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University of California
Santa Barbara

Capillary dynamics of polymer solutions, and their influence on cohesive particulate flow

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

Doctor of Philosophy

in

Mechanical Engineering

by

Sreeram RAJESH

Committee in charge:

Professor Alban Sauret, Chair
Professor Eckart Meiburg
Professor Paolo Luzzatto-Fegiz
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March 2026

The Dissertation of Sreeram Rajesh is approved.

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March 2026

Acknowledgements

To my advisor, Alban Sauret, I want to thank him for this opportunity of a lifetime. From the first email I received from you while I was at home under lockdown to starting my first experiments with the partially open labs, the infinite number of Slack DMs, helping me write the papers, and giving me the opportunity to explore different ideas, working with you has forever shaped in me a certain way of approaching any problem in life.

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I'm sure I have unintentionally missed a few names, for which I deeply apologize.

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by Sreeram RAJESH

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2. **Rajesh, S.**, Thiévenaz, V., and Sauret, A. (2021). “Transition to the viscoelastic regime in the thinning of polymer solutions.” *Soft Matter*, 18(16):3147—3156 [[144](#)].
3. **Rajesh, S.**, Thiévenaz, V., Peddada, S. S., and Sauret, A. (2022). “Pinch-off of bubbles in a polymer solution” *Journal of Non-Newtonian Fluid Mechanics*, 310:104921 [[145](#)].
4. **Rajesh, S.**, and Sauret, A. (2025). “Impact and spreading dynamics of a drop of fiber suspension on a hydrophilic solid substrate” *Journal of Colloid and Interface Science*, Vol. 692, 137518 [[143](#)].

5. **Rajesh, S.**, Tinianov, R. S., and Sauret, A. “Axial Forces in capillary liquid bridges of polymer solutions” *In Preparation*.
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◇ UCSB Senate Travel Grant Award	2023, 2025
◇ UCSB Graduate Student Association Conference Travel Grant	2023, 2024
◇ Mechanical Engineering Summer Support	2021–2024
◇ Society of Rheology Travel Award	2024

UNIVERSITY OF CALIFORNIA SANTA BARBARA

Abstract

PhD in Mechanical Engineering

Capillary dynamics of polymer solutions, and their influence on cohesive particulate flow

by Sreeram RAJESH

Granular materials are collections of discrete, macroscopic solid particles that interact primarily through dissipative contact forces. In industrial processing—ranging from pharmaceutical wet granulation to the handling of construction materials and food powders—these systems are rarely dry. Instead, they are frequently mixed with liquid binders to control dust, induce agglomeration, or modify flowability. These interstitial binders are often rheologically complex fluids containing dissolved polymers, surfactants, or suspended fines, rather than simple Newtonian liquids. Similarly, in soils, complex materials such as extracellular polymeric substances (EPS) or mucilage secreted by bacteria and plants help stabilize soil. The presence of such viscoelastic additives fundamentally alters the cohesive forces between grains, thereby modifying bulk transport behavior.

At the particle scale, these complex fluids bind grains together through the formation of capillary bridges. The resulting particle-scale forces are governed not only by surface tension and viscosity but also by the fluid’s elasticity and extensional rheology. In Chapter 1, we discuss the prevalence of non-Newtonian binders in industrial applications and the necessity of understanding particle-polymer interactions. In Chapters 2 and 3, we

present investigations on the fundamental capillary flows of polymer solutions in droplet and bubble pinch-off configurations. In Chapters 4 and 5, we detail the development of a custom apparatus and the subsequent quantification of the axial forces arising from viscoelastic liquid bridges. Finally, in Chapter 6, we investigate the bulk flow of cohesive particulate materials, bridging the gap between microscale force measurements and macroscopic granular dynamics.

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Chapter 1

Introduction

1.1 Introduction

The flow of granular materials is ubiquitous in both natural flows and industrial processes, ranging from the transport of sand and mud [92, 107] and the erosion of coastal cliffs (Fig. 1.2(b)) to the movement of microplastics in the ocean [135, 197] and the handling of bulk solids in manufacturing [49]. These flows represent complex, heterogeneous systems involving dynamic interactions between solid, liquid, and gaseous phases. The rheology and transport of these multiphase systems are often modified by dissolved substances such as pollutants, surfactants, or polymers (specifically mucilage and binders). In natural environments, polymeric cohesion could arise from bacterial biofilms, which are composed of secreted extracellular polymeric substances (EPS) [158] or mucilage released by plant roots into the nearby soil. By coating particulate matter, these polymeric films act as biological glues that alter the erosion thresholds of soil layers and the transport dynamics of microplastics in aquatic bodies.

Parallel to these natural phenomena, industrial processes utilize binders to engineer specific material properties. In the food and pharmaceutical industries, binders are employed to enhance texture, ensure the mechanical integrity of tablets, and achieve controlled drug release [73, 136]. Similarly, in the mining and mineral sectors, binders are critical for pelletization and dust control, transforming fine ores into durable, free-flowing agglomerates that are safer to transport and more efficient for downstream processing. Polymeric binders—ranging from natural starches and gums to synthetic options like polyvinylpyrrolidone (PVP)—are particularly valuable in these applications, as their molecular structure allows for precise control over viscosity, adhesion, and biodegradation [49, 73, 136].

1.2 What are Granular Materials?

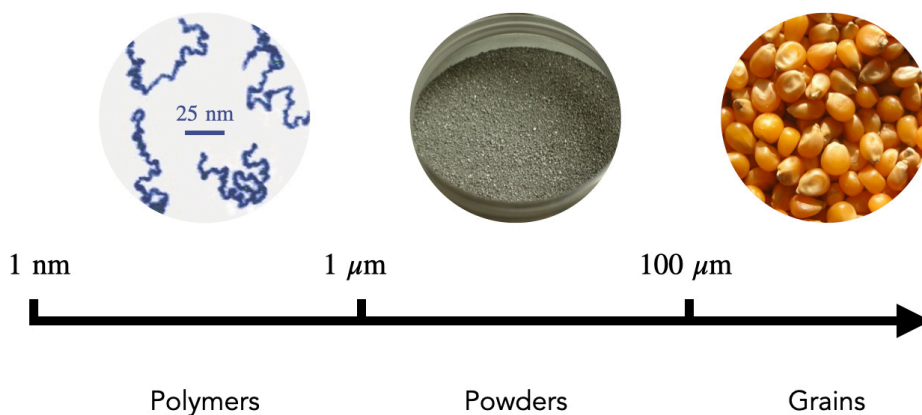


FIGURE 1.1: Classifications of materials discussed in this thesis by size: from polymers to granular materials

Granular materials are collections of discrete, macroscopic solid particles, generally defined as being larger than $100\ \mu\text{m}$ —a scale where thermal fluctuations (Brownian motion) are

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negligible compared to external forces. Examples of these systems are ubiquitous, ranging from everyday substances such as food grains and sand to industrial materials such as recycled concrete aggregates, and even cosmic structures such as the debris that forms Saturn’s rings. The collective behavior of these materials is driven primarily by athermal interactions, including gravity, friction, and inelastic collisions [4, 123]. Frequently, their dynamics are governed by bridging mechanisms that induce cohesion; this can arise from liquid bridges formed by humidity or added fluids, or from solid bridging (sintering) at high temperatures. This macroscopic scale stands in sharp contrast to that of polymers. While granular particles are visible to the naked eye, a polymer coil is orders of magnitude smaller, typically spanning only a few nanometers, depending on its molecular weight.

In this work, we focus on the cohesive transport of granular materials, where the primary interaction arises from liquid-bridge cohesion. Specifically, we investigate how the presence of polymers modifies these particle-scale interactions. Unlike simple Newtonian fluids, polymer solutions introduce complex rheological behaviors when stretched between grains. We are particularly interested in the onset of elasto-capillary stresses—forces generated by the resistance of polymer chains to stretching—and how these microscopic, non-Newtonian dynamics fundamentally alter the bulk flow behavior of cohesive granular systems.

1.3 Polymeric Cohesion in Natural Systems

In nature, the influence of cohesion often arises from the secretion of extracellular polymers that act as biological glues across diverse environments. One primary driver of this cohesion is the growth of bacterial biofilms, which develop when cells attach to surfaces, such as soil or submerged microplastics, and exude a complex matrix of extracellular polymeric substances (EPS). Another significant source of biological cohesion is root mucilage, a

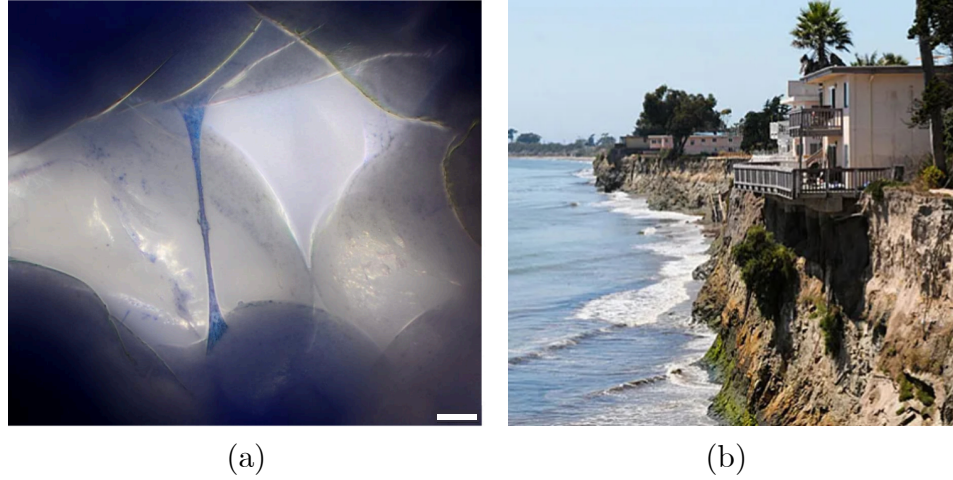


FIGURE 1.2: (a) Capillary liquid bridges of Mucilage (Polymeric gel) between soil particles help cement soil particles. Scale bar represents $50\ \mu\text{m}$ [Reproduced from the work of Carminati *et al.* [26]] (b) A house in Isla Vista hanging precariously over a cliff [Photo by Noozhawk].

polymeric gel exuded by plant root tips as they penetrate the soil [26]. By forming stable, interconnected networks between particles, these biopolymers fundamentally alter the mechanical and hydraulic properties of the medium, providing a level of structural integrity that simple water-based adhesion cannot achieve. Bacterial biofilms are ubiquitous in sediments, particularly within aquatic bodies [188]. Once bacteria attach irreversibly to a surface, they begin the production of biofilm matrix components, leading to the growth and formation of fully mature, cohesive colonies [158]. The prevalence of these microorganisms and the subsequent formation of EPS create significant cohesive forces between sediment particles [106]. Despite this, many existing physical models for sediment transport fail to account for the specific cohesive forces arising from particle-polymer interactions [66]. While recent studies have begun to consider particulate cohesion, they often rely on simplified versions based on the capillary bridges of Newtonian liquids [1, 2] or uniform chemical coatings [62, 165]. In real systems, however, cohesive forces emerge from discrete polymer bridges formed between particles (see Fig. 1.2). Accurately

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capturing the transport of such cohesive sediments requires a model that explicitly accounts for these complex particle-polymer interactions. These interactions are also central to understanding the environmental challenges posed by microplastic particles (MPs) [117, 135, 197]. Produced by the breakdown of industrial and human plastic waste, MPs (typically smaller than 5 mm) provide ideal surfaces for biofilm colonization [see Fig. 1.3(a) - (b)], which leads to the formation of MP aggregates, significantly modifying their size and density. Consequently, the transport properties of these biofilm-laden aggregates differ markedly from non-cohesive plastic particles; for instance, in lab-based studies of settling dynamics [Fig. 1.3 (c) - (f)], we note that polymer-laden particles exhibit modified transport behavior compared to their non-cohesive counterparts. However, the capillary scale mechanisms governing the particle-polymer interactions remain poorly understood.

