of magnetic fields. In figure 5.9a, again we see no significant difference between field and no field data across all magnet configurations, this time for 0.11 M DyCl_3 , using the quartz nozzle.

5.4.2 Prefactor Variation

Analysis was also carried out to investigate how the prefactor, A , changes over time, as shown by Deblais *et al.* (2018) [110]. The prefactor was calculated by restating equation 5.1 in terms of the dimensionless time t^* , to obtain $(D_{min}/D_0)^{3/2} = A^{3/2}t^*$. This equation allows for the instantaneous calculation of the prefactor over the range of measured filament diameters, using the literature values of static surface tension

($\sigma = 72$ mN/m) and density ($\rho = 997$ kg/m³) to calculate t^* . The results of the calculations are plotted in figures 5.7-5.9, subfigures (c) and (d) for water and 0.11 M DyCl₃ using both nozzles. Calculated prefactors over time for each individual filament are shown in (c) of each figure, with simulations from Deblais *et al.* over-plotted for reference. Note that these simulations are for different nozzle OD than investigated here and are therefore not expected to agree with our results but provide a qualitative comparison. Prefactor values for 10 different filament measurements are included for each field. Part (d) of each figure shows an average prefactor value over these 10 filaments per field over time, with the standard deviation indicated by the shaded regions. The spread in data points close to pinch-off seen in all plots is due to the increased error in D_{min} measurements for small diameters as detected diameters reach the resolution limit of 3 and 12 μ m for the steel and quartz nozzles respectively.

In figure 5.7b and 5.7c, we can see the instantaneous prefactor values for each field follow the same trend. The data follows a similar trend to that predicted by the simulations, showing that the prefactor is not in fact constant over the pinch-off process, however, for $t^* \gtrsim 0.1$ it is close to 0.9 as measured by Hauner et al. [108]. Figure 5.8b and 5.8c also display this fluctuating prefactor, with data agreeing across the different field configurations. The fluctuating prefactor is also seen in figure 5.9b and 5.9c for 0.11 M DyCl₃ using the quartz nozzle. Prefactor values for the different field configurations follows the same trends, with the exception of field 2, at times far from pinch-off. Here, we see the prefactor values lie below that of other fields, most apparent in 5.9c.

5.5 Discussion

Our plots for minimum filament diameter during the pinch-off process show no variation in pinch-off behaviour in the presence of any of our four magnetic field

configurations, which include both gradient and more uniform fields. Our data for water and 0.11 M DyCl_3 across both nozzles follow the same trend, indicating no change in dynamic surface tension in the presence of a magnetic field. The value obtained here for the dynamic surface tension of water under no magnetic field using the steel nozzle, while agreeing that the dynamic surface tension of water is higher than that of the static surface tension, is 8% higher than the value measured by Hauner *et al.* using the same prefactor value they found experimentally, 0.9. However, this calculation does not take into account that the prefactor in equation 5.1 used to calculate the dynamic surface tension from the filament thinning is not constant. Our measured instantaneous prefactor results across both fluids show similar variations in the prefactor as shown by Deblais *et al.* [110]. We do see a considerable spread in the prefactor data at times very close to pinch-off for measurements using the 3.02 mm quartz nozzle, compared to those for the 0.91 mm nozzle. This is due to the larger pixel size in these measurements, for both water and DyCl_3 , as lower magnification was necessary to fit the full fluid filament into the frame, along with a portion of the nozzle used to scale the data.

It is important to note that the known magnetic body forces acting on the droplet do not influence surface tension driven nature of the pinch-off process. In a gradient field, our fluid filament is acted upon by two forces, the magnetic gradient, $B\nabla B$, and the Maxwell stress,

$$\sigma_{Mij} = \frac{1}{\mu_0} B_i B_j - \frac{1}{2\mu_0} B^2 \delta_{ij}, \quad (5.3)$$

where μ_0 is the magnetic susceptibility of the fluid, B is the magnetic field, and δ_{ij} is the Kronecker's delta. These forces act as body forces on the filament modifying the effective force of gravity on the filament. Pinch-off dynamics are not affected by gravity, as is evident by the lack of a gravity term in the scaling law, equation 5.1. This is because pinch-off occurs at filament diameters far below the capillary

length, 2.72 mm for water. A small percentage change in the effective gravitational force due to the presence of magnetic body forces would only change the capillary number by a small amount, and so one would expect to see no effect of these body forces during pinch-off. The effective gravity, g_{eff} can be calculated from the angle of filament tilt shown in figure 5.5, for field 2. If we consider the angle of the DyCl_3 filament, 8° , a larger tilt angle than we see for water ($\sim 1^\circ$) due to its higher magnetic susceptibility, we obtain a 1% change in g_{eff} , resulting in a new capillary length of 2.71 mm for this field. This is small enough a change that pinch-off remains unaffected by body forces due to the field, even in the case of a gradient field, such as field 2.

One does, however, see some small deviation in prefactor variation in field 2 for the DyCl_3 filament at times far from pinch-off, seen in figure 5.9c. The scaling law does not apply in this regime and body forces can no longer be neglected, resulting in deviations from the thinning dynamics in no field. This effect is not seen for measurements with water in field 2, as the change in the effective gravity due to the additional body forces due to the field is negligible due to the low magnetic susceptibility of water.

5.6 Conclusions

The results we obtained in studying the pinch-off behaviour of both water and DyCl_3 clearly show that magnetic fields, both gradient and more uniform, have no effect on dynamic surface tension up to a field strength of 0.5 T. The known magnetic body forces do not affect the surface tension driven nature of the pinch-off, so any differences that would occur would not be due to a change in surface tension, but due to the body forces.

While we have shown that the pinch-off process can not be modified with a magnetic field, it remains crucial to jetting. As such it is important to investigate

how this process is affected by the addition of 2D nanoparticles, which is addressed in the next chapter.

Water, steel nozzle, 0.91 mm OD

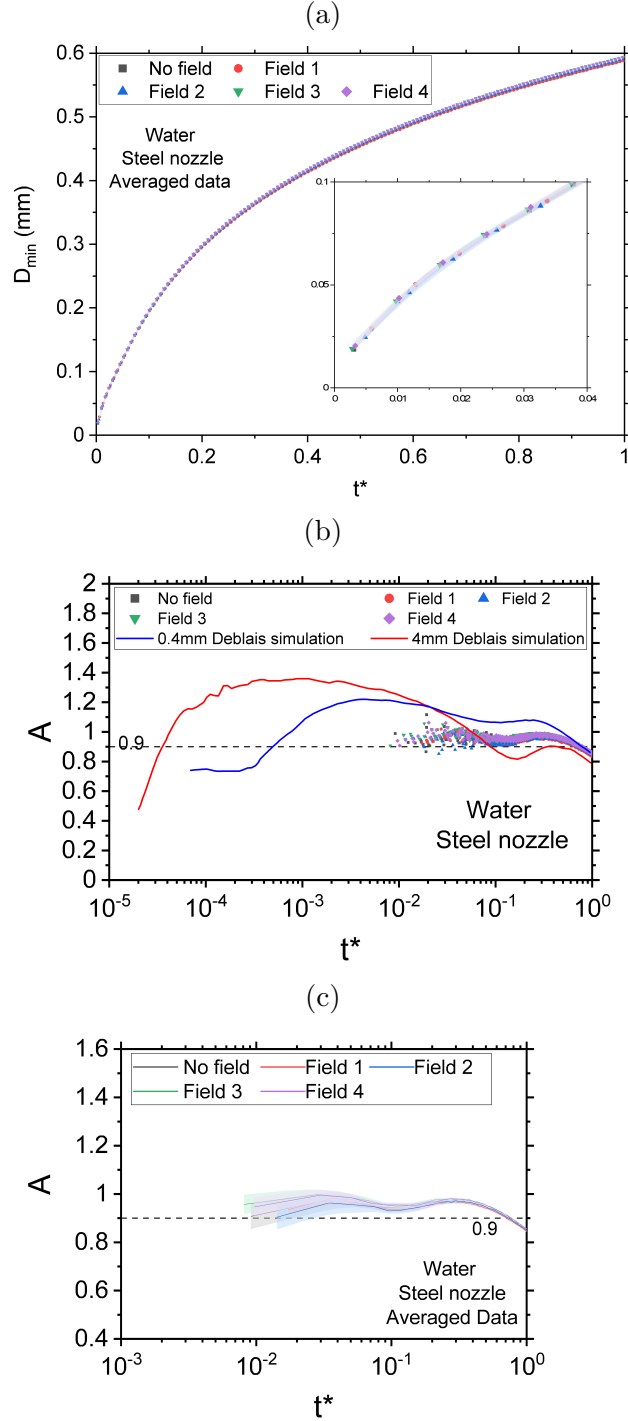


Figure 5.7: Pinch-off results for water using a 0.91 mm OD steel nozzle. (a) Averaged data for of D_{min} as a function of dimensionless time t^* , data close to pinch-off in inset. The shaded region denotes the standard deviation. (b) Calculated prefactor as a function of dimensionless time t^* for full dataset and (c) calculated prefactor as a function of dimensionless time t^* for averaged data. The horizontal dashed line in (b) and (c) indicates the prefactor proposed by Hauner *et al.*, $A = 0.9$.

Water, quartz nozzle, 3.02 mm OD

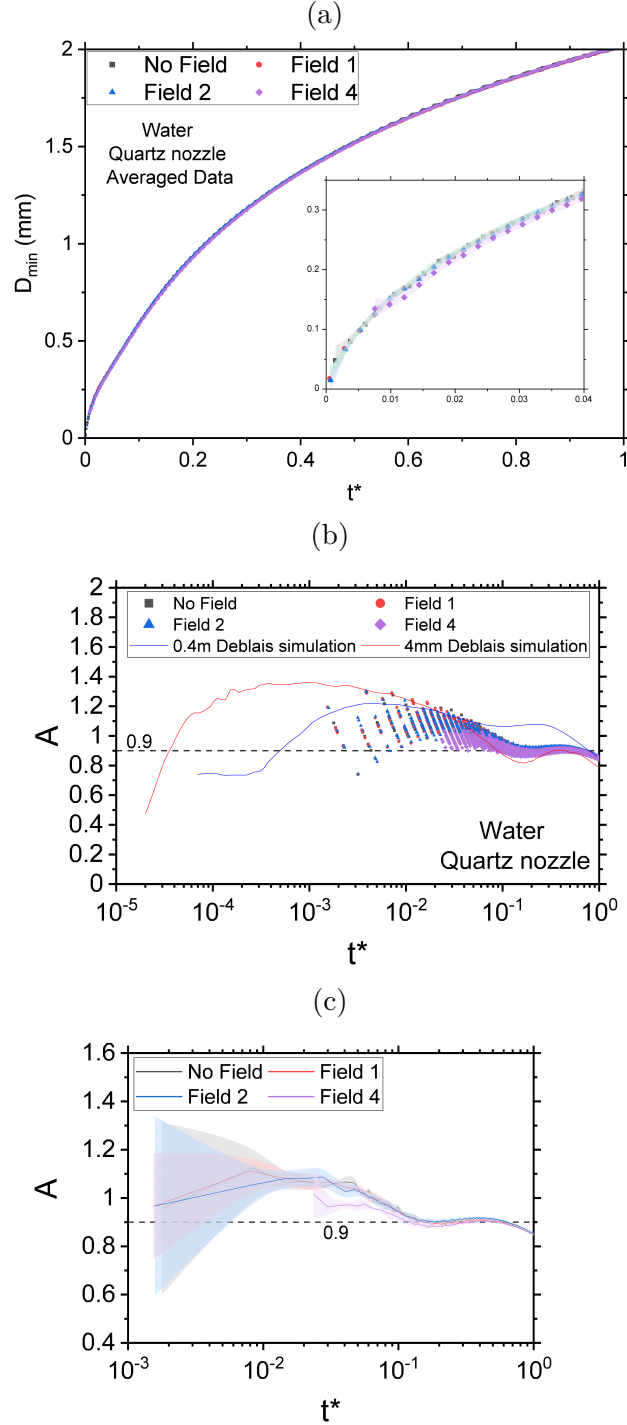


Figure 5.8: Pinch-off results for water using a 3.02 mm OD quartz nozzle. (a) Averaged data for of D_{min} as a function of dimensionless time t^* , data close to pinch-off in inset. The shaded region denotes the standard deviation. (b) Calculated prefactor as a function of dimensionless time t^* for full dataset and (c) calculated prefactor as a function of dimensionless time t^* for averaged data. The horizontal dashed line in (b) and (c) indicates the prefactor proposed by Hauner *et al.*, $A = 0.9$.

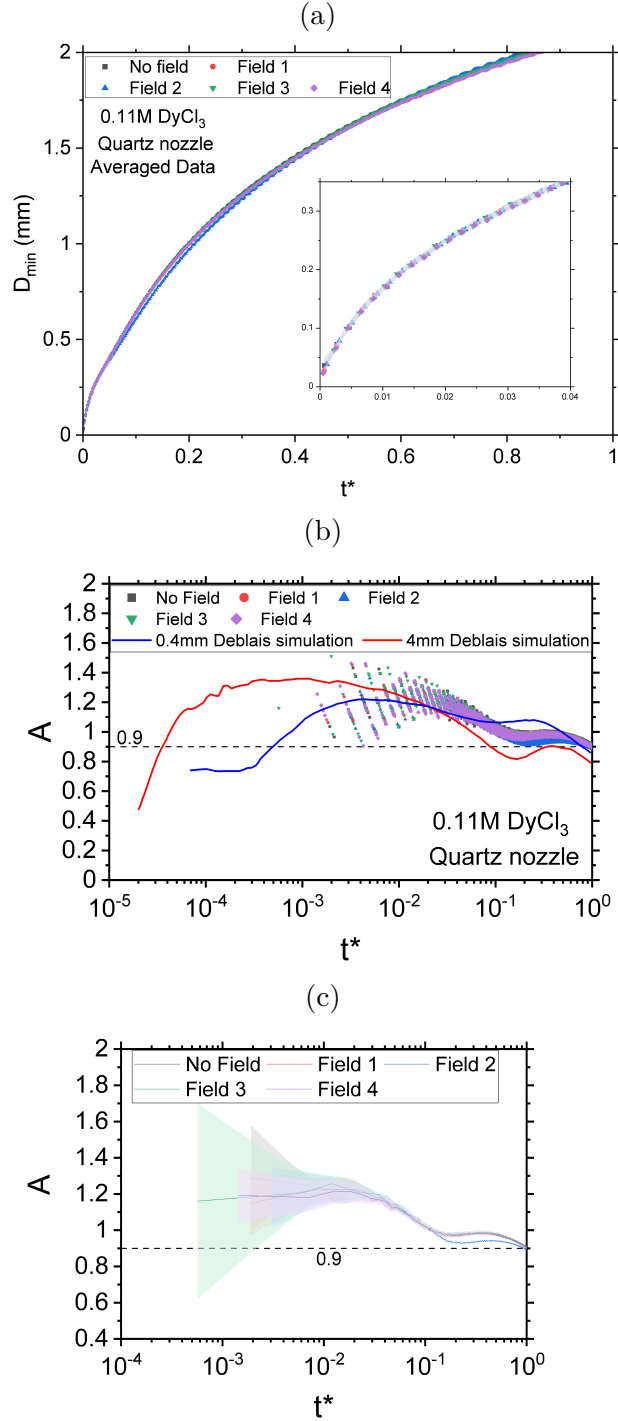
DyCl₃, quartz nozzle, 3.02 mm OD

Figure 5.9: Pinch-off results for DyCl₃ using a 3.02 mm OD quartz nozzle. (a) Averaged data for $D_{\min}$ as a function of dimensionless time t^* , data close to pinch-off in inset. The shaded region denotes the standard deviation. (b) Calculated prefactor as a function of dimensionless time t^* for full dataset and (c) calculated prefactor as a function of dimensionless time t^* for averaged data. The horizontal dashed line in (b) and (c) indicates the prefactor proposed by Hauner *et al.*, $A = 0.9$.