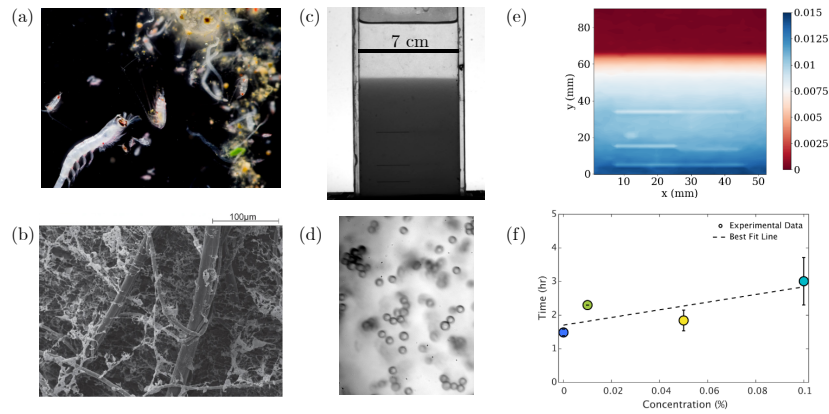


FIGURE 1.3: (a) Microplastic particles in the ocean [Credit: Morgan Trimble/Alamy Stock Photo]. (b) Polymeric bridges due to biofilms as observed under an SEM. [Credit: Mendrik *et al.* [117]] (c) A lab-scale experiment quantifying the settling dynamics of polymer-laden microplastic particles. (d) Settling dynamics experiment observed with 10x magnification. (e) Evolution of the settling front of the microplastic particles. The legend on the right, from red to blue, indicates increases in local volume fraction. (f) Influence of initial polymer concentration on the settling time of the aggregates.

The mechanical advantage of such polymeric binders is further demonstrated by the role of root mucilage at the root-soil interface (Fig. 1.2). According to Carminati *et al.*

(2017) [26], root mucilage significantly enhances the stability of liquid bridges between soil particles compared to bridges formed by water alone. While pure water bridges are highly unstable and break up rapidly as soil dries—draining toward particles and leaving air-filled gaps—the polymeric nature of mucilage creates viscoelastic bridges that resist this failure. Polymers simultaneously decrease surface tension and increase viscosity, which raises the capillary number, the ratio of the product of viscosity and velocity to surface tension, preventing the bridges from snapping and allowing them to stretch into persistent, long filaments. These filaments act as biological glue, cementing soil particles together and providing superior mechanical stability to the rhizosphere, thereby facilitating the formation of a stable rhizosheath. For the plant, this polymer-driven cohesion is far more beneficial than simple water-based adhesion because it maintains continuous physical and hydraulic contact during drought, preventing hydraulic failure as roots shrink.

1.4 Industrial Binders for Mixing and Granulation

Viscoelastic interactions of polymeric binders are of particular relevance to the processing of granular materials and powders for various industrial processes, from the formation of free-flowing granules to reducing the size distribution of mineral ores, agglomerates, and controlled reaction with particulate ingredients in milling and fluidized bed drying [49, 78, 191].

In industrial processing, the use of polymeric binders is essential for inducing the inter-particle cohesion required to transform fine powders into stable, free-flowing granules. This granulation process is critical for achieving a controlled size distribution, which ensures product quality and handling efficiency across diverse applications, such as the production of instant coffee, the formulation of pharmaceutical tablets, and the sintering

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of copper concentrates in mining. Ennis *et al.* [49] implemented a mechanistic approach to characterize these phenomena by shifting from purely empirical observations to models based on the collisional dissipation of relative kinetic energy. Specifically, they introduced the concept of using physically relevant population balance kernels that account for a capillary-scale description of viscous liquid bridges, often categorized by a dimensionless binder Stokes number. While these foundational models primarily address Newtonian binders, they provide the necessary framework for extension to complex polymeric systems. However, to successfully apply this to industrial polymers, a refined description that accounts for the specific capillary forces and stabilizing effects of polymer-based liquid bridges is vital to initiate accurate predictive modeling.

In the mining and mineral sectors, fragmentation remains a significant challenge, as durable agglomerates often require substantial energy input to break them down into their constituent parts. Industry currently relies on high-energy methods, such as turbulent jets in opposed-jet mills, to fragment these materials, though these processes often suffer from poor energy efficiency. Similar dynamics are observed in fluidized granular beds—commonly used for powder drying or high-shear mixing of binders—where gas-solid flow can lead to large particle-particle separations as the bed expands and individual grains are entrained in the fluidizing medium. These complex fragmentation and drying processes can be modeled through mechanistic frameworks, such as population balances that incorporate breakage and selection functions, or through Discrete Element Method (DEM) simulations. To improve the predictive accuracy of these models, particularly when dealing with viscoelastic binders that resist breakage, a thorough understanding of capillary-scale polymer interactions is necessary to characterize how these biological or synthetic glues influence the fracture and rebound thresholds.

1.5 Elasto-Capillary Dynamics of Polymer Solutions

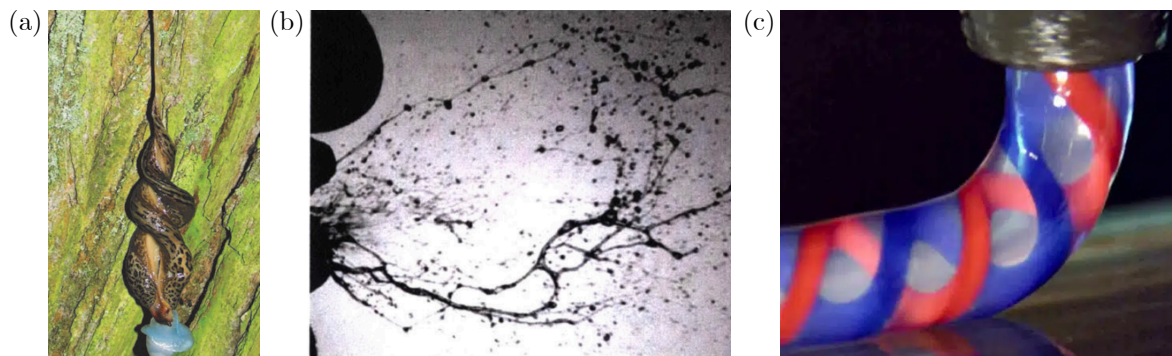


FIGURE 1.4: (a) Leopard slug mating ligaments demonstrate how high extensional viscosity in natural polymers allows a single mucus thread to stretch significantly without breaking [T. Hiddessen, Image via Wikimedia Commons]. (b) Viscoelasticity in mucosal fluid during a sneeze enables the formation of long, stable filaments that resist surface-tension-driven fragmentation into droplets [Reproduced with permission from Springer Nature: Springer, *Experiments in Fluids*, Visualization of sneezing, Scharfman *et al.*, 2016 [160]]. (c) In 3D printing, polymer extension is engineered to maintain a continuous liquid filament between the nozzle and substrate, preventing premature bead breakup [Reproduced with permission from Springer Nature: Nature, Rotational multimaterial printing of filaments with subvoxel control, Larson *et al.*, 2023 [96]].

From the biofilm-laden transport of particulate soil to the industrial handling of powder systems, the solid-liquid capillary interactions within liquid bridges are key in defining interparticle cohesive forces at bulk scales. Beyond their relevance to bulk solids handling, capillary-scale dynamics are of interest in a wide range of applications, from the rise of water in capillary channels in plants to blood flow in vessels and insects walking on water [64]. Consequently, capillary flow dynamics has been the subject of extensive investigation.

Capillary-scale interactions of polymers, in particular, have captured the interest of numerous researchers. These are often inspired by natural phenomena, such as the mating

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ritual of leopard slugs (*Limax maximus*), where the animals produce a concentrated mucus that forms a viscoelastic ligament [152]. This polymeric thread exhibits high extensional viscosity, allowing it to stretch into a stable, meter-long filament that supports the weight of both slugs. Similar stability is observed in the splashing dynamics of saliva during a sneeze, where the presence of mucins—long-chain glycoproteins—enables the fluid to resist immediate breakup [160]. Unlike Newtonian fluids that atomize rapidly, the viscoelasticity of mucosalivary fluid allows long liquid filaments to remain stable outside the respiratory tract, as the polymers undergo significant extension to counteract the surface tension that would otherwise drive fragmentation. Similarly, capillary-scale polymer interactions are significant in processes such as 3D printing [96]. In these processes, the extension of polymers must be accounted for when designing and predicting flows, as the viscoelastic ink must form a continuous liquid filament spanning the gap between the nozzle and the substrate without breaking. A thorough understanding of how these polymers extend and interact at the capillary scale is vital for optimizing printability, as it dictates the stability of the extruded thread and prevents issues like nozzle clogging or unintended bead breakup [159].

Even dilute polymer concentrations modify the capillary-scale extensional flows in several notable ways - a behavior that differs from shear flow for the same solution, where little to no shear thinning is observed. Extensional flows in such polymer solutions, known as Boger fluids, exhibit several stages in the thinning dynamics. The initial stage typically resides in the Newtonian regime, shown in Fig. 1.5(a), where the thinning is dominated by Newtonian effects such as capillarity, inertia, or viscosity. In this state, the dissolved polymers remain fully coiled and do not interact with the surrounding solvent; consequently, the thinning dynamics typically follow a capillary instability or power-law thinning [33, 48, 129]. Without polymers, the local strain-rate in the liquid

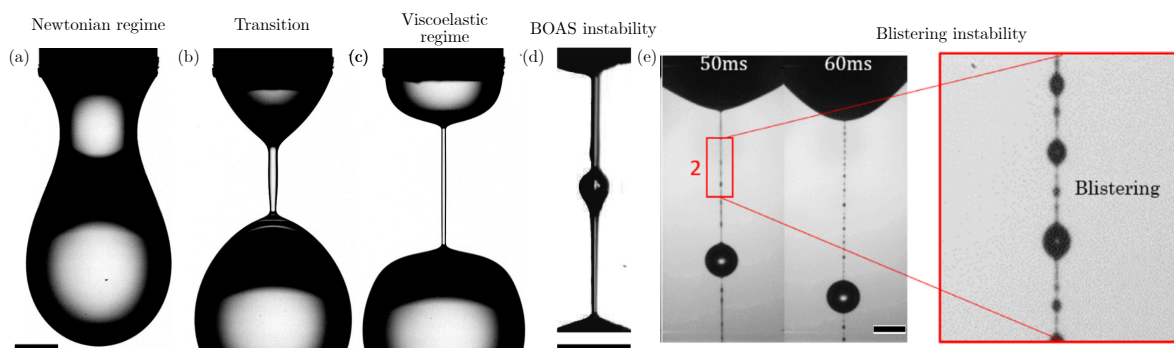


FIGURE 1.5: (a) - (c): Sequential stages of liquid bridge thinning, showing the (a) Newtonian regime, (b) the transition, and (c) the viscoelastic regime where the formation of a stable, cylindrical ligament occurs. (d) The onset of the beads-on-a-string (BOAS) instability is a capillary-driven phenomenon in which surface tension forms spherical beads connected by thin, viscoelastic filaments. [Wagner *et al.* [185], Reprinted figure with permission from Phys. Rev. Lett.] (e) The blistering instability is characterized by a pearling effect that originates from flow-induced phase separation and the coupling of elastic stress with local polymer concentration. [Deblais *et al.* [36], Reprinted figure with permission from Phys. Rev. Lett.]

bridge would eventually diverge into a singularity, leading to bridge rupture. However, if dissolved polymers are present, the local strain rate eventually reaches the limit of the coil-stretch transition, resulting in an abrupt uncoiling of the chains [63]. Once fully stretched, the resulting excluded volume effects become localized, and the stretched polymers stabilize the liquid bridge. This stabilization suppresses the singularity [3], and leads to the formation of characteristic long, cylindrical, and stretchy ligaments, as illustrated in Fig. 1.4(a)-(b).