Chapter 6

Pinch-off of Aqueous GO Suspensions

6.1 Introduction

As we have shown in previous chapters, the addition of nanoparticles to a fluid can have a profound influence on the dynamics - or not, as we saw in the case of droplet spreading. Building on the work detailed in the previous chapter, we expand our investigation on droplet detachment to include non-Newtonian fluids in order to assess their effect on this process. How do non-Newtonian fluids pinch off?

Many studies have been carried out with an aim to answering this question, and in some cases, no variation from Newtonian dynamics is observed [120]. A 2013 study by Aytouna *et al.* showed this to be true for yield stress emulsions of castor oil in water and shear-thinning solutions of xanthan in glycerol-water. Some yield stress fluids have shown to obey a power-law thinning behaviour, in which $\frac{D_{\min}}{D_0} \propto \tau_c^{n_{PO}}$ with n_{PO} ranging from 0.32 to 0.92 [121]. Power law fluids such as Carbopol solutions and even mayonnaise have also been show to obey this scaling [122]. Interestingly, the power law scaling exponent for these samples agreed well

with with power law exponent, n , where $\tau_c \propto \dot{\gamma}^n$ determined from the shear rheology, and has been shown to be the case for a wide range of different complex fluids [123].

In this chapter, we examine the pinch-off behaviour of non-Newtonian GO suspensions in 50%v/v ethanol-water mixtures with time resolution that far exceeds that achieved previously in the literature [18, 124]. We reveal a regime close to pinch-off in which the rate of pinch-off is retarded, which becomes more pronounced with increased particle loading. We also explore the affect of aggregates during pinch-off, and show similarities in the dynamics for this system and that of a non-Brownian spherical particle laden fluid.

6.2 Experimental Methods

An identical experimental setup to that described in section 5.3 was utilized to image the filament pinch-off of suspensions of varying GO concentration. Samples of GO in 50%v/v ethanol-water were prepared using the method detailed in chapter 2. Additionally, measurements for each sample were repeated after sonication was carried out using a Sonics Vibra-cell sonic tip, which has a maximum power output of 750W. An amplitude of 30% for a duration of 30 minutes and a pulse interval of 5 seconds on, 5 seconds off was used to ensure the samples were not overheated. Samples were also submerged in a cold water bath during sonication. High-speed videos of pinch-off were obtained at a frame rate of 89,000 fps with pixel sizes ranging from 6 to 24 μm . This high frame rate allows us to probe the dynamics in a region closer to pinch-off than previously achieved, however it restricts our analysis to smaller timescales due to the limitation of dataset size in the high-speed camera. As such, we do not consider filament dynamics at longer timescales ($\tau_c > 0.05\text{s}$).

A revised boundary detection algorithm was implemented for the image processing of the fluid filaments in this study. In the previous chapter, boundary detection of the free surface was carried out using a simple Moore-Neighbor tracing algo-

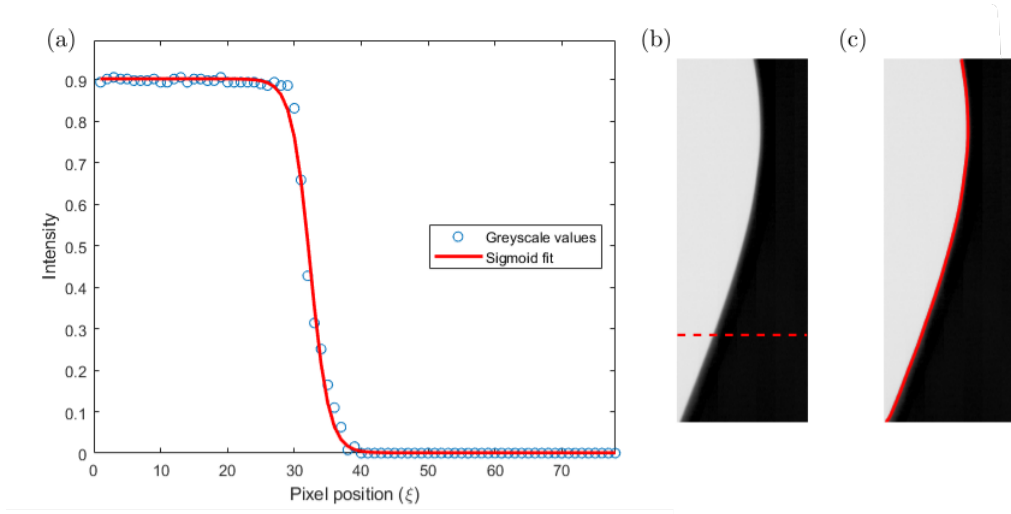


Figure 6.1: (a) Greyscale intensity as a function of pixel position (ξ) across left boundary of forming filament for a given pixel row, (b) source image with plotted pixel row indicated by red dashed line, (c) final detected boundary for left side of free surface.

rithm based function inbuilt in MATLAB which requires prior image thresholding to be implemented. In order to improve boundary detection and achieve sub-pixel resolution, a modified version of the method described by Vega *et al.* (2009) was introduced [125]. The grey intensity profile along the boundary of the free surface can be described by a sigmoid function, g , of the form

$$g(\xi) = \frac{g_1 - g_2}{1 + \exp[(\xi - \xi_0)/W]} + g_2 \quad (6.1)$$

where ξ is the pixel position and g_1 , g_2 , W and ξ_0 are fit parameters. An example of such a fit is shown in figure 6.1. g_1 and g_2 capture the plateau values either side of the boundary, W captures the edge width and ξ_0 is the midpoint of the profile which is extracted as the boundary location for a given row of pixels. Such fits were carried out using a least squares method for each pixel row using the pixel-resolution boundary position determined by Otsu's method as a starting value for ξ_0 , and constraining the fit to within two pixels of this point [126]. An example of the final boundary for the left side of the image can be seen in figure 6.1c.

6.3 Results

6.3.1 Filament Profiles

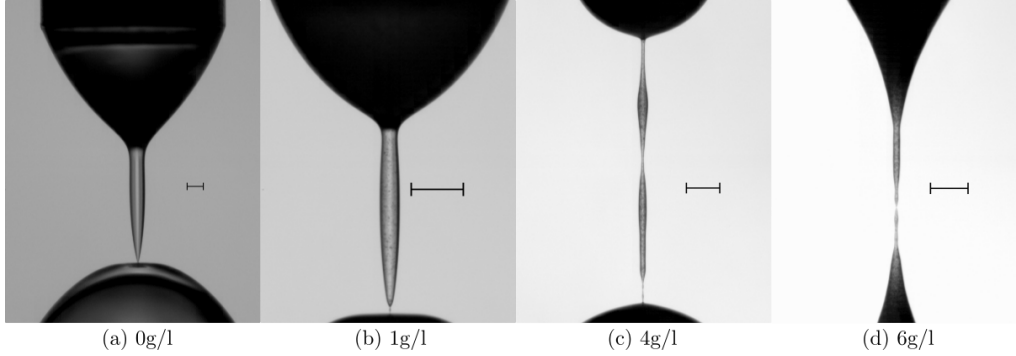


Figure 6.2: Final filament profiles before pinch-off for (a) 0g/l, (b) 1g/l, (c) 4g/l and (d) 6g/l GO in 50%v/v ethanol-water without prior sonication. The scale bar in each image represents 0.5 mm.

Figure 6.2 shows the profiles of a fluid filaments within 11 μ s of breaking for samples of increasing GO concentration from left to right prior to sonication. Qualitative analysis of the characteristic shapes of these profiles provides a useful insight into the underlying dynamics. As one would expect, the profile for our 0g/l concentration presents the classic shape that is seen for the pinch-off of an inviscid Newtonian fluid, seen in (a) [100, 127]. Here the filament tapers to a minimum diameter that is located at the top of the detaching drop. It has been noted at this point that an overturning of the free surface of the moving drop obscures the tip of the filament in the final moments prior to rupture [128].

When we introduce a low concentration of GO, such as the 1g/l sample in image (b), the profile shape remains for the most part unchanged, perhaps with the exception of a small "tail", a narrow section of filament between the top of the detaching drop and the rest of the conical filament. This "tail" is reminiscent of the filament seen in viscous Newtonian pinch-off, and is shown in more detail in figure 6.3 [129].

The filament shape, however, changes drastically at higher concentrations of GO. At 4g/l GO the previous characteristic inviscid Newtonian fluid shape is no

longer observed. Here, the diameter of the filament fluctuates down its length with two regions of notably larger diameter, which we describe as "bead-like". In this case, pinch-off occurs in the thin filament section closest to the detaching drop, but filament breakage occurs at different points along the fluid filament across repeated measurements, with a variety of fluctuating filament shapes observed. Rupture always occurs in a region where the filament diameter is at a local minima.

The filament profile at this concentration still consists of three distinct regions: The extended thinning neck, the detaching drop and remaining nozzle volume. When we move to a higher concentration, as seen at 6g/l in 6.2 (d), a further drastic change in filament profile is observed. These three regions are no longer distinct, and we see a more gradual transition from nozzle to minimum diameter point to drop with an over all thicker filament. This profile is strikingly different to that observed for the zero concentration sample in frame (a).

An important observation across these samples is the presence of agglomerates within the filament, which can be seen in all non-sonicated samples. An example of this can be seen in figure 6.3. We expect that the presence of agglomerates within the samples is a result of aging of the GO stock which is diluted to different concentrations as detailed in chapter 2. The same batch of stock was used for the experiments carried out in chapters 3 and 4 and the measurements carried out here, however while measurements for the previous chapters were carried out simultaneously, this study took place approximately 18 months subsequent. As discussed in chapter 2, aging does occur in these suspensions, although not appreciably over the course of measurement of a given sample.

Given a much larger effective particle size in our suspensions than expected for a suspension of mono-layer GO platelets, literature studies of spherical particle laden suspensions were examined to compare to the observed profiles presented here. Similarities can be drawn between the profiles presented by Furbank *et al.* (2004),

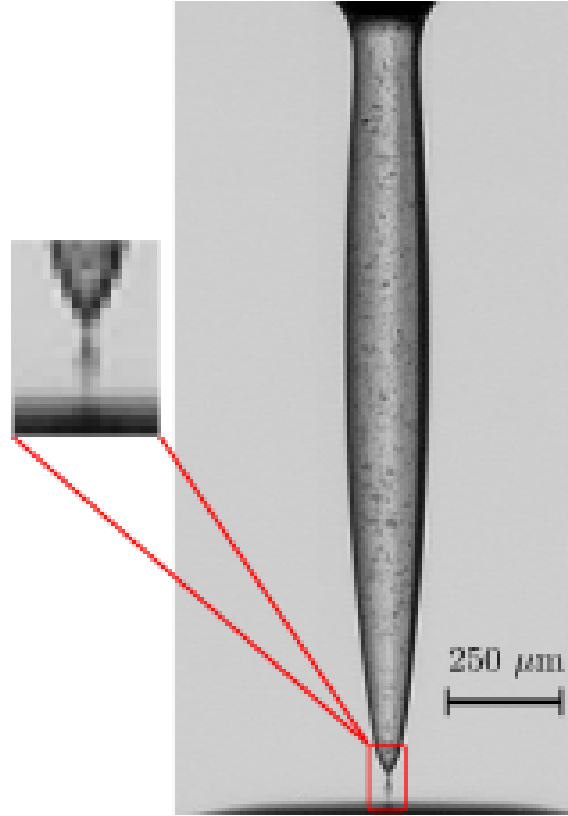


Figure 6.3: Filament of 1g/l GO in 50%v/v ethanol-water with no prior sonication.

displayed in figure 6.4 [130]. The evolution of pinch-off for a suspension of 212-250 μm PMMA in a 23%wt. ZnCl_2 /water solution and poly-alkylene glycol from their experiments of pinch-off in silicone oil shown in figure 6.4 highlights the influence of such particles in the final filament profile before rupture. A region of increased diameter can be observed in frame (d), where two particles are trapped in the filament as the filament approaches the particle size. The trapping of particles in the thinning filament restricts the contraction of the filament in the region surrounding the particles.

While the scale and geometry of the particles in the study by Furbank are still quite different to the agglomerated GO suspensions, we believe a similar process takes place. At sufficiently high GO concentration, such as the 4g/l sample in figure 6.2 (c), the presence of agglomerates in the thinning filament restricts the further reduction in diameter in localised regions resulting in a non-uniform filament profile.

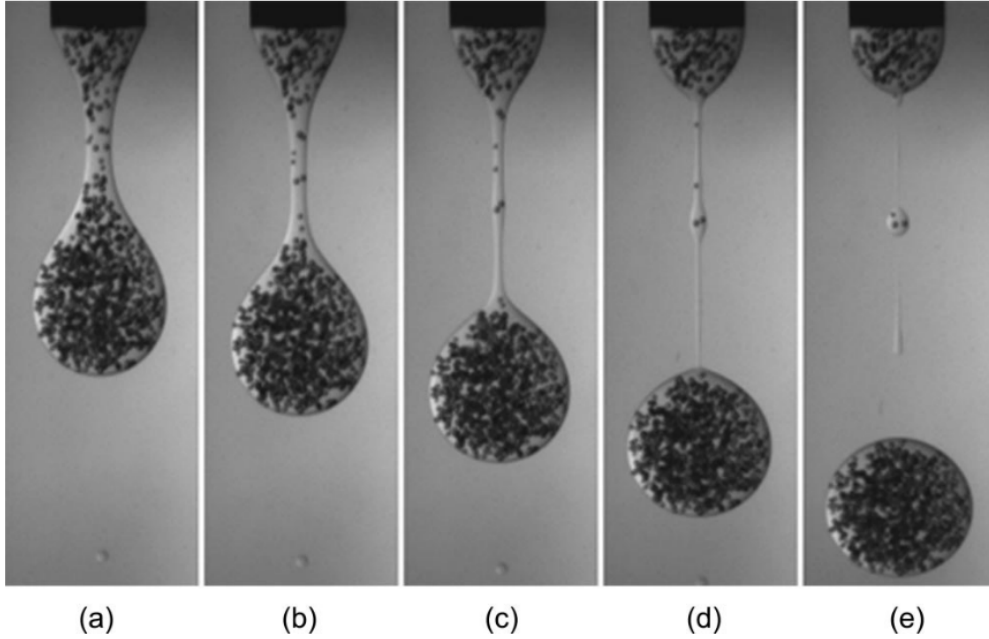


Figure 6.4: Evolution of a suspension thread up to and slightly beyond pinch-off for PMMA in 23%wt. ZnCl_2 /water solution and UCON 90,000, $\phi = 0.05$, $d = 0.32$ cm, $d_p = 212\text{--}250$ μm into silicone oil where the time between frames is $1/30$ s. Figure adapted from Furbank *et al.* (2004) [130].

In addition to this, Furbank reports that the shape of the filament and position of pinch-off varies considerably across repeated pinch-off events, dependant on the particle distribution in the filament. This variable profile was also seen in our 4g/l GO sample.

If it is the case that the two systems are analogous, one would expect a further increase in GO concentration to mirror the results for increased particle loading in the system examined by Furbank. Increasing the volume fraction from $\phi = 0.05$ in figure 6.4 to $\phi = 0.15$ shown in figure 6.5, they describe the filament shape as more "spindle-like". Particles are forced out of the forming filament as it thins into the orifice region and drop, producing the thicker, cone-shaped profile [130]. Comparing this profile with that shown in figure 6.2 (d) for 6g/l GO in 50%v/v ethanol-water, it is clear that a similar process is occurring, strengthening the argument that dynamics are similar in these two systems.

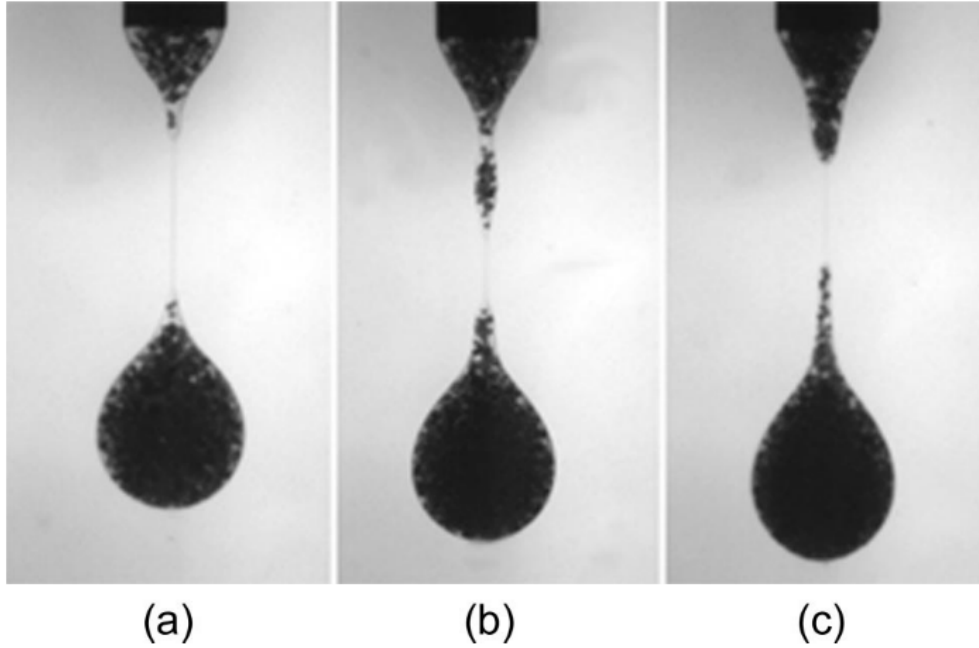


Figure 6.5: Representative pinch-off structures for the pendant drop formation of suspensions of (a) $\varphi = 0.15$, (b) 0.20 , and (c) 0.25 into ambient silicone oil for $d_0 = 0.32$ cm, $d_p = 212\text{--}250$ μm . Figure adapted from Furbank *et al.* (2004) [130].

Pinch-off of Sonicated GO Suspensions

While the flocculated samples proved an interesting system to examine, investigating samples that are relatively agglomerate-free such as those studied in previous chapters is where the goal of this project lies, as outlined in the introduction. To refresh the flocculated samples they were sonicated as described in section 6.2. This was carried out for only 30 minutes for each sample in order to break up agglomerates while not breaking down the individual flakes of GO.

Figure 6.6 shows a comparison of the filament evolution for a sample of 1g/l GO in 50%v/v ethanol-water (a) before and (b) after sonication. While there is for the most part no appreciable change in the profile shape after sonication, there are no longer visible agglomerates within the thinning filament. Only one minute difference in the profile shapes can be observed - the "tail" described in the final shape before pinch-off for this sample in the previous section no longer occurs after sonication.

A comparison of final fluid filament profiles for samples (a) before and (b) after

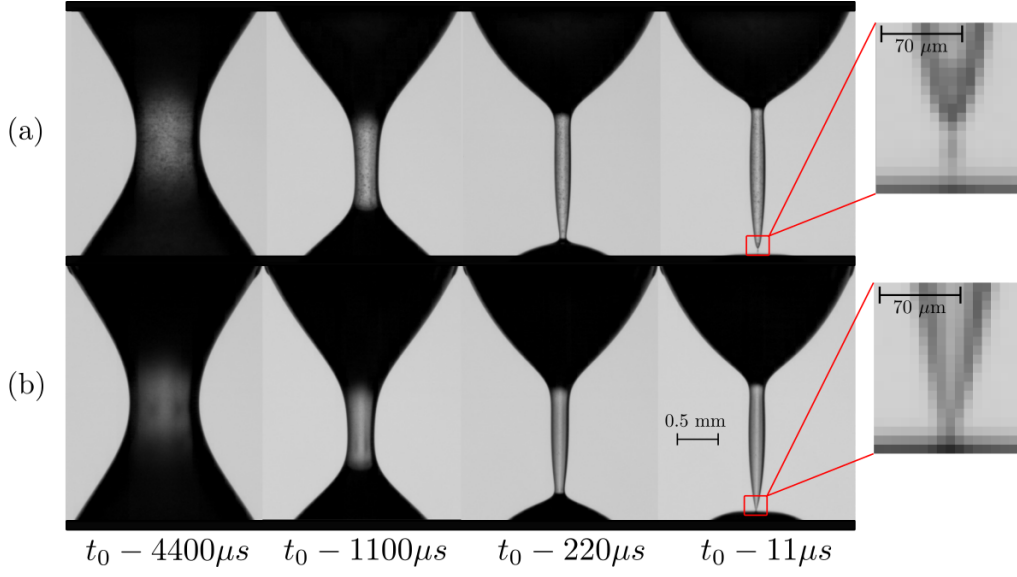


Figure 6.6: Thinning filaments of 1g/l GO samples at different times to pinch-off, t_0 , (a) before and (b) after sonication.

sonication is shown in figure 6.7. It is important to note that in each case sonication was carried out on the remaining sample volume after all measurements without sonication had been carried out, which is to say in each case it is the very same sample for a given concentration. At concentrations below 4g/l there is little difference in profile between samples before and after sonication, with the profiles matching the expected shape for an inviscid Newtonian fluid as previously discussed. At 4g/l however there is a marked difference in the profiles before and after sonication. Before sonication, we see the transition to the non-uniform profile while after sonication a Newtonian-like profile is retained. At 5g/l the profile of the sonicated sample is still uniform, but also narrows where the filament attaches to the orifice fluid volume. This filament also tapers more quickly to a minimum at the bottom of the filament than the classic inviscid Newtonian

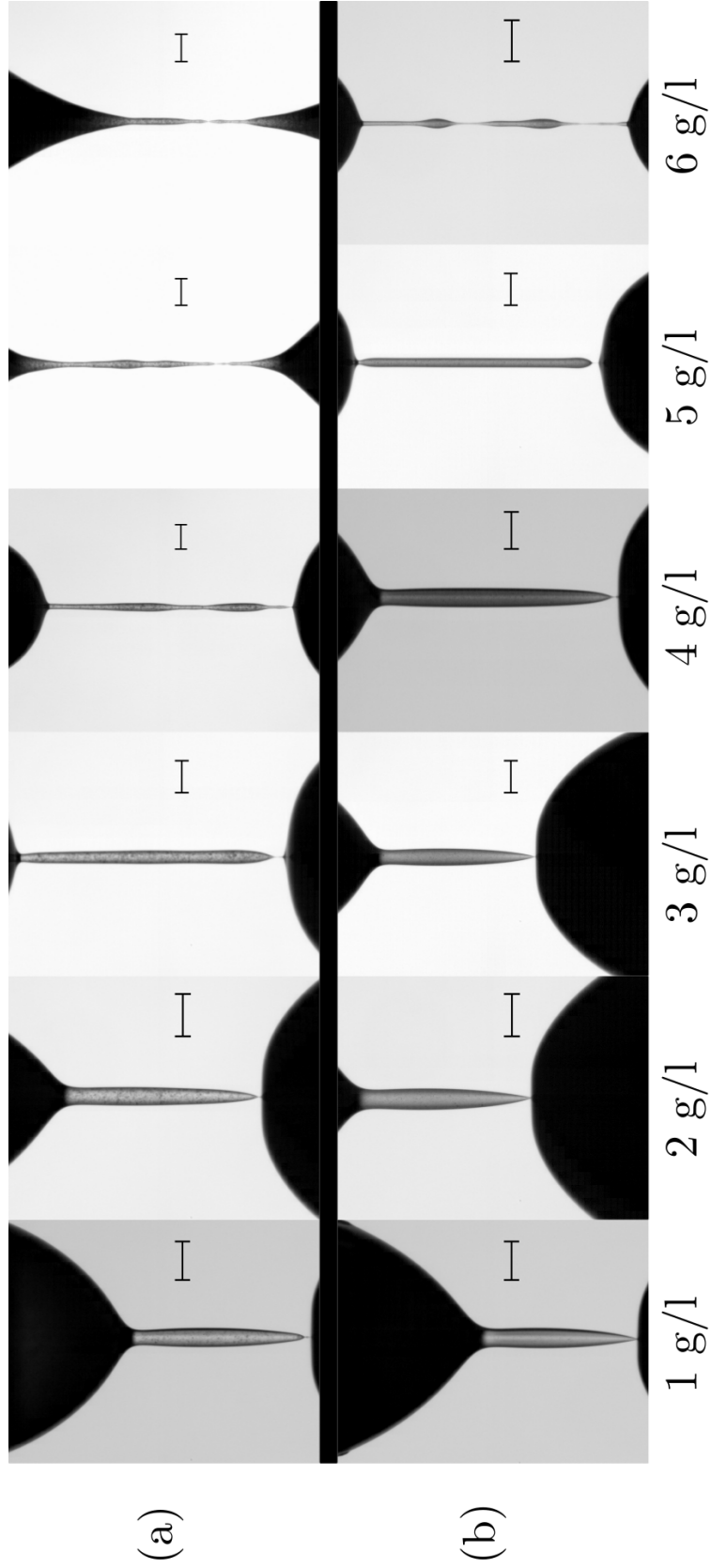


Figure 6.7: Final filament shape for samples of increasing GO concentration (a) before and (b) after sonication. Scale bar on each image represents 100 μm .

profile does. At 6g/l the sonicated samples show a non-uniform, bead-like profile similar to that observed for 4g/l before sonication. This shape is more pronounced in the 6g/l sonicated sample, however, with thinner filaments between each "bead".

6.3.2 Rheology & Characterisation of Samples

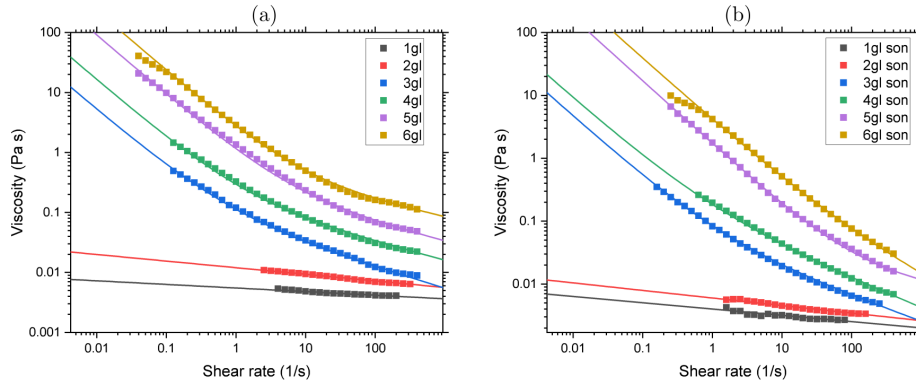


Figure 6.8: Viscosity curves for samples of varying GO concentration (a) before and (b) after sonication. The overplotted lines represent fits to the Herschel-Bulkley fluid model (equation 2.5), with the fit parameters given in table 6.1.

Table 6.1: Herschel-Bulkley parameters for samples of GO in 50%v/v ethanol-water, before and after sonication.

GO concentration (g/l)	Before Sonication			After Sonication		
	τ_0	m	n	τ_0	m	n
1	0	0.0055	0.94	0	0.004	0.9
2	0	0.012	0.89	0	0.006	0.88
3	0.050	0.063	0.645	0.045	0.04	0.6
4	0.160	0.135	0.69	0.085	0.10	0.54
5	0.900	0.2600	0.70	1.700	0.04	0.8
6	2.300	0.500	0.74	3.750	0.05	0.45

Given the difference in filament profiles for GO samples before and after sonication, we must examine if there are any differences in the underlying rheology of the samples. Figure 6.8 shows the viscosity curves for samples of GO in 50%v/v ethanol-water (a) before and (b) after sonication. The solid lines indicate Herschel-Bulkley fits to the data, with the parameters given in table 6.1. Viscosity is higher for the samples before sonication. This is made clearer in figure 6.9 (a), where the

viscosity at a fixed shear rate of 100s^{-1} is plotted for each concentration before and after sonication.

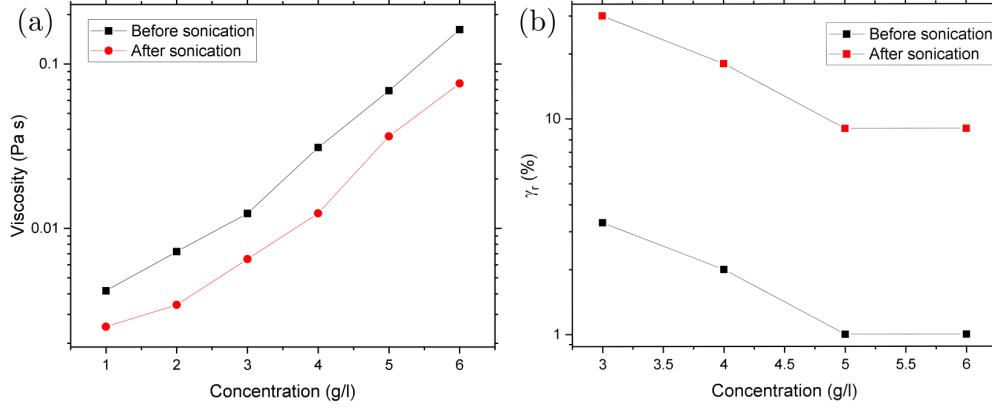


Figure 6.9: (a) Viscosity values of samples before and after sonication at a fixed shear rate of 100s^{-1} , extracted from figure 6.8. (b) Yield strain, γ_r as a function of concentration for GO samples before and after sonication.

Oscillatory Rheology

The yield strain, γ_r , was determined for samples before and after sonication from strain sweep measurements. An example of such a strain sweep is shown in the inset of figure 6.10, where the storage and loss moduli, G' and G'' , for a 6g/l GO sample are plotted as a function of strain. All strain sweeps were carried out at a frequency of 1Hz. A clear plateau can be seen in G' at low strain. We define γ_r here to be the point at which the plateau value, G_0' , begins to decrease. Figure 6.10 shows G' rescaled by G_0' as a function of the strain, γ rescaled by γ_r for different concentrations of GO before and after sonication. The sonicated samples have a sharper decrease in storage modulus after the sample begins to yield. Concentrations below 3g/l did not exhibit a storage modulus plateau in the strain sweep measurement, and as such are not shown.

γ_r is also plotted as a function of concentration for the higher concentration samples in figure 6.9b. After sonication, the yield strain value increases by a notable amount. A different gelation point for these samples is a contributing factor to this. Samples both before and after sonication exhibit a decrease in yield strain with

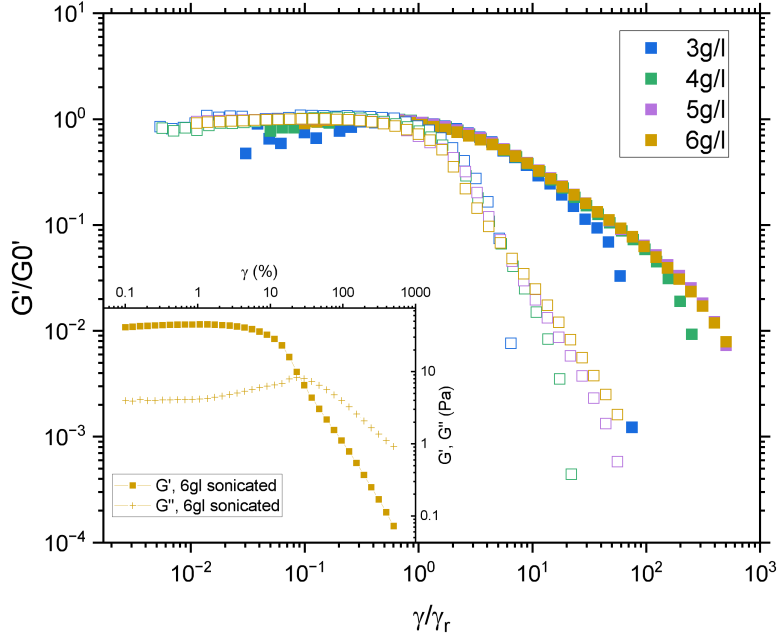


Figure 6.10: Storage modulus, G' , normalised by the plateau value, G'_0 , as a function of the strain amplitude, γ , rescaled by the yield strain, γ_r , at a frequency of 1Hz. Solid and open symbols represent samples before and after sonication respectively. Inset: strain sweep storage and loss moduli, G' and G'' , for 6g/l GO after sonication.

an increase in GO concentration. This is consistent with the study carried out by Barwich *et al.* (2022) on GO samples dispersed in water only [35].