The transition dynamics from the Newtonian to the viscoelastic regime (Fig. 1.5(b)) have remained elusive due to the extremely short time scales involved—often much shorter than the polymer relaxation time, as the bridge must be stretched faster than the chains can relax. Recent work by Thiévenaz *et al.* [175] revealed that the neck thickness during this transition in a particle-laden suspension depends on the solid volume

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fraction, indicating that both geometry and local strain rates influence the coil-stretch transition. Furthermore, by rescaling the strain rate associated with the minimum neck thickness by the critical transition strain rate, they demonstrated a universality during this transition. Understanding the role of polymers in this transition is essential for developing a continuous function for the capillary flow dynamics of polymer solutions in liquid bridges. Motivated by this, Chapter 2 investigates how polymer concentration, molecular weight, solvent viscosity, and initial droplet size influence the geometry of the liquid bridge during this transition. As discussed in detail later, we show that the universality of the strain-rate during transition extends across these parameters.

Once the thinning dynamics enter the viscoelastic regime, the evolution of the filament, which has an elongated and cylindrical shape, shown in Fig. 1.5(c), is described by:

$$h_{\min} = h_{\text{EC}} \left(\frac{Gh_{\text{EC}}}{\gamma} \right)^{1/3} e^{-\frac{t}{3\lambda_{\text{R}}}} \quad (1.1)$$

where h_{EC} is the thickness of the liquid neck at the onset of the elasto-capillary regime, λ_{R} is the characteristic time scale associated with fully stretched polymers relaxing back to a coiled state, and γ is the surface tension of the solution. The cylindrical ligament seen in Fig. 1.5(c) is essentially what is seen in the hanging threads of the leopard slugs or saliva ligaments shown in Fig. 1.4. The expression (Eqn. 1.1) has been investigated extensively [5, 7, 53] and is used in the present work to describe flow dynamics during droplet pinch-off (Chapter 2), bubble pinch-off (Chapter 3), and within capillary liquid bridges (Chapter 5). Although λ_{R} is not strictly the relaxation time of the polymers, it provides a useful time scale to describe the process, particularly for liquid bridges between solid particles; it is utilized in Chapter 5 to extend the study of rupture distances in capillary liquid bridges.

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In theory, according to Eqn. 1.1, a polymer chain can extend infinitely; however, real polymer chains possess finite extensibility. The final stages of thinning in polymer solutions are therefore characterized by the appearance of distinct "beads-on-a-string" (BOAS) structures or blistering instabilities. Wagner *et al.* [185] attributed the onset of such instabilities to asymmetry in the liquid bridge. According to Deblais *et al.* [36], the BOAS instability is primarily a capillary instability where surface tension drives the minimization of the liquid thread's surface area. While the polymers provide the elastic resistance that prevents the thread from snapping, the initial formation of these beads is often triggered by inherent geometric asymmetry in the liquid bridge. In contrast, the blistering instability is a pearling phenomenon that originates from flow-induced phase separation caused by a fundamental coupling between elastic stress and local polymer concentration [36]. Both BOAS and blistering instabilities are observed in the final stages of thinning described in this thesis, particularly in Chapters 3 and 5. However, as noted in Chapter 5, the capillary forces recorded during this stage are insignificantly small and unlikely to influence the bulk-scale properties of granular materials or powders; therefore, they are not investigated further here.

To characterize extensional flows, various flow configurations have been proposed and investigated. The most prominent methods, as illustrated in Fig. 1.6, rely on the capillary-driven self-thinning of liquid bridges or filaments to extract the rheological properties of complex fluids. The Capillary Breakup Extensional Rheometry (CaBER), popularized by Anna and McKinley [5], is a technique where a sample is rapidly stretched between two plates. However, it is often limited by a minimum measurable relaxation time of approximately 1 ms due to the dominance of inertial effects. To probe ultra-low viscosity fluids with sub-millisecond relaxation times, Keshavarz *et al.* [89] proposed the Rayleigh Ohnesorge Jetting Extensional Rheometry (ROJER), which utilizes the thinning of bridges

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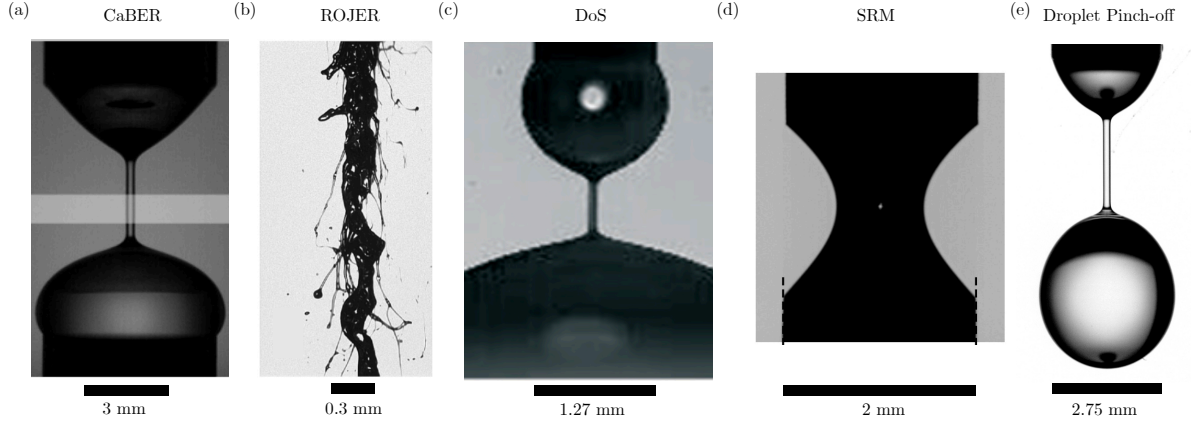


FIGURE 1.6: (a) CaBER involves a rapid step-strain followed by the passive filament thinning of a liquid bridge (b) ROJER utilizes high-frequency jet oscillations to probe thinning at much shorter time scales [Keshavarz *et al.* [89], Reprinted figure with permission from J. Non Newt. Fluids]. (c) DoS monitors the pinch-off of a liquid bridge formed as a pendant drop contacts a substrate. [Dinic *et al.* [42], Reprinted figure with permission from Soft Matter] (d) SRM employs a slow mechanical retraction to minimize inertial disturbances during the initial bridge formation, [Gaillard *et al.* [60], Reprinted figure with permission from Phys. Rev. Fluids]. and (e) Droplet Pinch-off investigates the self-similar thinning dynamics of a neck as a droplet detaches from a nozzle. These protocols allow for the resolution of viscous, elastic, and capillary forces across a wide range of fluid viscosities and relaxation times.

within an oscillating jet to resolve viscosities as low as 2.9 mPa·s. The Dripping-onto-Substrate (DoS) method, developed by Dinic *et al.* [42], offers a versatile alternative by measuring the thinning timescale of a liquid bridge formed between a dispensing nozzle and a substrate, capable of measuring relaxation times down to 0.1 ms. The Slow Retraction Method (SRM), used by Gaillard *et al.* [61] is specifically designed to minimize inertial disturbances during initial bridge formation, having reliably measured relaxation times as low as 10 ms. In the present work, we use the Droplet Pinch-off in Chapter 2 and capillary liquid bridges in Chapter 5, which are closer to the CaBER but not exactly the same. The droplet pinch-off method has been investigated by numerous researchers, such as Amarouchene *et al.* [3] and Tirtaatmadja *et al.* [177], who provide a canonical configuration for exploring self-similar thinning dynamics and the transition into

elasto-capillary regimes as a droplet detaches from a capillary needle. Collectively, these methods provide the necessary tools to resolve the complex interplay of viscous, elastic, and capillary forces across the diverse time scales encountered in polymeric solutions.

1.6 Capillary Flows of Liquid Bridges

Most existing descriptions of the capillary forces exerted by liquid bridges on solid particles have focused almost exclusively on Newtonian liquids [139, 194]. The primary objective of this thesis is to establish a thorough understanding of capillary flows in viscoelastic polymer solutions—exploring the effects of concentration, molecular weight, geometry, and solvent viscosity—and to connect these dynamics to the capillary forces exerted on solid particles. To achieve this, we investigate the transition to the viscoelastic regime in Chapter 2 using the droplet pinch-off method, as illustrated in Fig. 1.6(e). In Chapter 3, we explore the inverse problem through bubble pinch-off in polymer solutions. This study extends the symmetry associated with singularity in Newtonian fluids for droplet pinch-off and bubble pinch-off, shown by Burton *et al.* [21] and Thoroddsen *et al.* [176], to viscoelastic polymer solutions. Our findings successfully integrate polymer solutions in inviscid solvents into the Newtonian framework, revealing a Newtonian regime that maintains the same scaling exponent as water—even at high concentrations—followed by a transition to the exponential thinning dynamics characteristic of elasto-capillary flows. While recent studies [182] suggest that the onset of exponential thinning depends on the scale of the system that sets the bubble size, our work highlights the fundamental role of symmetry and provides a robust framework for the scales investigated herein.

A critical challenge in modeling these systems is the transition in the thinning dynamics from Newtonian to viscoelastic behavior. While we develop independent expressions for

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the axial forces in the two regimes in Chapter 5, a continuous description that connects them is currently lacking. Establishing the mechanisms governing this transition was one of the primary focuses of this research, since a continuous function is essential for numerical simulations. Consequently, a significant portion of this thesis, which has been published [144], was dedicated to characterizing the dynamics of this transition. The insights gained from these fundamental studies are applied to the development of specialized instrumentation and models. In Chapter 4, we describe the protocol for a custom capillary rheometer designed to measure the extensional flow of liquid bridges between model spherical particles. The results of these measurements are presented in Chapter 5, where we propose a first-order model to account for the axial forces exerted by polymeric liquid bridges on solid particles at various separation velocities. The velocity was chosen here as the controlling parameter for dynamics rather than an exponential separation like in CaBER or gravitational stretching due to the relevance of velocity in describing bulk granular flows. This model successfully extends particle-particle capillary force descriptions to polymeric systems, providing parameters that are particularly useful for Discrete Element Method (DEM) simulations. Finally, we conclude with a discussion in Chapter 6 on how microscopic polymer-driven capillary interactions influence the macroscopic behavior of bulk solid flows in industrial and natural systems.