Surface Tension

Surface tension measurements yielded a similar trend as that which was described in chapter 2, with little deviation between the values for samples before and after sonication, with the exception of a slight deviation between values for samples before and after sonication at 5 and 6g/l, shown in figure 6.11. This deviation, however, is not significant.

6.3.3 Thinning Dynamics

Figure 6.12 shows the rescaled minimum filament diameter evolution, D_{min}/D_0 , as a function of time to pinch-off τ_c for samples before sonication. Each concentration curve represents averaged experimental data across 3-6 repeated measurements. The

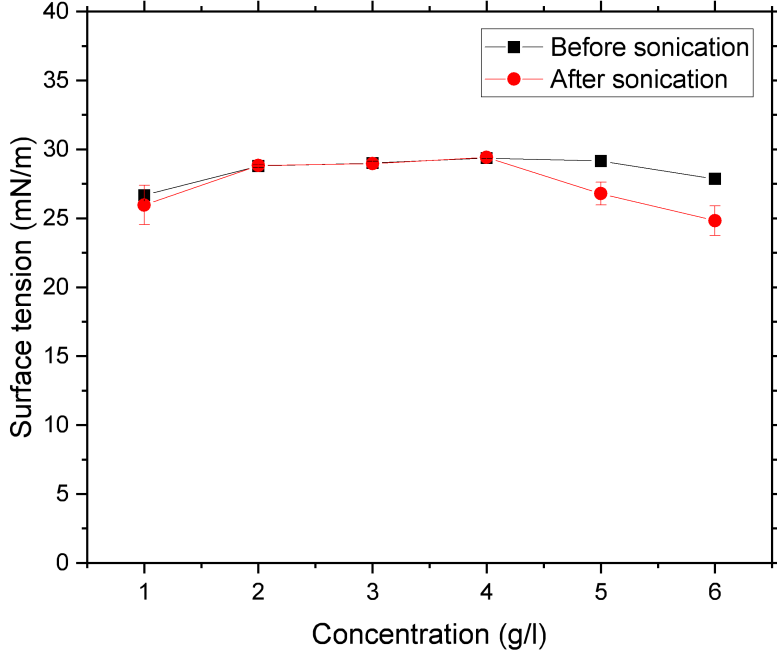


Figure 6.11: Surface tension *versus* concentration for samples of GO in 50%v/v ethanol-water before and after sonication.

zero concentration sample, simply 50%v/v ethanol-water fits the inviscid power law relation where $D_{min} \propto \tau_c^{2/3}$ [99]. At the lowest GO concentration, 1g/l, the thinning behaviour still follows this relation well. High concentration samples appear to follow a two stage thinning process. Further away from pinch-off, the thinning obeys the viscous power law scaling where

$$D_{min} \propto \tau_c. \quad (6.2)$$

This scaling was derived in a 1993 paper by Eggers, with the full form given by $D_{min} = 0.0304(\frac{\sigma}{\mu})\tau_c$ and is derived from the Navier stokes equations for an axisymmetric incompressible fluid (see appendix F.2 for details)[131].

Closer to pinch-off the behaviour shifts towards a different scaling of the form $D_{min} \propto \tau_c^{0.28 \pm 0.02}$. Intermediate concentrations gradually transition between the low and high concentration behaviours.

After sonication, low concentration samples follow the same thinning dynamics

as they did before sonication, as can be seen in figure 6.13. However, while samples began to transition from the inviscid scaling before sonication above a concentration of 1g/l, after sonication this transition does not occur until a concentration of 4g/l is exceeded. In addition to this, the high concentration samples transition to a different power law scaling close to pinch-off, of the form $D_{min} \propto \tau_c^{0.51 \pm 0.02}$

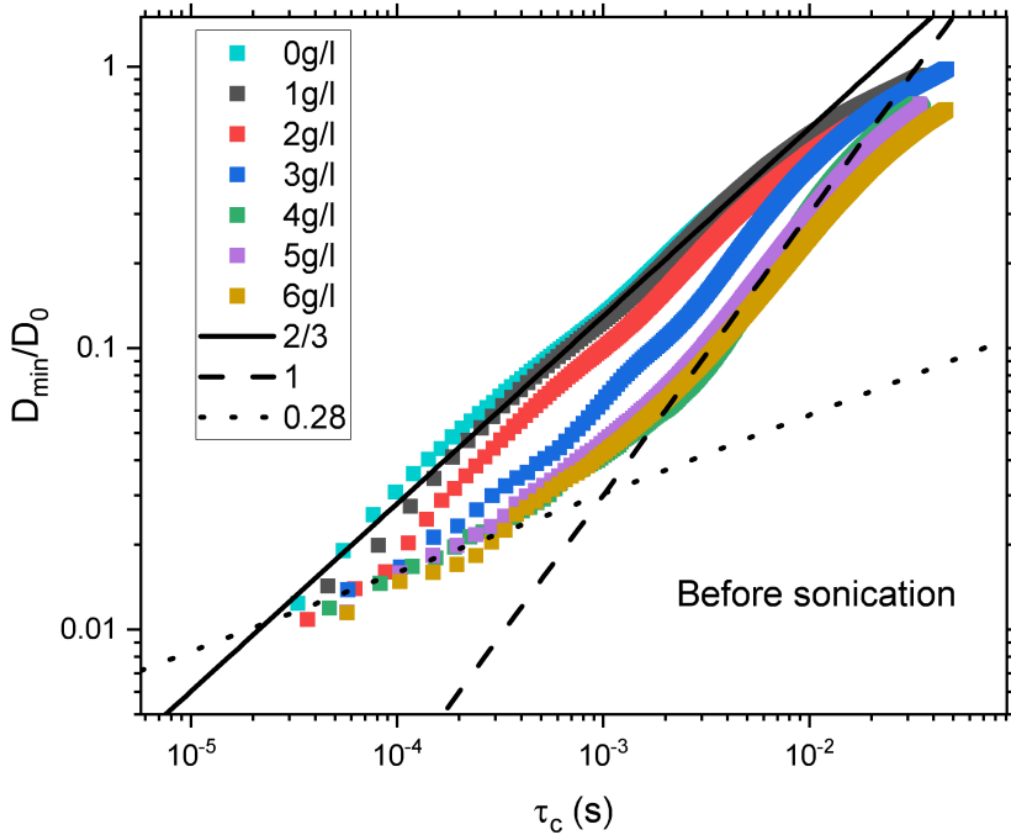


Figure 6.12: Rescaled filament diameter as a function of time to pinch-off for samples before sonication with increasing GO concentration in 50%v/v ethanol-water. The overplotted lines represent power law relations with varying exponent values given in the figure legend.

In both cases, before and after sonication, the final power law scaling, particularly for higher concentration samples, has a smaller exponent than both the viscous and inviscid Newtonian regimes. This means thinning is slowed close to pinch-off due to the addition of GO. Van Deen *et al.* (2013) showed that for suspensions of polystyrene spheres thinning is accelerated by the addition of particles in a small regime close to pinch-off in the case of small volume fractions ($\phi = 1 - 6\%$) [132].

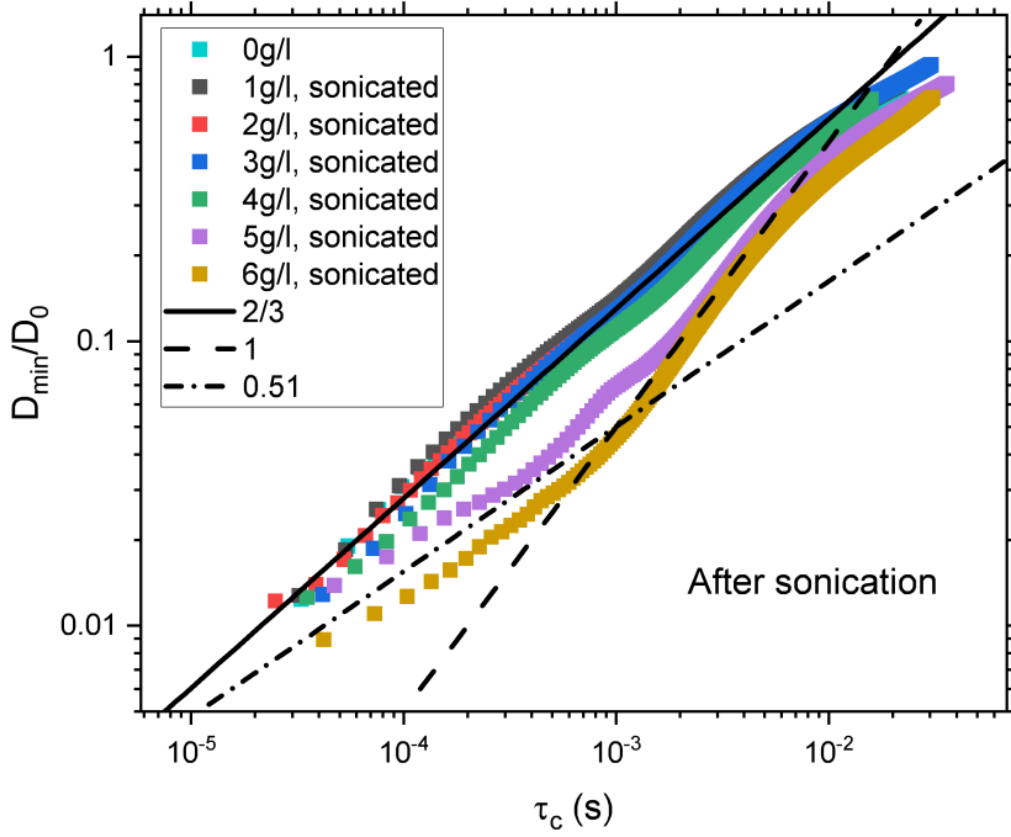


Figure 6.13: Rescaled filament diameter as a function of time to pinch-off for samples after sonication with increasing GO concentration in 50%v/v ethanol-water. The overplotted lines represent power law relations with varying exponent values given in the figure legend.

The spheres used ranged in diameter from 20-140 μm and were suspended in silicone oil. Due to the low volume fraction, the suspensions are effectively Newtonian with the viscosity given by the Einstein equation,

$$\mu = \mu_0 (1 + 2.5\phi), \quad (6.3)$$

for interstitial fluid μ_0 [133]. It is of note that these experiments were carried out with imaging frame rates of 4,000 fps, resulting in a much lower time resolution than those presented here.

The logarithmic derivative of the GO thinning data is shown in figure 6.14b and c. As the error in D_{min} is higher close to pinch-off which occurs on the leftmost side

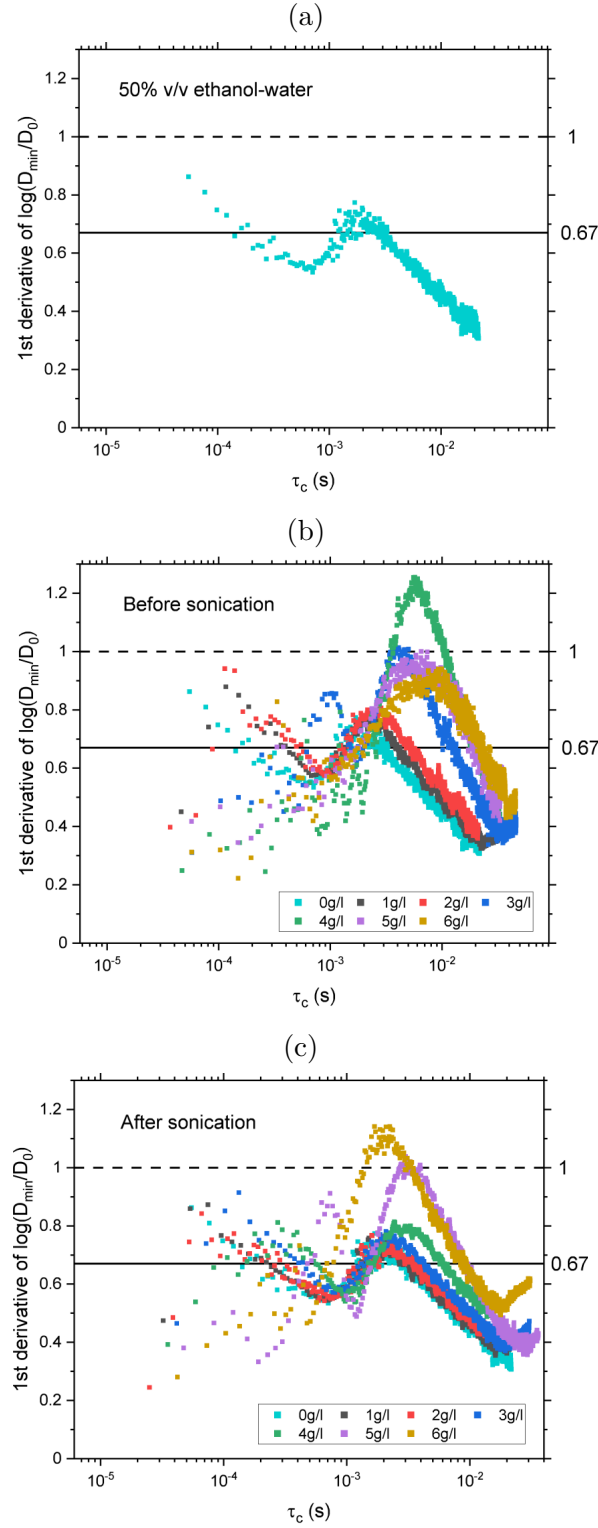


Figure 6.14: Logarithmic derivative of dimensionless minimum filament diameter, $D_{\min}/D_0$, for (a) 50 %v/v ethanol-water and GO samples (a) before and (b) after sonication.

of each plot, the derivatives become much noisier as this point is approached.

Figure 6.15 shows a comparison between the Newtonian experimental data collected here and the data for water and 0.11M DyCl₃ without a magnetic field from chapter 5. The minimum filament diameter, D_{min} is rescaled by $\left(\frac{\rho}{\sigma}\right)^{1/3}$ and plotted as a function of τ_c . Overplotting the scaling law for $A = 0.9$ shows that the scaling law represents the experimental results well at times close to pinch off, but all datasets lie slightly above the scaling law relation, suggesting a higher prefactor value would be more accurate.

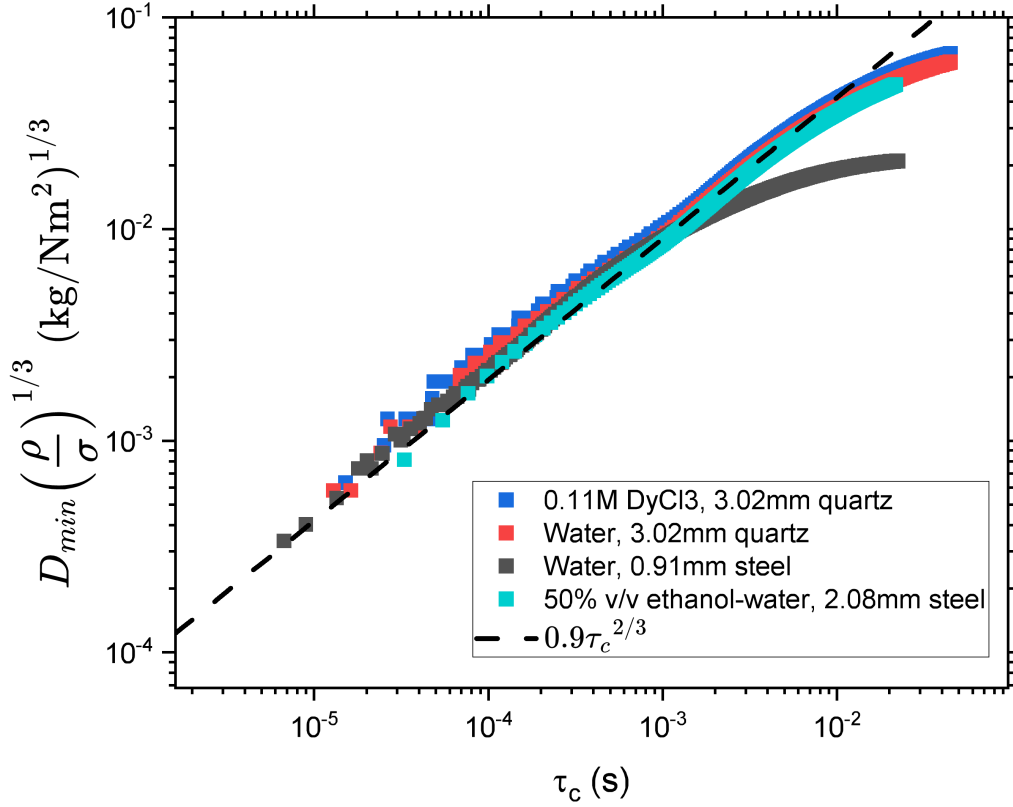


Figure 6.15: D_{min} rescaled by $\left(\frac{\rho}{\sigma}\right)^{1/3}$ for 50%v/v ethanol-water and water and 0.11M DyCl₃ with various nozzle diameters. Overplotted is the inviscid scaling law relation (equation 5.1) for $A=0.9$.

Figure 6.17 presents the GO thinning data in a manner similar to that in van Deen *et al.*. The data for each concentration is shifted by some value Δt such that it overlaps with the 0g/l data at some arbitrary value of D_{min}/D_0 , chosen here as

0.01. While Δt was added by van Deen in order to collapse the data at a given point here it must be subtracted in order for a collapse to be achieved. This figure demonstrates well the deceleration of filament thinning at higher concentrations of GO. Δt for each data set is shown in figure 6.18. In the case of van Deen's samples, a large Δt corresponds to a strong acceleration in thinning due to the presence of particles in the filament, but in our case it indicates a strong deceleration. We can also see that the thinning is more arrested in samples before sonication. The increase in Δt with increasing concentration indicates that it takes higher concentration GO samples longer to pinch-off compared to a 0g/l sample.

Governing equations were derived by Hameed and Morris in 2009 for a single particle trapped in a thinning jet [134]. They were derived from the Navier-Stokes equations for an axisymmetrical, incompressible, Newtonian fluid of high viscosity with a single solid spherical particle contained within. The equations for the axial velocity and interface at $z = h$ are given by

$$\begin{aligned} \frac{3}{2}Rw'' + \frac{R'}{2R} + 3R'w' - \frac{45\beta(z-h)^3R}{[R^2 + (z-h)^2]^{7/2}} + \frac{9\beta R(z-h)}{[R^2 + (z-h)^2]^{5/2}} + \frac{45\beta R^3(z-h)}{2[R^2 + (z-h)^2]^{7/2}} \\ - \frac{[90\beta R^2(z-h)^2 - 45\beta R^4]R'}{2[R^2 + (z-h)^2]^{7/2}} - \frac{[12\beta R^2 - 6\beta(z-h)^2]R'}{[R^2 + (z-h)^2]^{5/2}} = 0, \end{aligned} \quad (6.4)$$

and

$$\frac{\partial R}{\partial t} + \frac{R}{2}w' + w\frac{\partial R}{\partial z} = \beta \left[\frac{3R^3 - 6R(z-h)^2}{2[(z-h)^2 + R^2]^{5/2}} \right]. \quad (6.5)$$

These equations are solved by Hameed and Morris numerically using a finite difference scheme. $R(z, t)$ is the radius of the fluid neck, w is the component of velocity in the z direction and $\beta = \frac{5}{6}G(t)a^3$ for the strain rate $G(t) = -\frac{2}{R}\frac{\partial R}{\partial t}$ and particle size a . A prime denotes a derivative with respect to z .

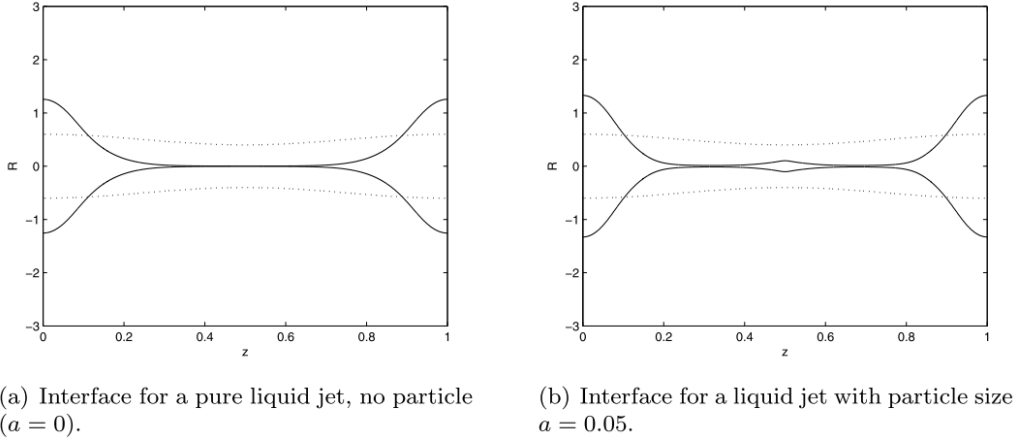


Figure 6.16: Jet evolution with centered particle for different particle sizes, adapted from Hameed & Morris (2009) [134].

The results from the numerical solution for two different particle sizes are shown in figure 6.16 for (a) $a = 0$ (no particle), and (b) $a = 0.05$. It is clear that the model predicts the characteristic bulging profile for a trapped particle. These governing equations also predict that the presence of a single particle should result in the deceleration of filament thinning contrary to the results of van Deen and in agreement with our data [135].

Another study on particle-laden pinch-off by Mathues *et al.* achieved a higher time resolution with frame rates of 9000 fps [136]. They detected a final regime in which thinning decelerates just before pinch-off not seen in previous studies [130, 132, 137, 138]. This deceleration was more pronounced for samples with larger particles. We saw the deceleration more pronounced in our samples before sonication. This would be consistent with the breaking up of flocculates during sonication. Determining the particle size distribution before and after sonication would help confirm this but was unfortunately outside of the scope of this study. They also found that an increase in volume fraction reduced the deceleration. They saw this across a range of volume fractions of $\phi = 2 - 25\%$, a significantly higher range than those explored in our GO samples here, which is equivalent to $\phi = 0.05 - 0.3\%$, however higher aspect ratio particles jam at lower volume fractions [139].

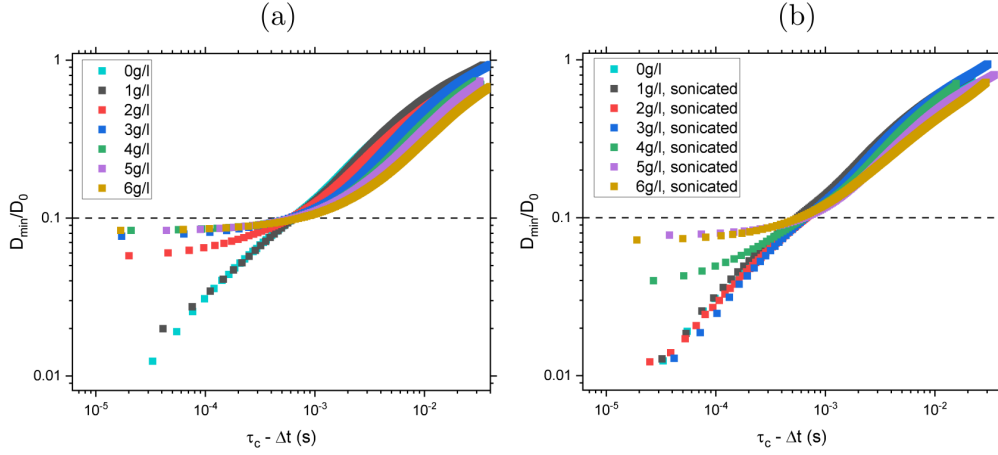


Figure 6.17: Shifted curves (a) before and (b) after sonication. Each curve is shifted by Δt in order to achieve a collapse of data at arbitrary value of $D_{min}/D_0 = 0.1$.

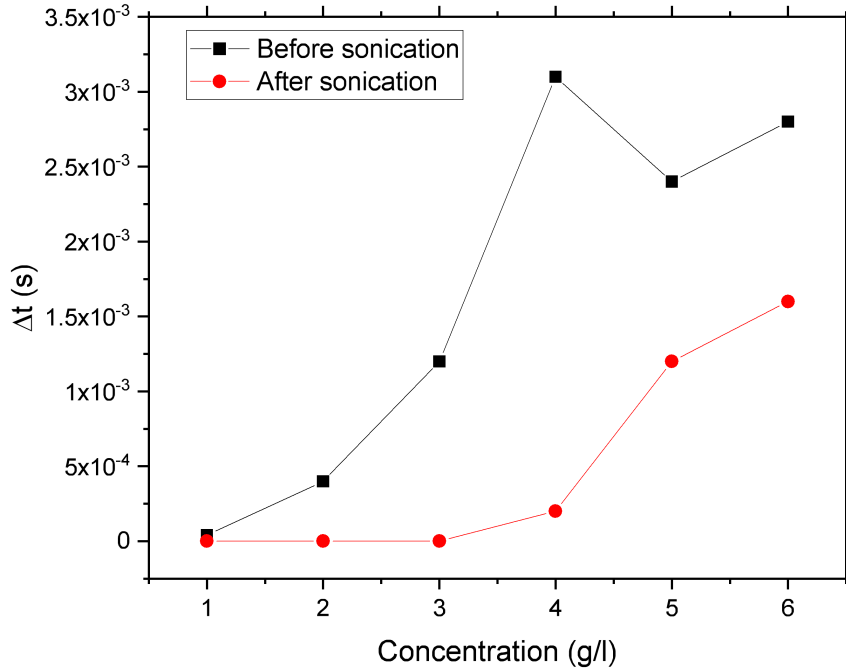


Figure 6.18: Δt shift factor as a function of concentration from figure 6.17.

It is also important to remember when making comparisons to the previously discussed literature on particle laden systems that both the geometry of the particles and the rheology of suspensions are significantly different to that of our GO suspensions - they are not non-Newtonian, at least at the volume fractions examined.

Filament thinning studies have been carried out on aqueous GO suspensions in papers by Corker *et al.* (2019) and Ng *et al.* (2020) [18, 124]. Both previous studies have been conducted using a CaBER (Capillary Break-up Extensional Rheometry) technique. Rather than examining the pinch-off of a detaching droplet from a nozzle, CaBER involves examining the liquid bridge that forms between two plates as they are separated. A critical difference between the aforementioned studies and the one presented here is that rather than following the evolution of the minimum filament diameter over time they examine thinning at the pinch-off point and at fixed positions along the filament. In their experiments, they do not observe the beaded filament structures reported here. This method, however, of imaging at fixed points allowed them to achieve a better spatial resolutions of 1.97 and 2 μm per pixel for Corker and Ng respectively, compared to our minimum of 6 μm per pixel.

At the lowest concentration of $\phi = 0.02$ observed by Corker and Ng, the suspensions follow the inviscid Newtonian scaling of $D \propto \tau_c^{2/3}$. Increasing concentration to $\phi = 0.05$, the viscous $D \propto \tau_c$ scaling is dominant. Further increase of GO concentration results in a transition to a power law thinning behaviour, where $D \propto \tau_c^{n_{PO}}$. Our suspensions differ in two key ways. Firstly, the mean lateral flake size for our samples is much smaller, 17 μm compared to 64 μm . Secondly, our suspensions are not dispersed solely in water, but in a 50%v/v mixture of ethanol and water, resulting in a significant difference in surface tension values. Because of this, it is not possible to directly compare similar sample concentrations between the Corker/Ng studies and the samples studied here.

The studies by Corker and Ng did not observe the deceleration of thinning close to pinch-off. It is likely this was not observed due to the significantly higher time resolution achieved here, 11.2 μs compared to 160 μs achieved by both Corker and Ng, which allowed us to probe times closest to pinch-off in more detail.

It is worthy of note that the final power-law scaling exponents do not correlate to

the Herschel-Bulkley exponents determined from the shear rheology. A 2012 study from Huisman *et al.* saw that this was the case for high-concentration bentonite suspensions in water which are extremely shear thinning, while low concentrations behaved like pure water [123]. Intermediate concentrations, however, exhibit more complex thinning dynamics, and the correlation no longer holds. The dynamics behind this is not well understood, and it is likely a similar process is occurring with our GO suspensions.

6.4 Conclusions

Significant changes in pinch-off profiles can be observed in suspensions of GO in 50%v/v ethanol-water as concentration is increased. This finding was facilitated by the implementation of a sub-pixel boundary detection algorithm, written in-house. Low concentration suspensions exhibit a characteristic inviscid Newtonian filament profile. Higher concentration samples develop a bead-like, heterogenous filament shape close to the detachment of the drop from the nozzle. We expect that this is due to the nanoparticles and any possible flocculates present in the sample becoming trapped in the filament, inhibiting the further thinning of the filament in localized regions.

For samples in which large aggregates of nanoparticles are present and can be observed under magnified imaging of the pinch-off filament, the onset of the heterogenous filament profile occurs at lower concentrations. In such samples, as the concentration exceeds this point, a further variation in pinching profile is observed that is more uniform and conical in shape. This is likely a result of a transition to jamming occurring as a larger number of particles and aggregates migrate from the thinning filament.

At times approaching pinch-off, low concentrations thin following the inviscid Newtonian scaling law (equation 5.1) while an increase in concentration results in a

transition to the viscous regime (equation 6.2). By achieving a time resolution that far exceeds that of pinch-off studies currently in the literature we observe a thinning regime not previously observed. In this regime, which occurs directly before pinch-off, the rate of thinning slows. This deceleration of thinning is more pronounced for higher concentration samples. A reduction in the size of flocculates in a sample reduces the degree of deceleration.

These results provide a new insight into the process of droplet detachment at times close to pinch-off. While the underlying mechanics are yet to be fully understood, further work may help to elucidate this matter.

Chapter 7

Conclusions & Outlook

7.1 Introduction

Exploring a range of dynamics in droplets of GO suspensions has not only enriched our understanding of fundamental processes but also holds profound implications for practical applications, particularly in the realm of inkjet printing with nanoparticle suspensions. In exploring the intricacies of these dynamic systems, we have navigated the complex interplay between various factors influencing droplet impact and jetting behavior, relevant not just to our specific system but to the dynamics of non-Newtonian fluids as a whole. As I conclude this thesis, it is imperative to reflect on the significant strides made and outline the path ahead.

In this chapter, we aim to consolidate the insights gained from our investigation and map out the direction for future research endeavors. The challenges encountered during this investigation serve as stepping stones toward a more comprehensive understanding of droplet dynamics of GO suspensions and those of other 2D nanoparticle suspensions. In acknowledging the limitations of our current study, we lay the groundwork for future researchers to build upon and refine our findings.