1.7 Why gap-dependent Force Measurements are Essential

At the grain scale, inter-particle cohesion is frequently approximated using the Bond number, $Bo = \rho g d^2 / \gamma$. In this simplified framework, the cohesion number is often treated as inversely proportional to the Bond number ($Co \propto Bo^{-1}$), leading to a force model



FIGURE 1.7: Thinning of a liquid bridge of (a) Water, and (b) PEO of $M_w = 4000$ kg/mol with 1% by mass concentration prepared in water. The liquid bridge is positioned between two beads of radius $R = 2$ mm and separated with a velocity, $v = 10$ mm/s.

that depends primarily on surface tension: $F = 2\pi R\gamma \cos \theta$ [80]. While computationally convenient, this approach is severely limited. It treats the cohesive force as a static constant, ignoring the critical influence of geometric variables such as liquid volume and, crucially, the separation gap between particles [103, 139].

More advanced models have attempted to correct this by accounting for the gap distance, particle velocity, and liquid volume. However, these improvements have been almost exclusively restricted to Newtonian fluids. This creates a significant knowledge gap because many practical fluid systems—as detailed in § 1.3 and § 1.4—are inherently non-Newtonian. Real-world cohesive granular flows often involve binders containing dissolved polymers (e.g., bacterial biofilms), clay suspensions, or surfactants. In these complex fluids, the microscopic force is no longer governed by surface tension and viscosity

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alone; it is fundamentally altered by the fluid’s rheological history and elasticity.

Consequently, current mechanistic models for bulk granular systems lack a description of polymer-mediated cohesion. This thesis addresses this specific deficiency. By quantifying the gap-dependent forces in viscoelastic liquid bridges (Chapter 5), we provide the necessary physical data to extend granular rheology models beyond the Newtonian limit. Given the ubiquity of polymers in industrial applications, such physically grounded models are essential for developing accurate kernels for processes like granulation and agglomerate fragmentation, where the interplay of strain rate and polymer rheology determines the bulk flow behavior.

Publications related to the thesis from the author

1. **Rajesh, S.**, Thiévenaz, V., and Sauret, A. (2021). "Transition to the viscoelastic regime in the thinning of polymer solutions." *Soft Matter*, 18(16):3147—3156 [[144](#)].
2. **Rajesh, S.**, Thiévenaz, V., Peddada, S. S., and Sauret, A. (2022). "Pinch-off of bubbles in a polymer solution." *Journal of Non-Newtonian Fluid Mechanics*, 310:104921 [[145](#)].
3. **Rajesh, S.**, Tinianov, R. S., and Sauret, A. "Axial forces in capillary liquid bridges of polymer solutions." *In Preparation*.

Chapter 2

Capillary flow dynamics in polymer solutions

Capillary flows are encountered in various situations, such as water rising in plants [99, 178], blood flow [27, 124], and in various industrial processes [100, 189]. A number of methods have been used to experimentally investigate them, such as capillary liquid bridges, droplet pinch-off, and the pinch-off of a bubble in a liquid (see Fig. 2.1). Although surface tension governs the thinning and break-up dynamics of a liquid across all configurations, the opposing forces can vary depending on the configuration.

As introduced in Chapter 1, the thinning dynamics of Newtonian liquid bridges have been investigated by numerous past studies. For instance, in the liquid bridge configuration [101, 198], shown in Fig. 2.1(a), the liquid is initially placed between two plates, or spheres, depending on the geometry of interest, and is then stretched at a prescribed rate. When the liquid is pulled apart, capillary forces due to surface tension cause the liquid bridge to adopt a particular shape that minimizes energy. Depending on the liquid

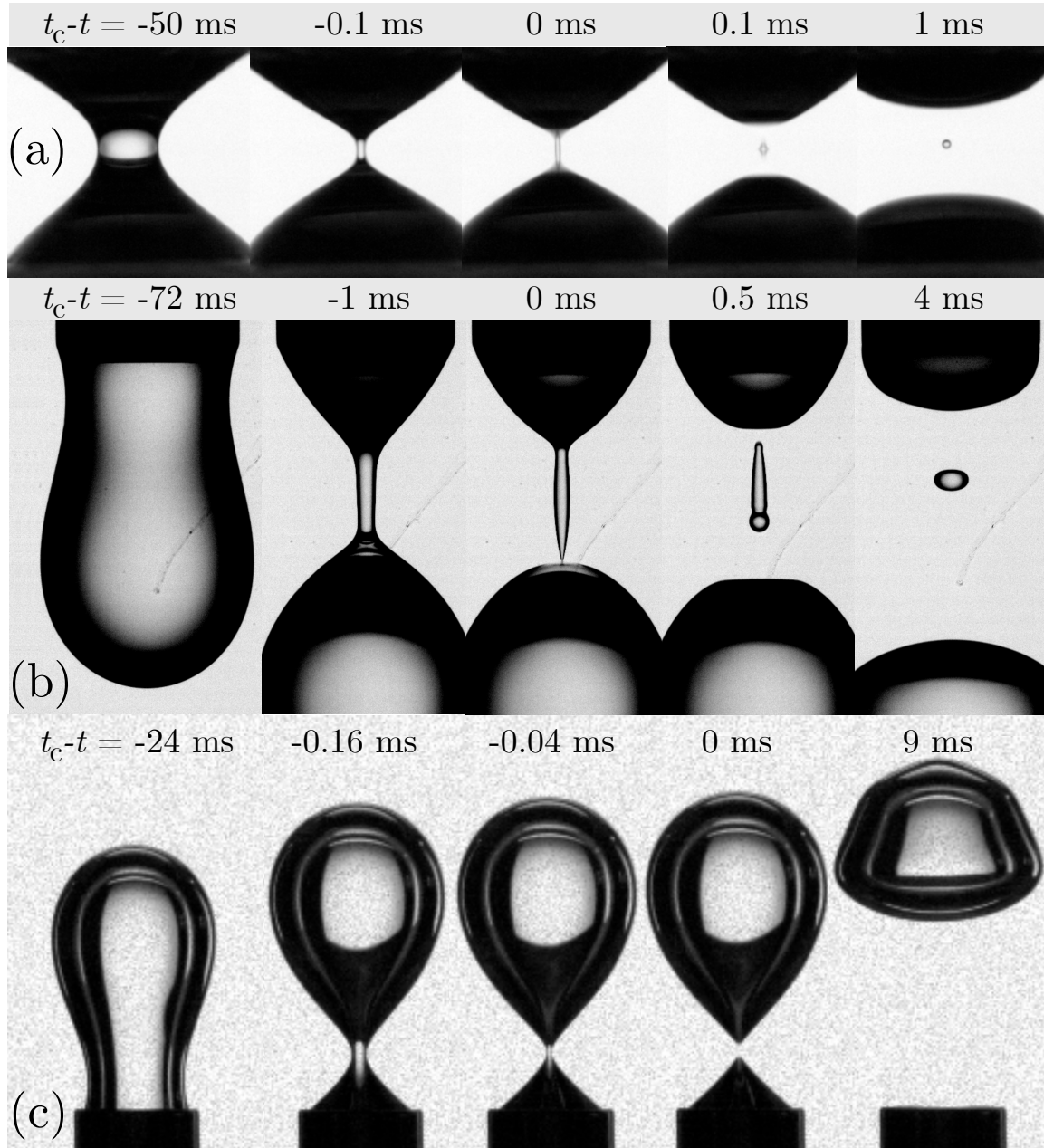


FIGURE 2.1: Thinning of a drop of 75/25% water/glycerol solvent (a) between two spherical particles. The particle diameter is 3 mm (b) as a droplet, from a nozzle, under the influence of gravity (c) Thinning of an air bubble in the solvent.

viscosity and the inertia imparted to the liquid, the thinning dynamics can either lead to an instability that causes the liquid bridge to rupture or to a break-up dynamics controlled by an inertio-capillary or visco-capillary balance. When we introduce polymers into the Newtonian solvent, the thinning dynamics are modified by the presence of polymers [5]. It has been established that the initial thinning dynamics of a polymer solution is similar to the Newtonian solvent in which it was prepared. However, the presence of polymers results in a suppression of the abrupt droplet break-up that is observed for Newtonian liquids [5]. Around the time when we expect the droplet to pinch-off, the thinning dynamics transitions to a viscoelastic regime, where the force balance is drastically modified.

Another configuration for capillary thinning dynamics is the droplet pinch-off, as shown in Fig. 2.1(b) for a Newtonian liquid. In the droplet pinch-off configuration, a small volume of droplet is formed by extrusion at the end of a nozzle. When the droplet accumulates sufficient volume, the weight of the droplet starts to pull it down. An opposing force due to surface tension maintains the contact of the drop with the nozzle as the droplet begins to thin. As the droplet thins, depending on the viscosity of the liquid, the thinning dynamics depends on the inertial forces [86], or the viscous forces [129]. Introducing polymers into the solvent leads again to a modification of the thinning dynamics similar to the liquid bridge configuration. In the following section, we explore in more detail the thinning dynamics of a drop of polymer solution. In particular, we investigate the transition dynamics of a drop of polymer solution from its initially Newtonian-like thinning to a viscoelastic thinning.

Transition to the viscoelastic regime in the thinning of polymer solutions

The work summarized here has been published as S. Rajesh, V. Thiévenaz, and A. Sauret (2022). "Transition to the viscoelastic regime in the thinning of polymer solutions". Soft Matter 18, 3147-3156.

2.1 Introduction

The formation of liquid droplets is a common phenomenon in everyday life [91, 183, 184] in situations as diverse as sneezing [120, 160], spraying of pesticides [105], inkjet printing [40, 104], bioprinting of tissues,[121], or combustion [79, 192]. When a liquid droplet detaches from a nozzle, the neck that binds the droplet to the nozzle thins down and eventually breaks. The break-up corresponds to a finite-time singularity [47]. In many industrial applications, the liquid is not a homogeneous Newtonian fluid but often contains particles, solutes, cells, or other components. At certain length and time scales, these components interact with the flow and sometimes influence capillary flows dramatically. The instantaneous and localized change in rheology can even temporarily suppress the singularity.

In the case of polymers, the question of the time scale of the flow arises. At rest, a polymer chain adopts the shape of a coil to maximize its entropy, but under a strong extensional flow it stretches: this is the coil-stretch transition [63]. This conformational change modifies the interactions with the surrounding fluid. In the coiled state, the chain has the approximate shape of a sphere: only the monomers on the surface contribute to

hydrodynamic friction. As the chain stretches, more of the monomer units are exposed to the external flow, and the polymer exerts more friction to the fluid. Therefore, the viscosity of a dilute polymer solution follows Einstein’s law at low strain rates but increases dramatically at high strain rates. Moreover, the chains can absorb some elastic energy so that the solution is viscoelastic.

The viscoelastic nature of a solution of polymers can be observed during the pinch-off of a drop. Initially, a drop of polymer solution seems to detach like a drop of a Newtonian liquid, but at some point, the neck turns into a long and slender filament [3, 35, 41, 44, 83, 172]. The thinning continues, but much more slowly than the initial necking, until the filament eventually breaks. In the meantime, capillary instability may cause one or more large droplets to appear on the filament, the so-called “beads-on-a-string” instability [13, 31]. A secondary “blistering” instability, occurring in the last stages of thinning and forming many tiny droplets along the filament, has also recently been described [36].