7.2 Spreading of Aqueous GO Suspensions

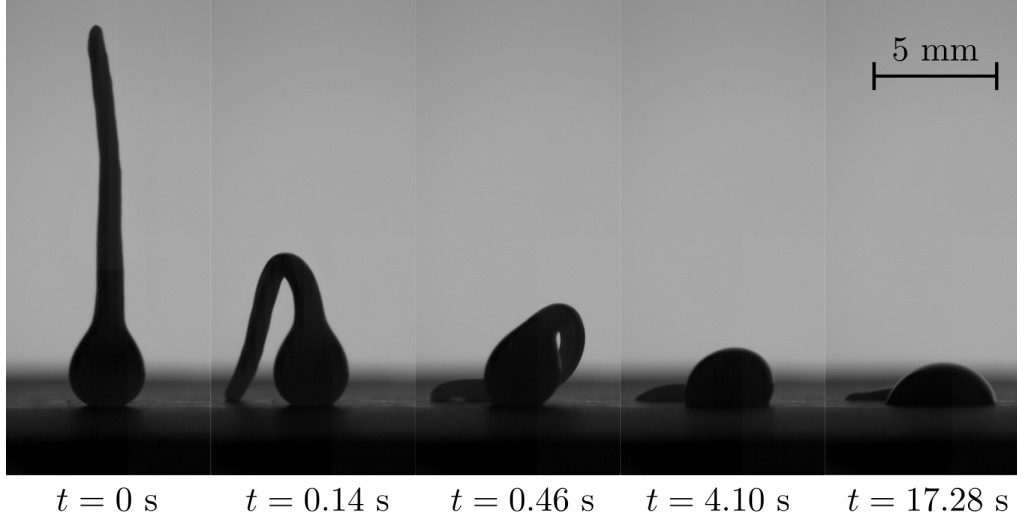


Figure 7.1: Impact morphology of a drop of 50% wt. suspension of cornstarch in a 85% wt. glycerol-water mixture on paper, $U_0 = 0.65$ m/s.

In chapter 3, we explored the effect of GO particle loading on the spreading dynamics of a 50%v/v ethanol-water mixture. Using a characteristic viscosity for given impact conditions and GO concentration, we were able to show that the spreading dynamics can be captured by a Newtonian spreading model derived by means of an energy balance. This new energy balance model has the advantage of having been successfully applied to a non-Newtonian fluid using a characteristic viscosity while also being analytically solvable for a constant viscosity fluid. Surprisingly, a single fit parameter value can capture the spreading behaviour over a wide range of impact velocities, despite the drop shape changing significantly.

While the model captures the behaviour well in the concentration range we have examined, this may not be the case for higher concentrations of GO, and it would be worthwhile to expand this study to a wider range of concentrations.

The relationship between contact angle and fit parameters in the new energy balance spreading model needs further refinement. To understand this better, further experimentation should be carried out using substrates of differing wettability. All droplet impact studies presented here for GO suspensions were limited to impacts

on glass substrates, which are hydrophilic. Spreading studies for GO suspensions on hydrophobic substrates would lend to enhancing our understanding of this relationship. Additionally, surface roughness also plays a role in spreading, and is something that has not been explored as part of this study. We know that surface roughness affects the spreading of Newtonian fluids [140], but the affect of surface roughness on the impact of non-Newtonian suspensions has not yet been examined. As such, expanding the work presented here to different substrates is pertinent.

The method of implementing a characteristic viscosity has allowed us to describe the behaviour of our shear-thinning, yield stress GO suspensions, and as such it is worth considering the extension of our investigation to other non-Newtonian fluids. such as other 2D nanoparticle suspensions or shear thinning liquids in general. Graphene oxide does not quite retain the excellent electrical and thermal properties of graphene or other nanoparticles such as carbon nanotubes. With the goal in mind of applying the insights developed here on droplet dynamics of 2D nanoparticle suspensions to refine inkjet printing of such suspensions for electronics, it is imperative to apply what has been learned here to other nanoparticle suspensions that retain these properties.

Some nanoparticle suspensions are shear-thickening. In this case, the viscosity of the suspension increases with shear rate, and suspensions of silica nanoparticles with carbon nanotubes (CNTs) are an example of this [142], with the effect more pronounced for higher concentrations of carbon nanotubes. Shear-thickening fluids are generally avoided in the context of inkjet printing due to the high shear rates in the printing nozzle that can result in clogging for these liquids due to their high viscosity at these rates [143]. An example of spreading for a shear-thickening cornstarch suspension is shown in figure 7.1. Spreading in this case occurs over a much longer timescale that those observed for GO suspensions, and axisymmetry of impacting drops is not always maintained [144, 145].

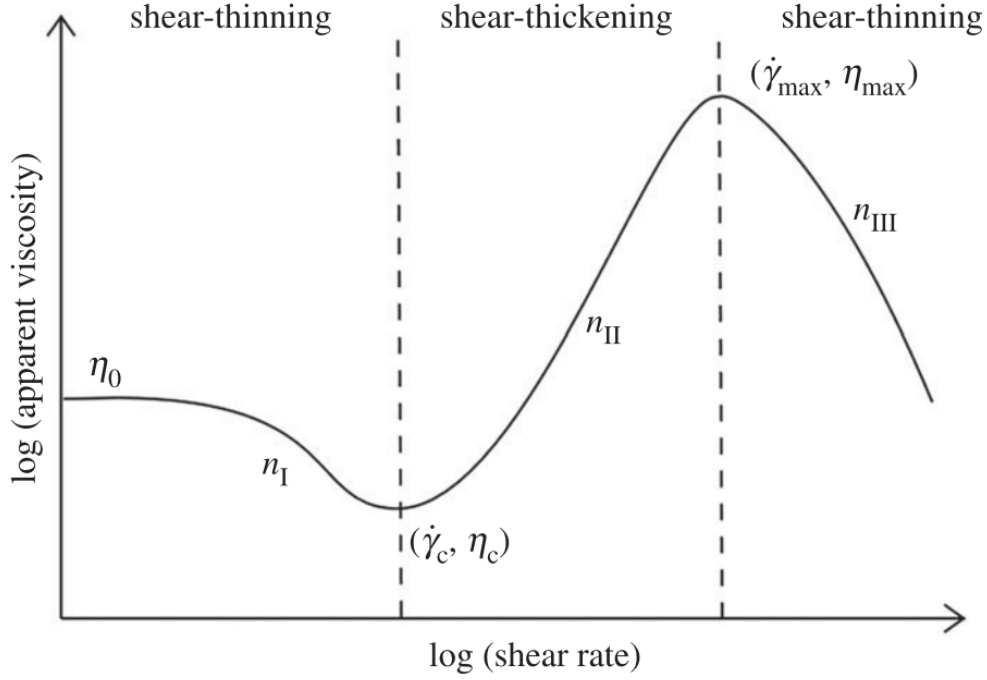


Figure 7.2: Qualitative viscosity curve for a shear-thickening fluid, Ionescu *et al.* (2020) [141].

Determining a characteristic viscosity in order to utilize the energy balance model is not trivial in the case of shear thickening fluids. A typical viscosity curve for a shear-thickening fluid is shown in figure 7.2, with three distinct regions where the fluid transitions from shear-thinning behaviour to shear-thickening and back again. There can also be distinct regimes after impact, particularly in the case of high concentration suspensions which initially undergo jamming on impact before relaxation [144, 145].

7.3 Splashing of Aqueous GO Suspensions

In contrast to the spreading results we obtained in chapter 3, when we examined the splashing behaviour of GO suspensions in chapter 4, use of a characteristic viscosity was not sufficient to predict the velocity at which impacting drops of GO suspensions would transition from spreading to splashing with the Riboux model or Almohammadi model [77, 81]. We saw that as the GO concentration is increased, the

threshold splashing velocity increases significantly. We also observed a suppression of splashing beyond a threshold viscosity for both GO suspensions and Newtonian water-ethanol-glycerol mixtures.

Droplet sizes typically used in inkjet printing are significantly smaller than those investigated here, in the 30-100 μm range. Given this, it is essential to further explore droplet impacts for drops of this scale. Some additional measurements were carried out using a MD-P-801 autodrop dispensing system that dispenses droplets by means of a piezo-driven pipette which operates with nozzle sizes of 30-70 μm . An example of a drop produced using this system is shown in figure 7.3. The maximum impact velocity achieved with this system was 2.9 m/s, which unfortunately was not sufficient to produce splashing outcomes for the micron-scale drops, and falls well below the typical impact velocities used in inkjet printing of around 10 m/s [146].

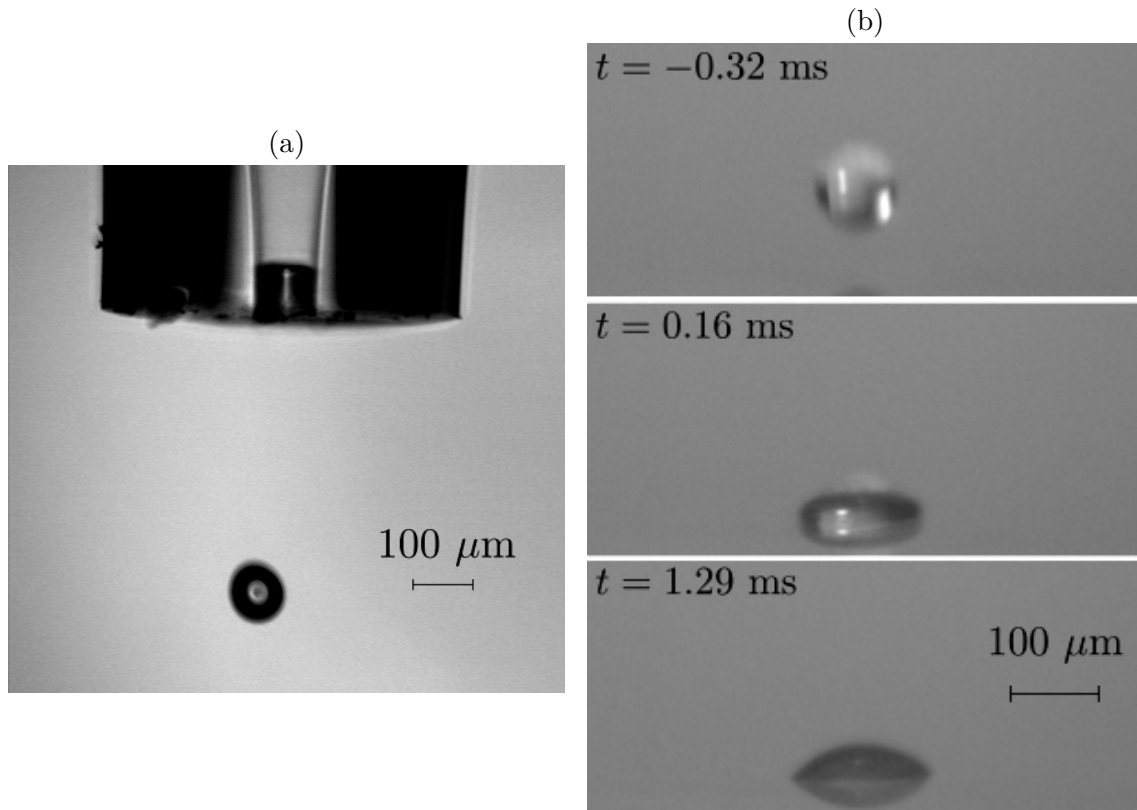


Figure 7.3: Droplets of 50%v/v ethanol-water generated using MD-P-801 autodrop dispensing system (a) upon ejection from capillary, (b) impact on glass substrate

7.4 Pinch-off of Fluid Filaments in Magnetic Fields

In chapter 5, we explored whether surface tension can be controlled with a magnetic field by examining the pinch-off behaviour of water and DyCl_3 . This study was motivated by results seen by the crop spraying technology company MagrowTec. Their spraying system implements permanent magnets in the spraying manifold that affects drop adhesion on crops and reduce drift by up to 70%, with a suppression of smaller drops in sprays reported [11, 97]. The median droplet size in a spray, D_{50} is given by

$$D_{50} = Cb\alpha_p^{-1/6}We^{-1/3}, \quad (7.1)$$

where C is a dimensionless constant, $C \approx 1.9$, b is the characteristic length given by the minor axis of elliptical nozzle opening and $\alpha_p = \frac{\rho_{air}}{\rho_{liquid}}$. Given that the size distribution has a surface tension dependence, we investigated whether the magnetic fields were affecting the surface tension of the fluid.

Although our findings indicate that magnetic fields have no discernible impact on the surface tension of water, our study has provided valuable insights into the inviscid scaling law and its inherent limitations. We showed that the prefactor included in the scaling law is not always constant, and that even for essentially inviscid fluids such as water, viscous effects are still important close to pinch-off, confirming previous results by Deblais *et al.* [110].

It is clear that much more work will be required to understand the physics underlying the results seen with MagrowTec's spray technology. Ongoing work is being carried out examining droplet impacts on leaves with high-speed imaging of such impacts for magnetized water underway, an example of which is shown in figure 7.4. This work is being undertaken to assess how magnetic treatment of water affects the adhesion of droplets on leaves after impact. Preliminary results so far have not

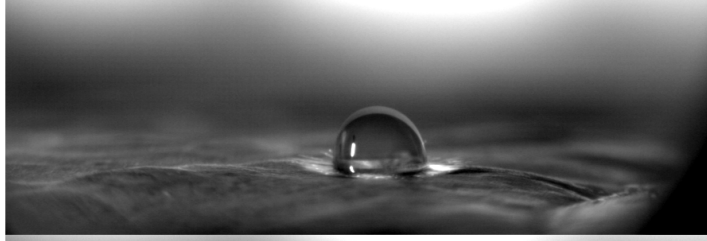
revealed any differences in contact angle or wetted area between magnetized and non-magnetized samples [11].

7.5 Pinch-off of Aqueous GO Suspensions

We saw that for low concentration GO suspensions the thinning dynamics followed that which one would expect for an inviscid fluid. As the concentration increased, the pinch-off filaments were no longer heterogeneous, with "bead-like" structures forming and the thinning follows the Newtonian viscous scaling law. The observed structures display similarities to pinch-off examined in the literature for particle laden, non-Brownian suspensions, suggesting the beading structure is a result of aggregates of GO becoming trapped in the filament. The high frame rate used in these experiments exposed a region close to pinch-off in which thinning is slowed even for samples without GO. Sonication of the samples results in a delay in the transition from inviscid to viscous behaviours, and resulted in a different final power law scaling in the decelerated thinning regime close to pinch-off. Other studies on aqueous GO suspensions in the literature [18, 124] did not observe the decelerated regime, which is likely due to the significantly lower frame rates used.

The results detailed above provide a solid foundation to build upon with further research. Determining the flocculate size before and after sonication would provide a much clearer picture of why the GO samples behave as they do during pinch-off, but was unfortunately out of the scope of the study presented here. Dynamic Light Scattering (DLS) is a technique used to measure the size of particles or molecules in a suspension or solution that would be appropriate [147]. DLS is based on the principle of analyzing the fluctuations in scattered light intensity caused by Brownian motion of particles suspended in a fluid. As particles move randomly due to thermal motion, they cause fluctuations in the intensity of light scattered by the suspension. These fluctuations are proportional to the size of the particles and their diffusion

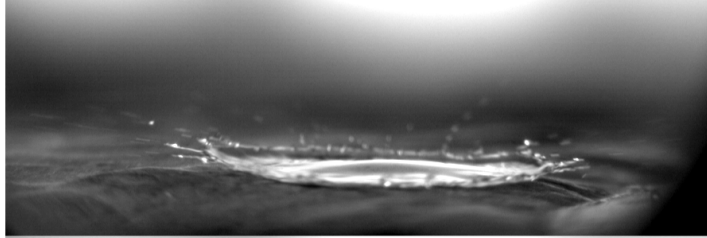
$t - t_0 = 0.15$ ms



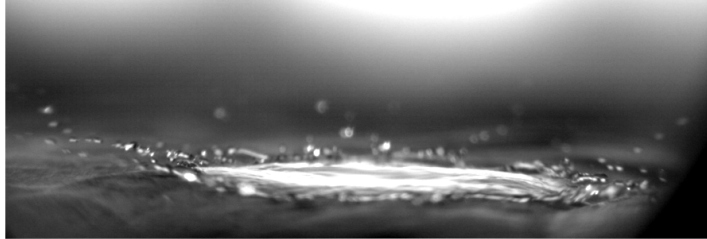
$t - t_0 = 0.3$ ms



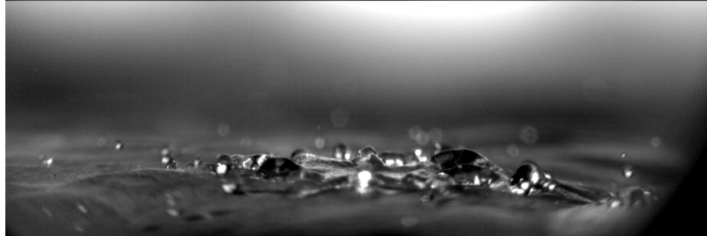
$t - t_0 = 0.7$ ms



$t - t_0 = 1.7$ ms



$t - t_0 = 5.75$ ms



$t - t_0 = 16.35$ ms



$t - t_0 = 50.5$ ms



Figure 7.4: Impact of drop of magnetized water on *Brassica oleracea* var. capitata.

coefficient. Along similar lines and in combination with the above, it would be beneficial to repeat these measurements with a new batch of GO stock. We would expect this to have a lower degree of agglomeration.

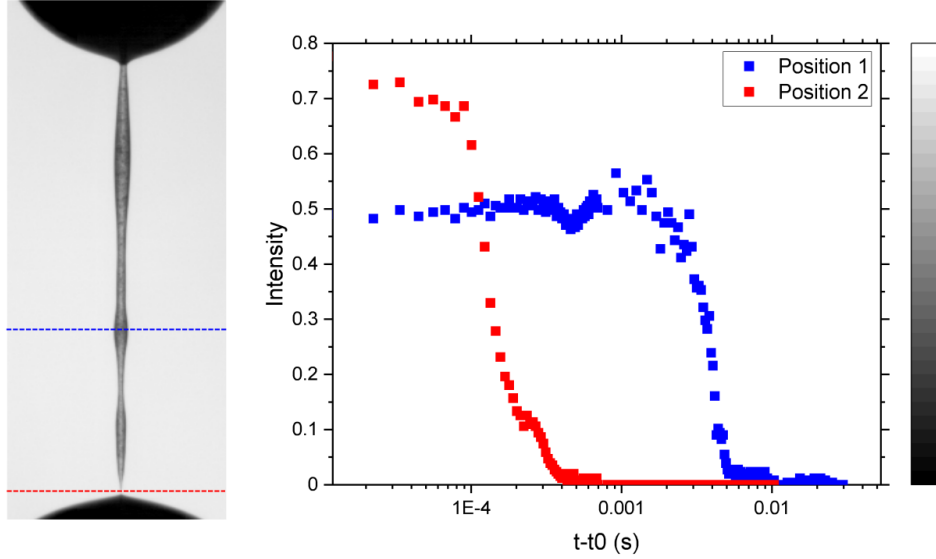


Figure 7.5: Greyscale pixel intensity at two points along filament axis for a 4g/l GO sample before sonication as a function of time.

There is some further analysis that can be carried out on pinch-off of GO suspensions using the existing data here that would also provide more insight into the dynamics in the fluid filaments. It was noted throughout the recorded pinch-off events that the greyscale intensity of the filament varied both over time and over the length of the filament. We would expect that this is dependent on the filament diameter, with more light penetrating through the suspension at small diameters. Considering the visible aggregates in the filaments of samples before sonication present as dark particles, it may be possible to estimate the local concentration of the suspension in the thinning filament at a given point in the filament by scaling with the filament radius at that point. Figure 7.5 shows the time evolution of the greyscale intensity for two pixels along the center line of a filament of a 4g/l GO sample, one at the position where pinch-off occurs (position 2, red) and the other at the position of one of the "beads" (position 1, blue). The corresponding positions are indicated in

the image to the left of the plot. Due to time constraints and considering that this experiment marked the culmination of my PhD research, I was unable to conduct this additional analysis beyond the preliminary plot shown here.

While we have gained some insight into the pinch-off dynamics of our shear-thinning suspensions, there are certainly gaps in our understanding of the process for most, if not all non-Newtonian fluids, shear-thickening fluids, for example. Figure 7.6 shows the pinch-off of a shear-thickening cornstarch suspension. In this case the fluid filament is much longer than that of our GO suspensions. There also remains the open question on how particles affect the rate of pinch-off at later times, with an acceleration observed by Van Deen *et al.* and a deceleration observed here, and predicted by Hammel and Morris [132, 134].

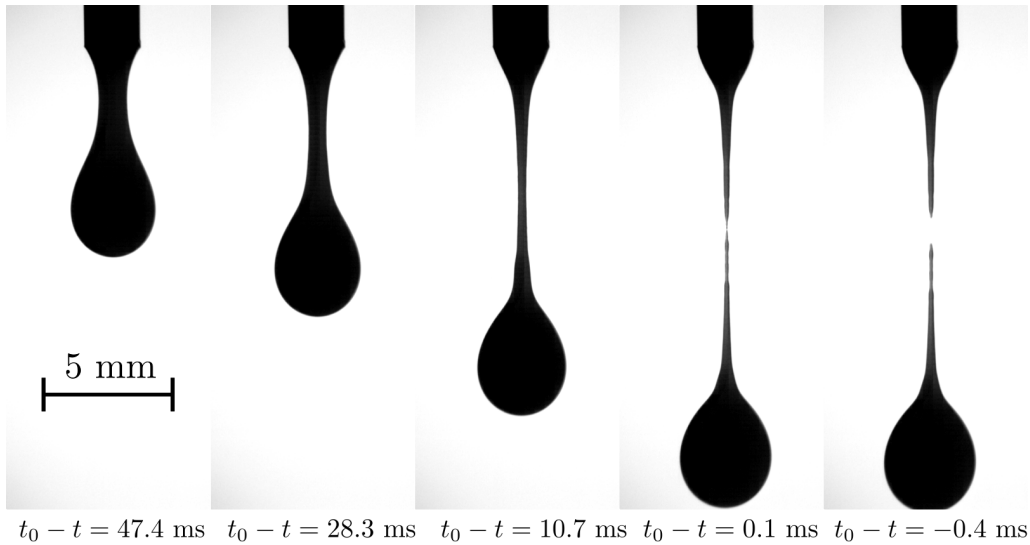


Figure 7.6: Pinch-off of 35%wt. suspension of cornstarch in a 85%wt. glycerol-water mixture.

Concluding Remarks

In closing, this thesis has delved into the intricate dynamics of droplets of graphene oxide (GO) suspensions through meticulous examination of spreading, splashing, and pinch-off phenomena, shedding further light on the unique characteristics of non-

Newtonian fluids in droplet dynamics. Examining the insights garnered from our investigations, it becomes evident that there are still additional avenues of inquiry and significant work remains to truly understand the underlying mechanisms. By acknowledging the boundaries of our current study and delineating pathways for future study, we set the stage for continued progress in elucidating the complexities of 2D nanoparticle suspensions and advancing applications in inkjet printing and beyond.

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Appendix A

Fits to Lee *et al.* Spreading Model (2016)

Table A.1: Fit parameters from figure 3.13.

GO concentration (g/l)	A	B	C	β_0
0	1.56	1.09	2.60	2.47
0.5	2.12	2.12	1.73	2.33
1	2.47	2.33	1.57	2.24
1.5	1.72	1.52	1.94	2.30
2	1.63	1.44	2.14	2.24
3	1.50	1.25	2.12	2.07
4	2.13	1.80	1.41	1.80
5	1.26	2.08	2.44	1.93
6	1.82	3.53	1.85	1.74

Appendix B

Drag Coefficient of a Smooth Sphere

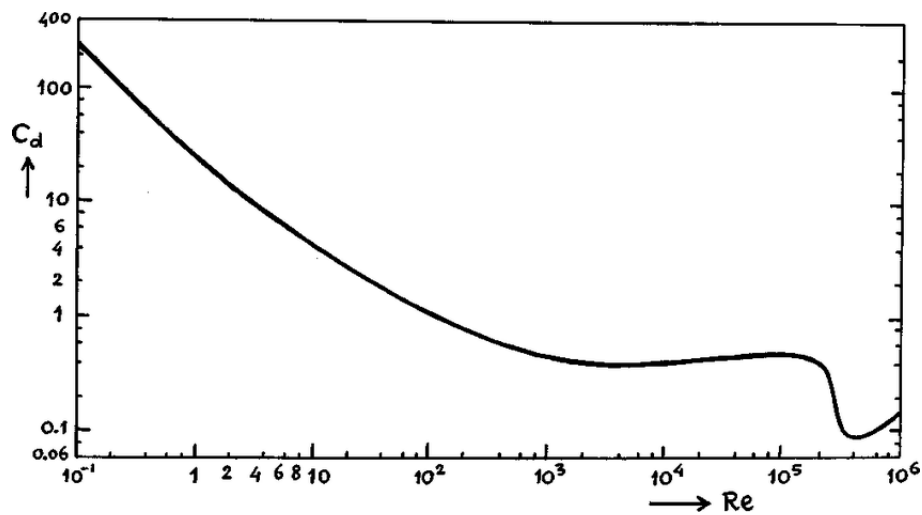


Figure B.1: The drag coefficient C_d of a sphere as a function of the Reynolds number Re . Figure adapted from Timmerman & Van der Weele (1999) [148].

Appendix C

Fluid Properties of Literature data on Spreading

C.1 Newtonian Samples

Table C.1: Physical properties of literature data. GW denotes glycerol-water mixtures.

Source	Sample	Substrate	Viscosity (mPa s)	Surface tension (mN/m)	Density (kg/m ³)	θ_D (deg.)	α fit
Scheller <i>et al.</i> (1995) [49]	GW A	Polystyrene	1.0	72.0	992	-	3.6
	GW C	Polystyrene	2.9	71.5	1082	-	2.8
	GW H	Polystyrene	16.0	68.5	1169	-	1.8
	GW I	Polystyrene	31.0	68.0	1190	-	1.8
	GW J	Polystyrene	300.0	65.0	1236	-	0.4
Lee <i>et al.</i> (2015) [67]	Ethanol	Steel	1.2	23	789	44	0.8
	GW	Steel	10	68	998	121	3.8
Laan <i>et al.</i> (2014) [60]	Water	Steel	1.0	73	998	-	3.4
	GW 1:1	Steel	6.0	65.69	1124	-	4.0
	GW 1:3.2	Steel	51.0	64.5	1204	-	1.2

C.2 Non-Newtonian Samples

Table C.2: Physical properties of non-Newtonian literature data.

Source	Sample	Substrate	Surface tension (mN/m)	Density (kg/m ³)	α fit
Balzan <i>et al.</i> (2021) [32]	Water	Steel	72.0	997	4.6
	BIF1 10%TS	Steel	51.1	1025	3.6
	BIF1 20%TS	Steel	53.4	1040	3.8
	BIF1 40%TS	Steel	54.2	1120	4.6
	BIF1 45%TS	Steel	54.7	1130	3.0
	BIF3 45%TS	Steel	57.5	1190	1.0
	WMP 45%TS	Steel	52.5	1130	10.4
	WPC 20%TS	Steel	51.9	1060	5.2

Table C.3: Rheology of non-Newtonian literature data

Source	Sample	τ_0 (mPas)	m	n
Balzan <i>et al.</i> (2021) [32]	Water	-	1.00 ± 0.01	1.00 ± 0.01
	BIF1 10%TS	0 ± 1	1.80 ± 0.02	1.00 ± 0.01
	BIF1 20%TS	4 ± 1	3.2 ± 0.2	0.99 ± 0.01
	BIF1 40%TS	4 ± 1	22.5 ± 1.0	0.96 ± 0.01
	BIF1 45%TS	4 ± 1	47.6 ± 0.5	0.95 ± 0.01
	BIF3 45%TS	5 ± 1	65.5 ± 2.0	0.94 ± 0.01
	WMP 45%TS	5 ± 1	130.0 ± 0.5	0.90 ± 0.01
	WPC 20%TS	3 ± 1	385 ± 5	0.67 ± 0.01

Appendix D

Turbulent Drag Derivation

Turbulent drag gives a non-linear relationship between the drag force and velocity,

$$F_d = \frac{1}{2} C_d \rho A v^2 \quad (\text{D.1})$$

where ρ is the density of the surrounding fluid, C_d is the drag coefficient, and A is the cross-sectional area of the falling spherical droplet. Typical velocities of drop impact are ~ 1 m/s, and drop radii ~ 1 mm, so the Reynolds number $Re > 1$, and as such Stokes drag does not apply. The drag coefficient is not a constant as it depends on the Reynolds number which changes as the drop falls due to changing droplet velocity.

The equation of motion for this drag force is as follows:

$$\begin{aligned} m \frac{dv}{dt} &= mg - \frac{1}{2} C_d \rho A v^2 \\ m dv &= dt (mg - \frac{1}{2} C_d \rho A v^2) \\ \int m \frac{dv}{mg - \frac{1}{2} C_d \rho A v^2} &= \int dt \end{aligned}$$

with m the droplet mass and v the droplet velocity. Letting $p = mg$ and $q =$

$\frac{1}{2}C_d\rho A$, we consider the integral

$$\int \frac{dv}{p - qv^2} = \frac{1}{p} \int \frac{dv}{(1 - \frac{q}{p}v^2)}$$

Making the substitution $u = \frac{i\sqrt{q}}{\sqrt{p}}v$, $du = \frac{i\sqrt{q}}{\sqrt{p}}dv$, the integral becomes

$$\frac{-i}{\sqrt{pq}} \int \frac{1}{1 + u^2} du = \frac{-i}{\sqrt{pq}} \arctan u + C$$

Where C is an arbitrary constant of integration. We know that $\operatorname{arctanh}(z) = \frac{1}{i} \arctan(iz)$, and so we obtain

$$\frac{\operatorname{arctanh}(\sqrt{\frac{q}{p}}v)}{\sqrt{pq}} + C$$

Inverting this results in an expression for the velocity as a function of time

$$v(t) = \sqrt{\frac{p}{q}} \tanh\left(\frac{\sqrt{pq}}{m}t + D\right) \quad (\text{D.2})$$

with D a further arbitrary constant.

Imposing the initial condition $v(0) = 0$,

$$\begin{aligned} \sqrt{\frac{p}{q}} \tanh D &= 0 \\ \implies v(t) &= \sqrt{\frac{p}{q}} \tanh\left(\frac{\sqrt{pq}}{m}t\right) \end{aligned}$$

Substituting back p and q , the final equation for the turbulent velocity reads

$$v(t) = \sqrt{\frac{2gm}{AC_d\rho}} \tanh\left(\sqrt{\frac{AC_d g\rho}{2m}}t\right) \quad (\text{D.3})$$

As hyperbolic tangent functions have an asymptote of at $y = 1$, a falling droplet reaches a terminal velocity $v_T = \sqrt{\frac{2gm}{AC_d\rho}}$.

We can integrate the resultant velocity due to turbulent drag to obtain the relationship between the position of the droplet and time.