Rather than considering the process of viscoelastic thinning, which has been characterized extensively in the past, the present study focuses on its onset. The sudden change in the thinning dynamics are due to the coil-stretch transition, as reported by Amarouchene *et al.* [3]. At rest, a polymer chain adopts the shape of a coil to maximize its entropy. Since stretching reduces entropy, it is opposed by a resisting force that increases linearly with the deformation ε [34]. If the force applied onto the chain is strong enough, the coil will unwind and stretch [63]. However, as soon as the external force becomes comparable to the Brownian motion, the resisting force f becomes non-linear, $f \sim \varepsilon^{3/2}$, because the excluded volume hinders the stretching of the chain [161]. This was theoretically predicted in the 1970s by Pincus [138] and only recently proven experimentally [155]. Once the polymer is sufficiently stretched, self-avoidance effects weaken, and the chain exhibits an

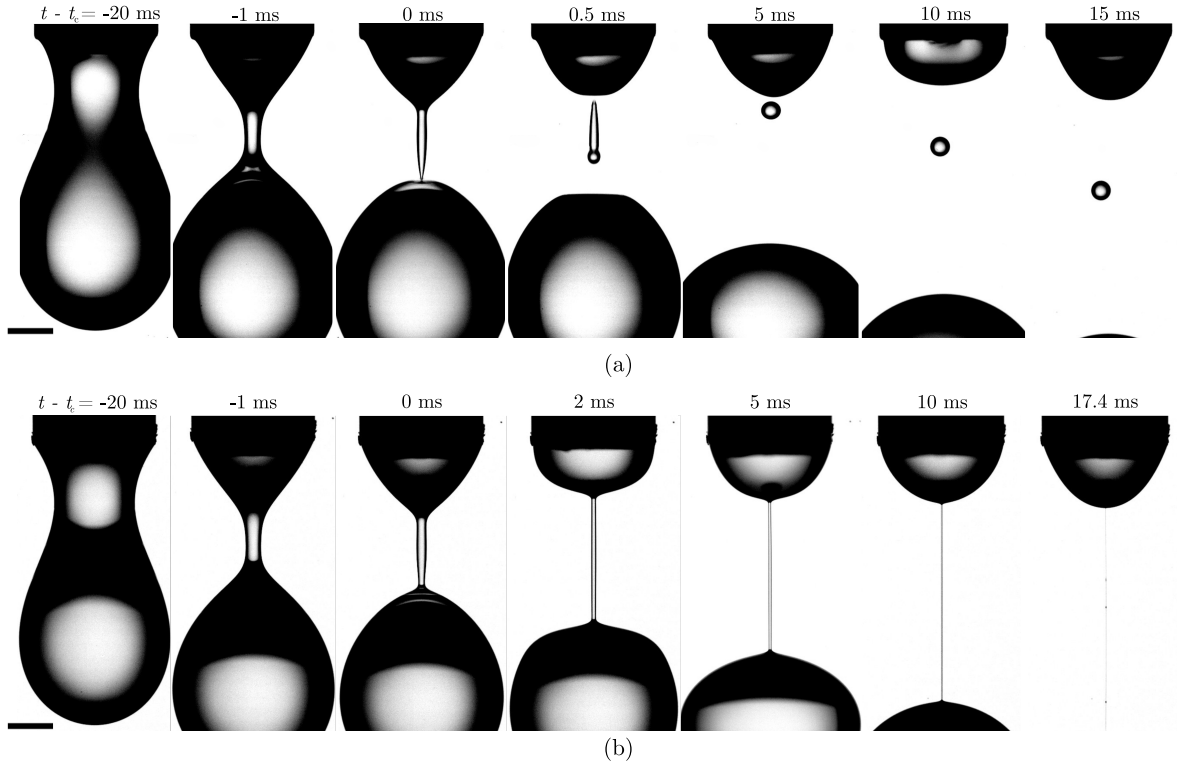


FIGURE 2.2: Pinch-off of a drop of (a) pure solvent (50/50 wt% water/glycerol) and of (b) a dilute polymer solution ($c = 0.5$ %wt 300K PEO in 75/25 wt% water/glycerol). Adding a small quantity of polymer prevents the singularity and the fast break-up of the liquid neck between the drop and the nozzle. The scale bars are 1 mm. The movies of these experiments are available in Supplementary Materials 2.6.

ideal behavior that opposes a linear resisting force [161]. In other words, past a sufficient elongation, stretching the polymer chains suddenly becomes easier.

To investigate the transition between the Newtonian and the viscoelastic regime, we consider here the pinch-off of drops of dilute polymer solutions, with different polymer concentrations, molecular weights, and solvent viscosities. We present in § 2.2 our experimental methods and the polymers used. We then recall the main features of the thinning of a polymer solution in § 2.3: first, the Newtonian regime, in which the solution thins down like an inviscid Newtonian liquid following a power law; then the viscoelastic regime, characterized by an exponential decay of the filament thickness. Existing results

for the relaxation time are also recovered. We then describe the thinning in terms of strain rate and identify two critical quantities that mark the coil-stretch transition: the critical strain rate $\dot{\epsilon}_c$ and the critical thickness h_c . We provide empirical scaling laws for the dependence of these parameters on the polymer concentration, solvent viscosity, and nozzle diameter. Finally, we show that the strain rate follows a self-similar dynamics around the transition, entirely controlled by the critical strain rate. This result enables us to highlight and discuss in § 2.4 the difference between two characteristic times, one associated with the coil-stretch transition and the other with the relaxation of the stretched polymer chains.

2.2 Experimental methods

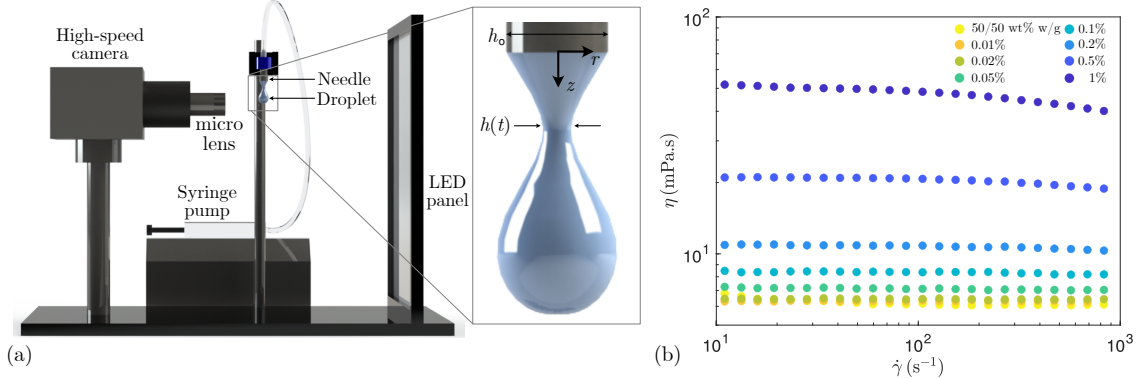


FIGURE 2.3: (a) Schematic of the experimental setup. $h_{\min}$ corresponds to the minimal diameter of the liquid thread. (b) Evolution of the shear viscosity η with the shear rate $\dot{\gamma}$ for polymer solutions prepared with different mass concentration c of 300K PEO in a 50/50 wt% water/glycerol solvent.

The experimental setup, shown in Fig. 2.3(a), consists of slowly extruding a dilute polymer solution through a nozzle to form a pendant drop, which then detaches when its weight overcomes capillarity. As the drop falls, it is bound to the nozzle by a liquid neck that thins and stretches into a long filament before eventually breaking. Most experiments

Chapter 2. Capillary flow dynamics in polymer solutions

PEO M_w (g/mol)	Composition (water/glycerol wt%)	c (wt%)	$[\eta]$ (m^3/kg)	c/c^*	η_s (mPa s)	η (mPa s)	λ_R (ms)
3×10^5	75/25	0.01-1	0.401	0.044-4.47	2.16	2.16-19.5	0.165-4.65
3×10^5	50/50	0.01-1	0.307	0.056-5.56	6.06	6.28-40.91	0.96-11.1
4×10^6	75/25	0.01-1	2.65	0.36-37	2.16	2.56-98.3	24-505

TABLE 2.1: Properties of polymer solutions used to carry out pinch-off experiments: M_w is the molar weight of the polymer, c the mass concentration in polymers, $[\eta]$ is the intrinsic viscosity, c^* is the critical overlap concentration, η_s is the viscosity of the solvent without polymer, η is the shear viscosity of the polymer solution, and λ_R is the relaxation time.

are performed using a nozzle with an outer diameter of 2.75 mm. Some additional experiments have been done with nozzles of outer diameter $h_0 = 0.4, 0.9$, and 1.6 mm (see Supplementary Materials 2.6). The quasistatic growth of the drop is achieved with a syringe pump (KDS Legato 110) at $Q = 0.2$ mL/min (see Supplementary Materials 2.6). We ensured that slightly changing the flow rate did not influence the dynamics reported in this study (see Fig. S1, supplementary data). The thinning is recorded using a high-speed camera (Phantom VEO710), a macro lens (Nikon Micro-NIKKOR 200 mm f/4 AI-s), and a microscope lens (Mitutoyo X2). The setup is backlit using an LED panel (Phlox), and the resulting resolution is about 10 μm /pixel. Depending on the composition of the polymer solution, the frame rate is varied between 500 fps and 10,000 fps to ensure a precise measurement of the instantaneous strain rate of the liquid neck (see Supplementary Materials 2.6). After the recording, we extract the liquid contour in ImageJ and use a custom-made Python routine to determine the neck thickness at its thinnest point, $h_{\min}$.

The polymer solutions are prepared by dissolving polyethylene oxide (PEO, Sigma-Aldrich) into a mixture of deionized (DI) water and glycerol (Sigma-Aldrich). We use PEO of two different molecular weights: $M_w = 300$ kg/mol and $M_w = 4000$ kg/mol, further referred to as 300K PEO and 4000K PEO. The mass concentration of PEO in the solution varies from $c = 0.01\%$ to $c = 1\%$. Varying the amount of glycerol (from 0 to 60% per weight)

enables us to tune the solvent viscosity (from $\eta_s = 1 \text{ mPa s}$ to $\eta_s = 10 \text{ mPa s}$). Water and glycerol are first mixed, then the PEO powder is added. The mixture is then placed on a roller mixer and gently mixed for at least 24 hours.

The surface tension of the solution is around 60 mN/m and does not vary significantly in the range of glycerol content and PEO concentration used here [30, 59]. We measured the viscosity of each solution using a rheometer (Anton Paar MCR 92) with a 50 mm -wide 1° cone-plate geometry. Fig. 2.3(b) shows the typical variations of the viscosity η with the shear rate $\dot{\gamma}$ and with the polymer concentration of 300K PEO for a 50/50 wt% water/glycerol solvent (see also Supplementary Materials 2.6). The viscosity of the PEO solutions increases with the polymer concentration. The shear viscosity of the PEO solutions remains Newtonian at small concentrations but exhibits a slight shear-thinning at the highest concentration used here. For each solution, we provide in Tab. 2.1 the concentration scaled by the critical overlap concentration c^* , defined as $c^* = 0.77/[\eta]$ [67], where $[\eta] = [(\eta - \eta_s)/\eta_s]/c$ is the intrinsic viscosity. For a solution of 300K PEO in a 50/50 wt% water/glycerol mixture, $[\eta] = 0.307 \text{ m}^3/\text{kg}$, and $c^* = 0.22\%$.

2.3 Results

Newtonian and viscoelastic regimes

In Fig. 2.4(a), we show the classical difference between the thinning dynamics of a drop of dilute polymer solution (in blue) and a pure Newtonian solvent (in red). We observe that the dilute polymer solution follows the same dynamics as the solvent, up to a certain point. In the regime of small Ohnesorge numbers ($\text{Oh} = \mu/\sqrt{\rho\sigma h_o} \lesssim 0.24$) considered here, this first regime can be described as the thinning of an inviscid Newtonian fluid,

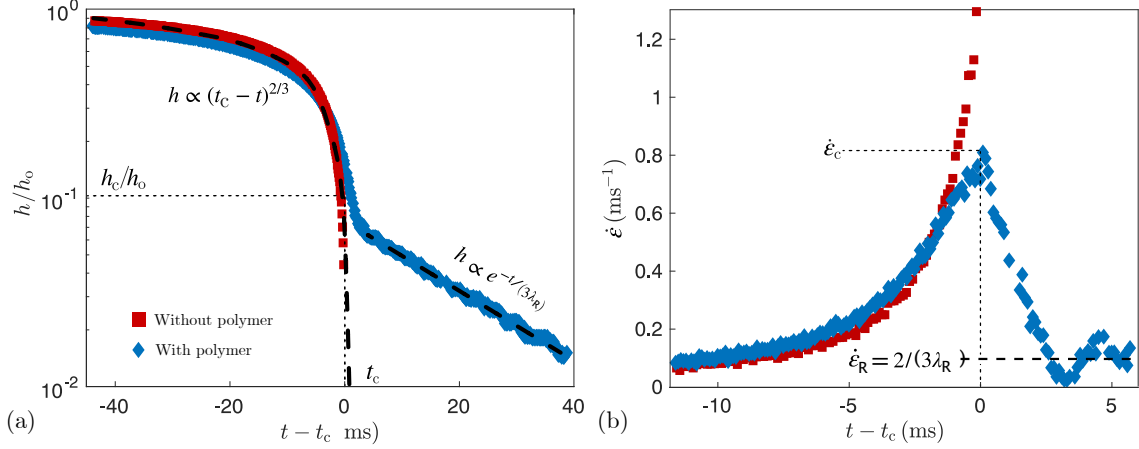


FIGURE 2.4: Time evolution of (a) the rescaled neck thickness $h_{\min}/h_o$ and (b) the strain rate $\dot{\epsilon}$ for the pure solvent (50/50 wt% water/glycerol, red squares) and a dilute polymer solution ($c = 0.5\%$ 300K PEO in 50/50 wt% water/glycerol, blue diamonds).

which is driven by the capillary pressure, to which inertia resists. The thickness of the neck $h_{\min}$ is given by the scaling law [86]:

$$h_{\min} = A(\eta) [\gamma(t_c - t)^2/\rho]^{1/3}, \quad (2.1)$$

where $A(\eta)$ is a prefactor that weakly depends on the viscosity of the solvent, as reported by Thiévenaz *et al.* [175]. Here γ and ρ are the surface tension and the density of the liquid, respectively. We can fit Eqn. (2.1) to both the solvent and dilute polymer solution in the Newtonian regime, and obtain a good agreement as shown in Fig. 2.4(a). Here, we define t_c as the fitting parameter of Eqn. (2.1). For the polymer solution t_c represents the moment of the transition from the Newtonian to the viscoelastic regime. Using this definition of t_c , we can define the critical thickness of the neck at transition as $h_c = h_{\min}(t_c)$.

Polymer solutions do not break at $t = t_c$ because of the presence of polymers. Initially coiled, the polymer chains unwind under the increasing stress, as shown in Fig. 2.5. This

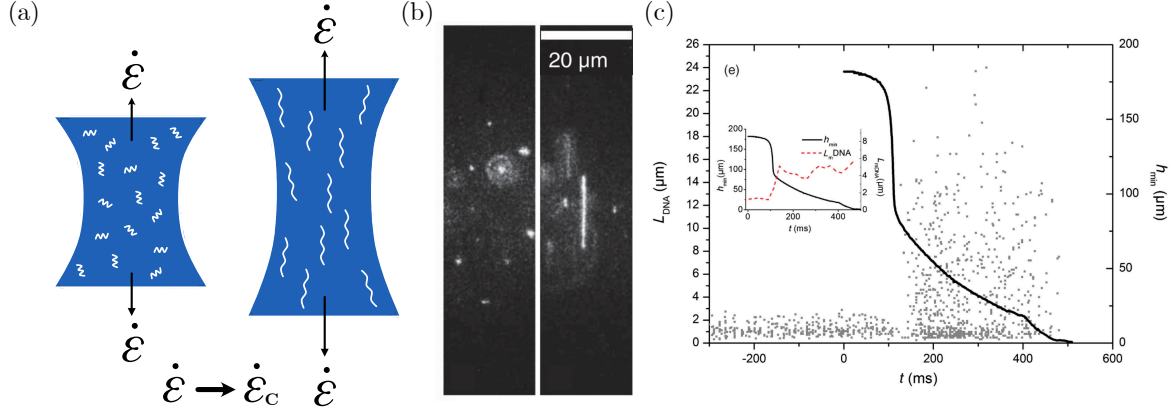


FIGURE 2.5: (a) Schematic of the coil-stretch transition when the local strain rate $\dot{\epsilon}$ exceeds the threshold $\dot{\epsilon}_c$ (b) Visualization of the coil-stretch transition of individual DNA molecules in a thinning liquid neck. [Left] Initial regime where molecules appear as bright specks, representing the coiled state. [Right] Onset of the transition at the center of the filament, where a single molecule is stretched into a linear conformation by the extensional flow. (c) Late-stage elasto-capillary regime showing a fully extended polymer chain, with its length L used to determine the molecular extension and local elastic stress. [Images from Ingrèneau *et al.*, [77], Reproduced under CC BY 3.0]

coil-stretch transition has been directly observed as well; for instance, to characterize the molecular dynamics during filament thinning, Ingrèneau *et al.* [77] utilized a dilute solution of λ -DNA labeled with YOYO-1 fluorescent dye, which served as model polymer chains in a droplet pinch-off configuration. The experimental setup employed a high-power laser and an EMCCD camera to capture the fluorescent emission of individual molecules as they flowed through the thinning liquid neck. In the early stages of thinning (Fig. 2.5 (b) left), the strain rate is low, and the DNA molecules appear as bright, localized specks, indicating they remain in a coiled conformation. As the neck reaches a critical thickness (Fig. 2.5 (b) right), a single molecule at the center of the filament undergoes the coil-stretch transition, appearing as a long, continuous white line of light while surrounding molecules remain coiled. Finally, in the late-stage elasto-capillary regime (Fig. 2.5 (c)), the strong extensional flow results in the full extension of the polymer chain, where its measured length L reaches a significant fraction of its total contour length L_0 , directly confirming

the molecular origin of the elastic stress that stabilizes the filament.

Once the polymer chains are unwound, they increase the viscosity of the solution and make it viscoelastic. As a result, for $t > t_c$, the thinning dynamics of the polymer solution slows down dramatically, and enters the viscoelastic regime. The neck becomes a long filament of uniform thickness, which thins down exponentially [5]:

$$h_{\min} \propto e^{-t/(3\lambda_R)}, \quad (2.2)$$

where λ_R is the longest relaxation time of the polymer, it has also been recently shown that the liquid interface exhibits a self-similar shape during the viscoelastic thinning of a polymer solution [35].

The viscoelastic thinning of dilute polymer solutions has been considered in many past studies [114]. In particular, it has been shown that by adding a dilute amount of polymer to a solvent, the dynamics can be described in terms of the thickness of the neck $h_{\min}$, or in terms of strain rate at the neck $\dot{\varepsilon} = (\partial v_z / \partial z)|_{h_{\min}}$, where v_z is the axial component of the velocity [3]. The latter can be expressed through the continuity equation:

$$\dot{\varepsilon} = -\frac{2}{h_{\min}} \frac{\partial h_{\min}}{\partial t}. \quad (2.3)$$

For a Newtonian fluid, the minimum neck thickness $h_{\min}$ vanishes at time t_c , which is the moment the neck breaks. The evolution of $\dot{\varepsilon}$ for both the water/glycerol mixture and the dilute solution of polymers is shown in Fig. 2.4(b). In terms of strain rate, the Newtonian regime of thinning given by Eqn. (2.1) provides the expression:

$$\dot{\varepsilon} = -\frac{4}{3} \frac{1}{t_c - t}. \quad (2.4)$$

Therefore, for an inviscid Newtonian fluid, the strain rate diverges at pinch-off. For a dilute polymer solution, t_c also corresponds to the moment when the strain rate is maximal and reaches the critical strain rate $\dot{\epsilon}_c = \dot{\epsilon}(t_c)$ before relaxing to a constant value. This constant strain rate in the viscoelastic regime is $\dot{\epsilon}_R = 2/(3\lambda_R)$.

2.3.1 Influence of the polymer concentration and solvent viscosity on the thinning dynamics

The different features of the two thinning regimes, Newtonian and viscoelastic, and of the transition between them depend on the molecular weight of the polymer, its concentration, and on the viscosity of the solvent. In Fig. 2.6(a), we show the thinning dynamics of solutions of 300K PEO, with mass concentrations varying between 0.01% (yellow) and 1% (dark blue), in a 50/50 wt% water/glycerol solvent. First, we observe no significant influence of the polymer concentration on the Newtonian regime. Indeed, all the solutions follow the capillary-inertial scaling law given by Eqn. (2.1). The small differences observed in this regime are due to the variations in shear viscosity reported in Fig. 2.14(b). The differences appear at the transition, *i.e.*, at $t = t_c$. Depending on the concentration of polymers, the critical thickness of the neck at the transition, h_c , is different. Indeed, we observe that the more polymer in the solution, the thicker h_c is. We shall consider the variations of h_c with the different experimental parameters later in the chapter. In the viscoelastic regime, all dilute polymer solutions follow the exponential decay law given by Eqn. (2.2), but with a different relaxation time λ_R . As expected, λ_R increases with the polymer concentration [39].