I will make the following substitution for clarity:

$$Q = \sqrt{\frac{2gm}{AC_d\rho}}$$

$$R = \sqrt{\frac{AC_dg\rho}{2m}}$$

It now remains to solve

$$x(t) = \int v(t)dt = Q \int \tanh(Rt)dt \tag{D.4}$$

We make the substitution $u = Rt$, $du = Rdt$,

$$\begin{aligned} \implies x(t) &= \frac{Q}{R} \int \tanh(u)du \\ &= \frac{Q}{R} \int \frac{\sinh(u)}{\cosh(u)} du \end{aligned}$$

Let $s = \cosh(u)$, and $ds = \sinh(u)du$

$$\begin{aligned} \implies x(t) &= \frac{Q}{R} \int \frac{1}{s} ds \\ &= \frac{Q}{R} \log(s) + C \\ &= \frac{Q}{R} \log(\cosh(Rt)) + C \end{aligned}$$

with C an arbitrary constant of integration. Imposing the initial condition $x(0) = 0$,

we obtain

$$\begin{aligned}\frac{Q}{R} \log(1) + C &= 0 \\ \implies C &= 0\end{aligned}$$

Finally we arrive at the expression for position in the turbulent drag case

$$x(t) = \frac{Q}{R} \log(\cosh(Rt)) \tag{D.5}$$

$$x(t) = \frac{2m}{AC_d \rho} \log\left(\cosh\left(\sqrt{\frac{AC_d g \rho}{2m}} t\right)\right) \tag{D.6}$$

Appendix E

Fits to Almohammadi *et al.*

Splashing Model (2019)

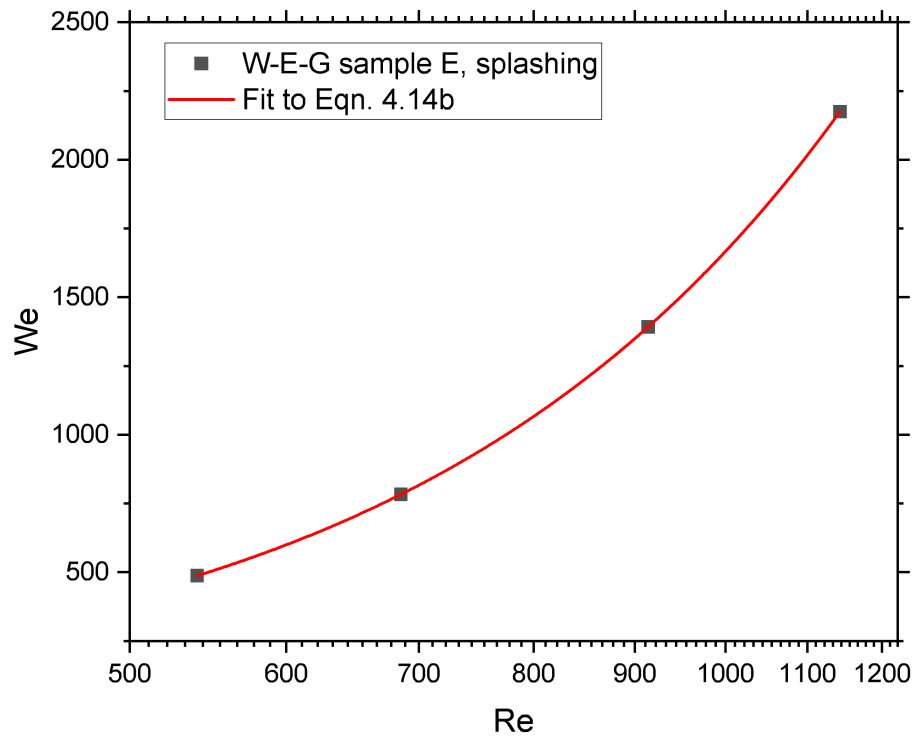


Figure E.1: W-E-G fit to equation 4.14b. The fit is made to projected splashing points along with the experimentally determined splashing threshold, and the fit parameters are $\beta_3 = 2$ and $K_3 = 0.00167$.

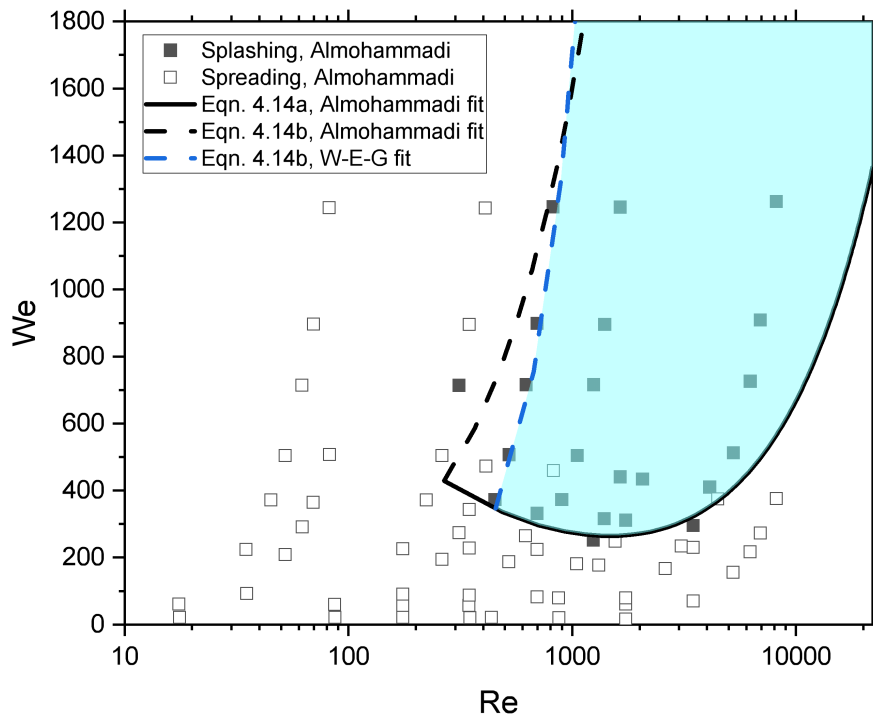


Figure E.2: Data from Almohammadi *et al.* compared to fits to equations 4.14a and 4.14b presented there, and W-E-G fit to equation 4.14b [77]. Fit parameters are given in tables 4.4 and 4.5. Arguably, both fits represent the data equally well.

Appendix F

Pinch-off Scaling Law Derivations

F.1 Inviscid Newtonian Fluids

The scaling law in equation 5.1 is derived by dimensional analysis, using the Buckingham π theorem. Here we wish to derive a function, f , that depends on surface tension, the characteristic time scale, density and filament diameter. On physical grounds we can exclude viscosity and gravity as the length scales of the neck are far from the viscous and capillary length scales.

$$f(\sigma, \tau, \rho, D) = 0, \quad (\text{F.1})$$

Here, we have 4 physical variables that have dimensions

$$[\sigma] = MT^{-1}, \quad [\tau] = T, \quad [\rho] = ML^{-3}, \quad [D] = L \quad (\text{F.2})$$

where M, T, and L are the independent units for mass, time and length respectively. Equation F.1 can be restated in the form

$$F(\pi_1) = 0 \quad (\text{F.3})$$

where π is a dimensionless grouping of the four physical variables. There is only one possible π for this function, as $p = n - k = 4 - 3$, where p is the number of dimensionless groupings, n is the number of physical variables and k is the number of independent units.

π is given by some combination of the variables,

$$\pi = \sigma^a \tau^b \rho^c D = (MT^{-1})^a (T)^b (ML^{-3})^c (L) \quad (\text{F.4})$$

$$= M^{a+c} T^{b-2a} L^{1-3c} = M^0 T^0 L^0 \quad (\text{F.5})$$

Solving for a , b , and c ,

$$a + c = 0 \quad c = 1/3 \quad (\text{F.6})$$

$$b - 2a = 0 \quad a = -1/3 \quad (\text{F.7})$$

$$1 - 3c = 0 \quad b = -2/3 \quad (\text{F.8})$$

therefore,

$$\pi = \sigma^{-1/3} \tau^{-2/3} \rho^{1/3} D = A \implies D = A \left(\frac{\sigma}{\rho} \right)^{1/3} \tau^{2/3} \quad (\text{F.9})$$

F.2 Viscous Newtonian Fluids

The universal scaling law for viscous pinch-off in Newtonian fluids was derived in Eggers (1993) [131] from the Navier stokes equations for an axisymmetric ($v_\phi = 0$), incompressible fluid for velocity $v(r, z, \phi)$, pressure $p(r, z, \phi)$ and density ρ

$$\begin{aligned} & \rho (\partial_t v_r + v_r \partial_r v_r + v_z \partial_z v_r) \\ & = -\partial_r p + \eta (\partial_r^2 v_r + \partial_z^2 v_r + \partial_r v_r / r - v_r / r^2) \end{aligned} \quad (\text{F.10})$$

$$\rho(\partial_t v_z + v_r \partial_r v_z + v_z \partial_z v_z) \quad (\text{F.11})$$

$$= -\partial_z p + \eta(\partial_r^2 v_z + \partial_z^2 v_z + \partial_r v_z / r) - \rho g$$

$$\partial_r v_r + \partial_z v_z + v_r / r = 0. \quad (\text{F.12})$$

These equations are simplified using a power law expansion in r for the velocity and pressure fields and retaining only the lower order terms, resulting in the coupled equations

$$\rho(\partial_t v + vv') = -\sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)' + 3\mu\frac{(h^2 v')'}{h^2} - \rho g \quad (\text{F.13})$$

$$\partial_t h + vh' = -v'h/2,$$

where ρ is the density, σ is the surface tension, R_1 and R_2 are the principal radii of curvature, μ is the viscosity, h is the width of the fluid filament, and prime refers to differentiation with respect to z . Despite the aforementioned approximation, this relation has shown to agree well with experimental data.

Using a self-similar scaling approach, a pair of Ordinary Differential Equations can be formed in terms of scaling functions $\phi(\xi), \psi(\xi)$, where ξ is the similarity variable $\xi = z'/t'^{1/2}$ for time and length to the singularity $z' = (z - z_0)/\ell_v$ and $t' = (t_0 - t)/t_v$ ($\ell_v = \mu^2/\sigma\rho$ and $t_v = \mu^3/\sigma^2\rho$). The ODE's are given as

$$\begin{aligned} \psi/2 + \xi\psi'/2 + \psi\psi' &= \phi'/\phi^2 + 3\psi'' + 6\psi'\phi'/\phi \\ \phi' &= \phi \frac{1 - \psi'/2}{\psi + \xi/2} \end{aligned} \quad (\text{F.14})$$

and can be solved to determine $h_{min} = D_{min} = 0.0304(\frac{\sigma}{\mu})\tau_c$.

Appendix G

Numerical Solution to Riboux & Gordillo Splashing Model (2014) - MATLAB

```
1  ***Riboux and Gordillo splashing velocity model***
2
3  ***Solution for single given R value
4
5  %Newton-Raphson numerical solution to find ejection time
   (te) and splashing velocity (vsp) of
6  %a given liquid and compare to de Goede approximation.
7
8  %read in parameters and experimental data from excel
9  excelfile = 'WEG_RG.xlsx';
10 sheet = 'Sheet 1';
11 T = readtable(excelfile,'Sheet',sheet,'ReadVariableNames'
   ,false);
```

```

12 A= table2array(T(:,2:end));
13 row =3;
14
15 %Definition of input parameter values:
16 sigma = A(row,1)*(10^(-3)); %Surface tension of liquid (N
    /m)
17 beta = 0.14; %Splashing ratio
18 mug = 1.85*(10^(-5)); %viscosity of surrounding gas (kg/
    ms)
19 rho = A(row,2); %density of liquid (kg/m^3)
20 R = A(row,3)/2; %Radius of droplet (m)
21 mu = A(row,4)*(10^(-3)); %viscosity of liquid (kg/ms)
22 lambda = 65*(10^(-9)); %Mean free path of gas molecules (
    m)
23 alpha = pi/3;
24 ku = 0.3;
25 rhog = 1.18;
26
27
28 %take input for x0, initial guess for te
29 te0= input('Enter initial approximation for ejection time
    (s): ');
30 places = input('Enter degree of accuracy required (
    decimal places): ');
31 dt = 5*(10^(((1)*places)-1));
32
33 for i=1:100
34

```

```

35     %get f(te0)
36     vsp0 = RGeqn_vsp( te0, sigma, mu, rho, R);
37     ht0 = hteqn(R, te0);
38     vt0 = vteqn(vsp0, te0);
39     kl0 = RGeqn_kl( ht0, lambda);
40     f0 = RGeqnf(kl0, mug, vt0, ku, rhog, ht0, sigma, beta
        );
41     %get f(te0 + h)
42     h=0.0001;
43     te0h = te0 +h;
44     vsp0h = RGeqn_vsp( te0h, sigma, mu, rho, R);
45     ht0h = hteqn(R, te0h);
46     vt0h = vteqn(vsp0h, te0h);
47     kl0h = RGeqn_kl( ht0h, lambda);
48     f0h = RGeqnf(kl0h, mug, vt0h, ku, rhog, ht0h, sigma,
        beta);
49     %get derivative at te0
50     fderiv0 = fn_Euler_FD(h,f0,f0h);
51
52
53     %Newton Raphson:
54     te_new = te0 - (f0/fderiv0);
55     %Check if xnew agrees within dx:
56     if abs(te_new-te0)<dt %break if successive values
        agree within dx
57     break
58     end
59     te0=te_new;

```

```
60 end
61 %te_new = te_new - rem(te_new,10^-places); %Displaying up
    to required decimal places
62
63 if i<100 %If above loop breaks before reaching the
    maximum iteration, display results
64     fprintf('Ejection time (s) : %f \n',te_new);
65     fprintf('No. of Iterations : %d\n',i);
66
67     %calculate splashing velocity, low ohnesorge
        approximation and ohnesorge number:
68     te = te_new;
69     vsp = RGeqn_vsp( te, sigma, mu, rho, R);
70     vapprox = ohnesvspfn(sigma, mug,rho,R);
71     ohnes = ohnesnofn(mu,R,rho,sigma);
72
73     fprintf('Splash velocity (m/s) : %f \n',vsp);
74     fprintf('Low Ohnesorge approximation (m/s) : %f \n',
        vapprox);
75
76     fprintf('Ohnesorge number : %f \n', ohnes);
77
78 else
79     fprintf('***Maximum iterations reached, no converging
        value found***');
80
81 end
82
```

```

83
84 %REF: https://uk.mathworks.com/matlabcentral/fileexchange
      /68885-the-newton-raphson-method
85
86 %FNS
87 function vsp = RGeqn_vsp( te, sigma, mu, rho, R)
88     %calc. vsp function
89 vsp = (((((3^(1/2))/2)*(mu/(rho*R))*(te^(-1/2))))+(((3/4)
      *((mu/(rho*R))^2)*(te^(-1)))) + (4.84*(sigma/(rho*R))*(
      te^(3/2))))^(1/2))/(2.42*(te^(3/2)));
90 end
91 function ht = hteqn(R, te)
92 ht = ((sqrt(12))/pi)*R*(te^(3/2));
93 end
94 function vt = vteqn(vsp, te)
95 vt = ((sqrt(3))/2)*vsp*(te^(-1/2));
96 end
97 function kl = RGeqn_kl( ht, lambda)
98     %calc. kl function
99 kl = (-2)*((log(19.2*lambda*((ht)^(-1))))-(log(1+(19.2*
      lambda*((ht)^(-1))))));
100 end
101 function f = RGeqn_f(kl, mug, vt, ku, rhog, ht, sigma,
      beta)
102     %calc. splash eqn function
103 f = (kl*mug*vt)+(ku*rhog*(vt^2)*ht) - (2*sigma*(beta^2));
104 end
105 function EFD = fn_Euler_FD(h, fte0, fte0h )

```



```
106 %euler forward difference derivative calculation
107         EFD = (fte0h - fte0)/h;
108     end
109     function ohnesno = ohnesnofn(mu,R,rho,sigma)
110     ohnesno = (mu*((R*rho*sigma)^(-1/2)));
111     end
112     function ohnesvsp = ohnesvspfn(sigma, mug,rho,R)
113     ohnesvsp = (((sigma)^(2/3))*0.12*((3)^(1/2)))/(2.22*((
        mug)^(1/2))*((rho*R)^(1/6))))^(6/5);
114     end
```