Similar to the effect of the polymer concentration, we can characterize the effect of the solvent viscosity. Fig. 2.6(b) shows the thinning dynamics of solutions of 300K PEO

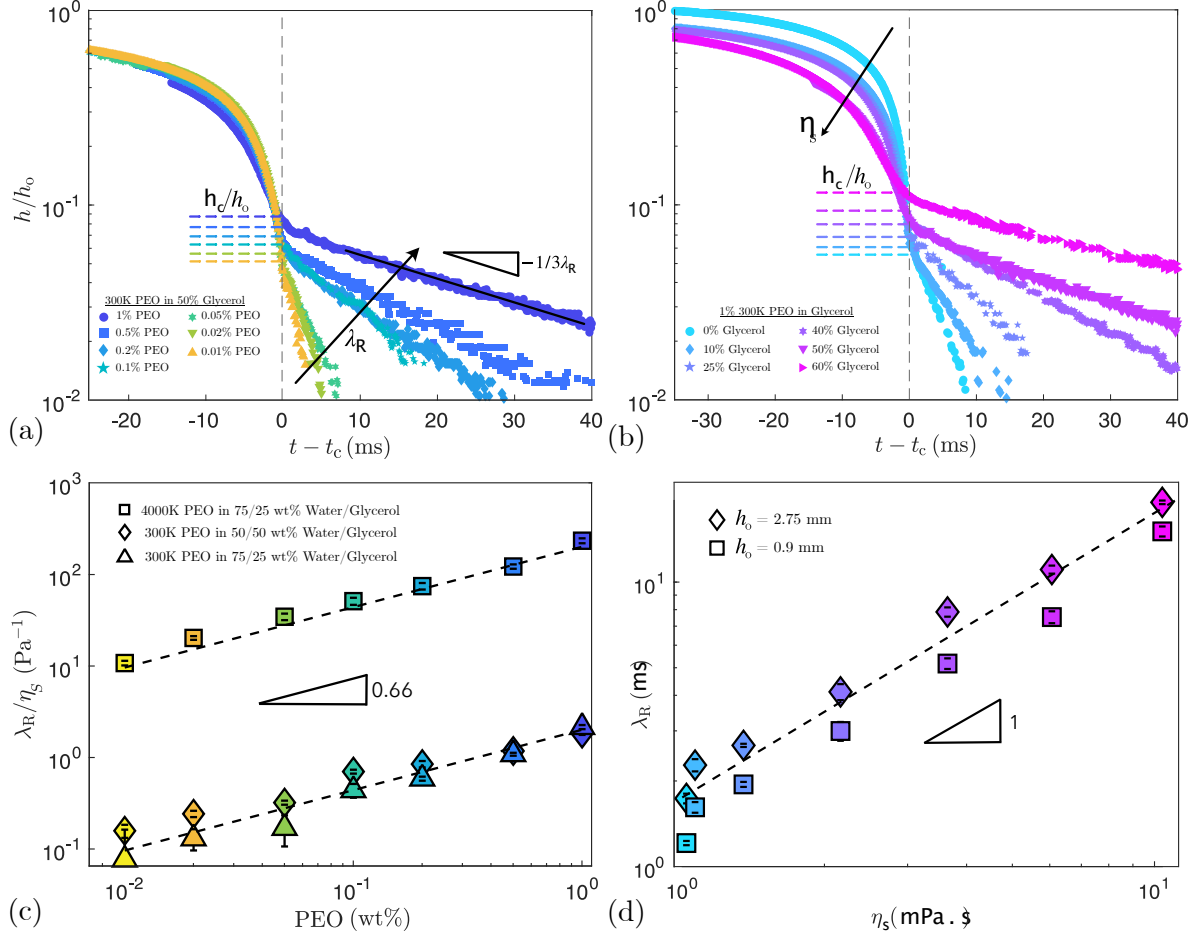


FIGURE 2.6: (a) Thinning dynamics for solutions of 300K PEO at various concentrations (from yellow: $c = 0.01\%$ to dark blue: $c = 1\%$) in a 50/50 wt% water/glycerol solvent. (b) Thinning dynamics for solutions with $c = 1\%$ of 300K PEO in solvents with different glycerol contents, hence different viscosity (from light blue: water only, $\eta_s = 1$ mPa s; to pink: 40/60 wt% water/glycerol, $\eta_s = 10.41$ mPa s). The data shown correspond to $h_0 = 2.75$ mm. (c) Relaxation time in the viscoelastic regime λ_R , rescaled by the solvent viscosity η_s , for increasing polymer concentration. The dashed lines represent the empirical law $\lambda_R/\eta_s \propto c^{0.66}$ [177], with a different prefactor depending on the molecular weight of the polymer. (d) Relaxation time λ_R as a function of the solvent viscosity η_s for two nozzle sizes. The dashed line represents the linear fit given by Eqn. (2.5).

Chapter 2. Capillary flow dynamics in polymer solutions

with a mass concentration of 1%, in water/glycerol mixtures where the mass fraction of glycerol is varied between 0% (light blue, pure DI water) to 60% (pink). At these moderate viscosities, the Newtonian regime still follows the capillary-inertial scaling law given by Eqn. (2.1). Nevertheless, as expected, a higher viscosity yields a slower thinning. The effect of the viscosity, in this case, is to change the prefactor in Eqn. (2.1) [175]. Similar to increasing the polymer concentration, increasing the solvent viscosity also increases the critical thickness at the transition h_c , as well as the relaxation time in the viscoelastic regime λ_R .

The relaxation time λ_R is of great interest to predict the thinning of dilute polymer solutions and has been the focus of many studies [150, 177]. In Fig. 2.6(c), we report the quantity λ_R/η_s when varying the polymer concentration c , and recover the result of Tirtaatmadja *et al.* [177]: $\lambda_R/\eta_s \propto c^{0.66}$. The relaxation time λ_R is also expected to scale like the longest relaxation time λ_z expected from the Zimm theory [201]:

$$\lambda_z \approx \frac{\eta_s M_w}{N_a k_B T}, \quad (2.5)$$

where N_a is the Avogadro number, k_B is the Boltzmann constant, and T is the temperature. In Fig. 2.6(d), we also recover this linear trend between λ_R and the solvent viscosity η_s .

This section was a reminder of classical results that focused solely on presenting the thinning dynamics, introducing the quantity of interest, and ensuring that we recover the results from the literature. The novelty in the analysis is presented in the following discussion, where we focus on the evolution of the strain rate at the transition. In particular, our results demonstrate that the transition also follows a self-similar evolution, whose only scale is the critical strain rate $\dot{\epsilon}_c$.

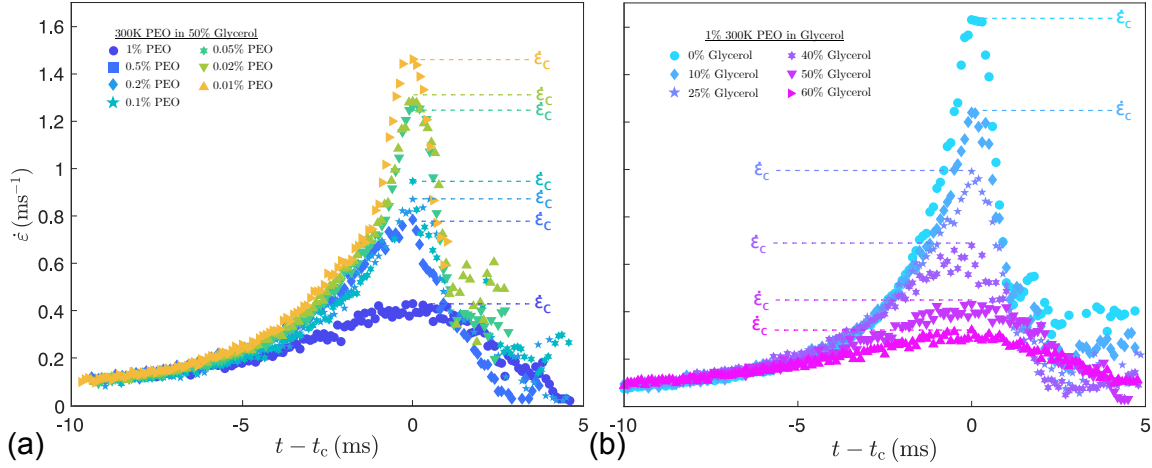


FIGURE 2.7: Time evolution of the strain rate $\dot{\epsilon}$ for dilute polymer solutions with (a) different concentrations of 300K PEO in 50/50 wt% water/glycerol solvent and (b) $c = 1\%$ 300K PEO in solvents with various water/glycerol mixtures. At the transition between the Newtonian and the viscoelastic regime ($t = t_c$) $\dot{\epsilon}$ reaches its maximum value $\dot{\epsilon}_c$.

As previously mentioned, the thinning of the polymer solution can also be described in terms of strain rate at the neck $\dot{\epsilon}$, defined in Eqn. (2.3). As illustrated in Fig. 2.4(b), $\dot{\epsilon}$ increases sharply during the Newtonian regime, reaches a maximum $\dot{\epsilon}_c$ at the onset of the coil-stretch transition, and immediately after quickly decreases. Fig. 2.7(a)-(b) show the evolution of $\dot{\epsilon}(t)$ for the experiments reported in Fig. 2.4(a)-(b). When the polymer concentration increases (Fig. 2.7(a), from yellow to blue), the curve $\dot{\epsilon}(t)$ flattens. A decrease in $\dot{\epsilon}_c$ implies the transition lasts longer. The trend is also similar when the solvent viscosity increases (Fig. 2.7(b), from light blue to pink). This similarity between the effects of polymer concentration and solvent viscosity suggests that a single mechanism drives the evolution of $\dot{\epsilon}_c$ at the transition.

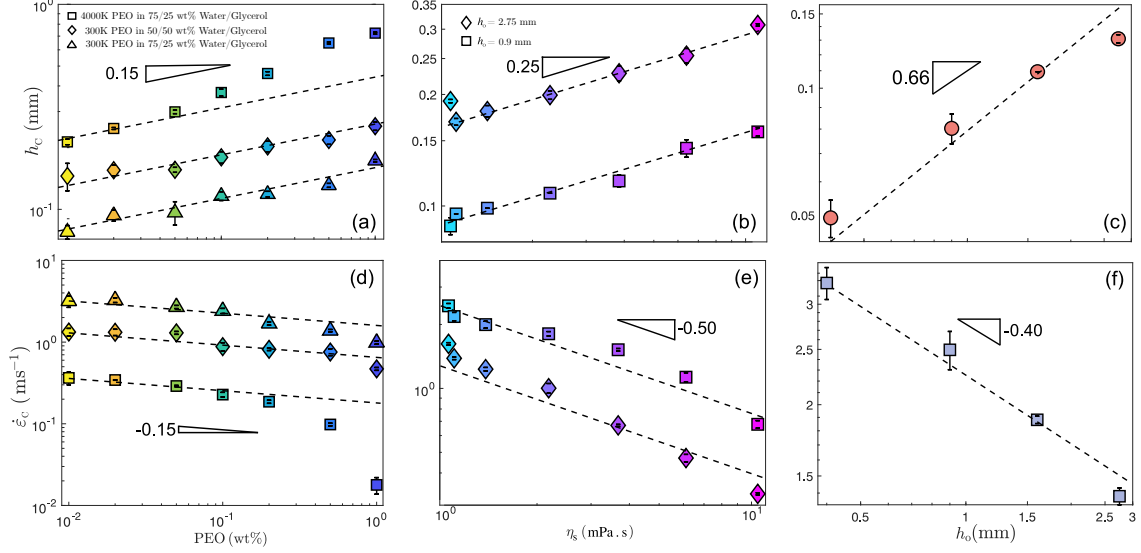


FIGURE 2.8: Evolution of (a)-(c) the critical neck thickness h_c and (d)-(f) the critical strain rate, $\dot{\epsilon}_c$ at the transition when varying (a) and (d) the concentration c of the polymer for 300K and 4000K polymers in different solvents, (b) and (e) the viscosity of the solvent η_s for $c = 1\%$ of 300K PEO, (c) and (f) the diameter of the nozzle h_0 for $c = 0.5\%$ of 300K PEO in a 75/25 wt% water/glycerol mixture.

2.3.2 Transition between the Newtonian and the viscoelastic regime

The critical thickness h_c and the critical strain rate $\dot{\epsilon}_c$ characterize the onset of the coil-stretch transition in the neck. These two parameters depend on all the experimental variables: the polymer concentration, the solvent viscosity, the polymer molecular weight, and the drop size. The evolution of $\dot{\epsilon}_c$ with those parameters can be fitted with power laws, as reported in Fig. 2.8(a)-(f).

As the polymer concentration increases, we observe an increase in the critical thickness h_c and a decrease in the critical strain rate $\dot{\epsilon}_c$ as reported in Fig. 2.8(a) and 2.8(d), respectively. Both quantities follow opposite power laws: $\dot{\epsilon}_c \propto c^{-0.15}$ and $h_c \propto c^{0.15}$. The prefactors of these scaling laws depend on the solvent viscosity and on the molecular

weight of the polymer. The more viscous the solvent and the higher the molecular weight, the lower $\dot{\epsilon}_c$ and the larger h_c . Therefore, increasing the viscoelastic behavior of the dilute polymer solution smooths the transition. For a high concentration of PEO (4000K, squares), the data match the scaling laws up to $c = 0.2\%$, which is about ten times larger than the overlap concentration ($c^* = 0.027\%$). Therefore, it appears that the present scaling law for h_c and $\dot{\epsilon}_c$ are valid for dilute and slightly semi-dilute solutions only.

Similarly, Fig. 2.8(b) and 2.8(e) show that as the viscosity of the solvent increases, $\dot{\epsilon}_c$ decreases and h_c increases, following the power laws $\dot{\epsilon}_c \propto \eta_s^{-0.50}$ and $h_c \propto \eta_s^{0.25}$. These scaling laws also depend on the diameter of the nozzle h_0 as demonstrated in Fig. 2.8(c) and 2.8(f). We naturally recover the same trend: a wider nozzle leads to a lower critical strain rate $\dot{\epsilon}_c$ and to a larger critical thickness h_c . We obtain the following scaling laws: $\dot{\epsilon}_c \propto h_0^{-0.40}$ and $h_c \propto h_0^{0.66}$. Finally, we can sum up the different contributions of these scaling laws:

$$\dot{\epsilon}_c \propto c^{-0.15} \eta_s^{-0.50} h_0^{-0.40}; \quad h_c \propto c^{0.15} \eta_s^{0.25} h_0^{0.66}. \quad (2.6)$$

2.4 Discussion

2.4.1 Characteristic thinning rate of the neck during the transition

The characterization reported in Fig. 2.8(a)-(f), and summed up in Eqn. (2.6), suggests that the product $h_c \dot{\epsilon}_c$ does not depend on the polymer concentration. We also notice that this quantity has the dimension of a velocity, and we therefore define this parameter as a critical velocity $v_c = h_c \dot{\epsilon}_c$ of the neck during the transition. Fig. 2.9 plots the evolution of

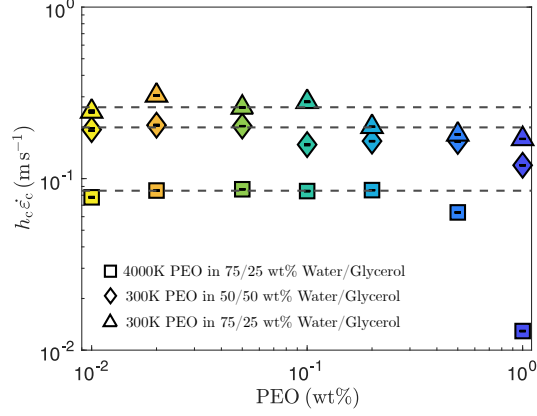


FIGURE 2.9: Evolution of $h_c \dot{\epsilon}_c$ with the concentration of PEO for different solvents and molecular weights of the polymer. The horizontal dotted line shows constant values of v_c .

v_c when varying the polymer concentration, for different viscosities of the solvent and polymer molecular weight. As expected, v_c is independent of the polymer concentration in the dilute regime. We observe the same abrupt decrease in the case of the 4000K PEO when the concentration c crosses 0.2% ($c = 7.4c^*$), consistent with the dilute regime limit. The value of v_c depends on the molecular weight of the polymer. Indeed, we measure for the 300K PEO $v_c = 0.26$ m/s in 75/25 wt% water/glycerol ($\eta_s = 2.16$ mPa.s) whereas we obtain $v_c = 0.08$ m/s for 4000K PEO. Note that according to Eqn. (2.6), v_c also has a weak dependence on the solvent viscosity, following $\eta_s^{-0.25}$. This dependence is recovered when comparing the values obtained in the 50/50 wt% water/glycerol ($\eta_s = 6.06$ mPa.s) where $v_c = 0.185$ m/s and in 75/25 wt% water/glycerol.

2.4.2 Self-similarity of the strain rate

As previously mentioned in the description of Fig. 2.7(a) and 2.7(b), the effect of the polymer concentration on the evolution of the instantaneous strain rate $\dot{\epsilon}(t)$ is similar to the effect of the solvent viscosity η_s . Besides, the inverse of the critical strain rate,

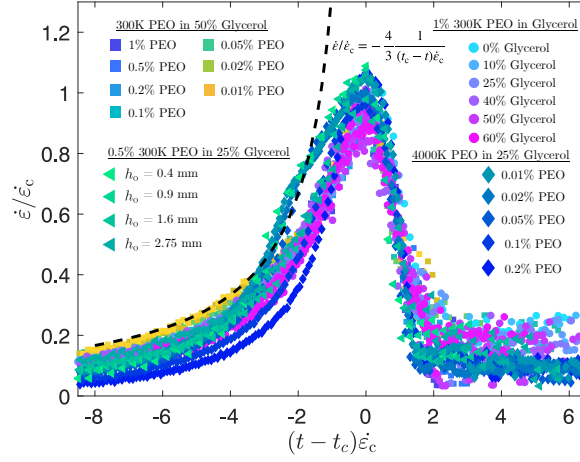


FIGURE 2.10: Evolution of the strain rate around the transition, rescaled by the critical strain rate: $\dot{\epsilon}/\dot{\epsilon}_c$ as a function of $(t - t_c) \dot{\epsilon}_c$. The data plotted include different polymer concentrations ($c = 0.01\%$ to 1%), viscosity of the solvent ($\eta_s = 1$ to 10 mPa s), molecular weights (300K and 4000K), and nozzle diameters ($h_0 = 0.4$ to 2.75 mm).

$\dot{\epsilon}_c^{-1}$, has the dimension of a time, so that we can use $\dot{\epsilon}_c^{-1}$ as a typical time scale of the transition.

Fig. 2.10 shows the time evolution of the strain rate around the transition, rescaled by the time scale $\dot{\epsilon}_c^{-1}$, *i.e.*, $\dot{\epsilon}/\dot{\epsilon}_c$ as a function of $(t - t_c) \dot{\epsilon}_c$. In this figure, we included every parameter that we have investigated: the polymer concentration c , the molecular weight M_w , the solvent viscosity η_s , and the nozzle diameter h_0 . The dashed lines represent the strain rate expected from Eqn. (2.4) in the Newtonian regime. The experimentally measured strain rates have a time shift of a few ms. We obtain a good collapse of all the data onto a single master curve, which leads to two key findings. First, the transition to the viscoelastic regime follows a self-similar dynamic. Second, there is only one physical quantity associated with this transition, the time scale $\dot{\epsilon}_c^{-1}$. In particular, since the nozzle diameter h_0 is the only macroscopic length scale in the system, the good collapse of all our data implies that there is no macroscopic length scale in the mechanism of the transition from the Newtonian to the viscoelastic regimes.

The rescaling by $\dot{\epsilon}_c$ is even more universal. A previous study showed that adding solid particles to a given polymer solution with fixed polymer concentration, molecular weight, and solvent viscosity, leads to the same rescaling [175]. The presence of rigid particles only influenced the value of $\dot{\epsilon}_c$ without changing the mechanism of the transition. The present study extends this result to the case of any dilute solution of polymer in a good solvent.

2.4.3 Interpretation of the critical strain rate

We have shown in the previous section that the dynamics of the transition to the viscoelastic regime can be captured by the single parameter $\dot{\epsilon}_c$. Although we are not able to provide a theoretical model for the evolution of the critical strain rate with the different parameters, we can qualitatively explain its variations.

Two forces drive the thinning of the neck: the weight of the falling drop and the capillary pressure at the neck. Since the size of the falling drop is the result of the balance between its weight and the capillary force that held it to the nozzle, the weight of the drop is also linked to the capillary forces. As the neck deforms, the local viscous stress acting on the polymer chains increases until it becomes sufficient to unwind the chains [3]. We can therefore consider that the critical macroscopic strain rate $\dot{\epsilon}_c$ is linked to the critical microscopic stress. The stronger the local stress, the more easily the polymer chains unwind. All things being equal, if the solvent is more viscous, then the viscous stress acting on each polymer chain will be stronger. If we use a wider nozzle, then the falling drop will be heavier and pull more strongly on the neck, and so the local stress will also increase.

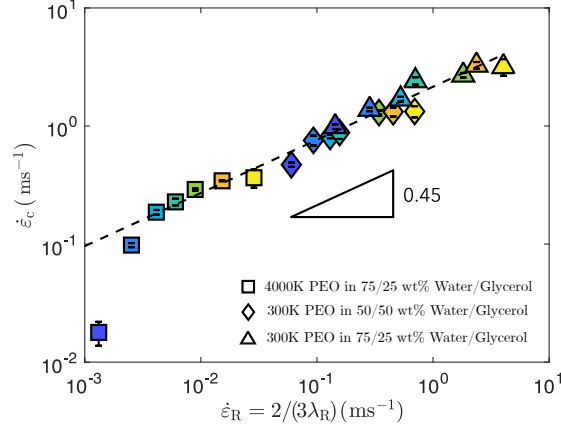


FIGURE 2.11: Critical strain rate $\dot{\epsilon}_c$ as a function of the strain rate in the viscoelastic regime $\dot{\epsilon}_R$. The dashed line represents the best power-law fit, $\dot{\epsilon}_c \propto \dot{\epsilon}_R^{0.45}$, excluding the two leftmost points that are not in the dilute regime.

The effect of the polymer concentration is more complex. On the one hand, increasing the concentration increases the viscosity of the solution, and probably increases the local stress on the polymer chains. On the other hand, in the dilute regime, the viscosity of polymer solutions increases linearly with the concentration following Einstein's law [151]. If the sole effect of concentration on $\dot{\epsilon}_c$ was through the linear increase in the viscosity, we should have similar exponents in the scaling laws given by Eqn. (2.6). However, this is not the case: $\dot{\epsilon}_c$ depends on the concentration in a much weaker way than it depends on the viscosity. Therefore, we can only conclude that in this dilute regime, the coil-stretch transition of a polymer chain is primarily controlled by the solvent viscosity, and secondarily by the concentration in polymers.

One can interpret $1/\dot{\epsilon}_c$ as the relaxation time of the polymer in the solvent: to stretch the polymer chain, one must deform it faster than it naturally relaxes. Fig. 2.11 compares the critical strain rate at the transition $\dot{\epsilon}_c$ to the constant strain rate in the viscoelastic regime $\dot{\epsilon}_R$. There are two main observations to be made. First, in most of our experiments, an order of magnitude separates $\dot{\epsilon}_c$ and $\dot{\epsilon}_R$. The strain rate at the transition $\dot{\epsilon}_c$ is about

Chapter 2. Capillary flow dynamics in polymer solutions

ten times stronger than the strain rate in the viscoelastic regime $\dot{\epsilon}_R$. Second, although $\dot{\epsilon}_c$ and $\dot{\epsilon}_R$ vary in the same way, they do not follow a linear relationship. Instead, the best power-law fit yields $\dot{\epsilon}_c \propto \dot{\epsilon}_R^{0.45}$. Note that this fit excludes the highest concentrations ($c > 0.2\%$) for the 4000K PEO, which are not in the dilute regime.

This difference between the two relaxation times can be qualitatively explained by considering their reference states. λ_R is the longest relaxation time of the polymer, *i.e.*, the relaxation time of the fully stretched polymer chain. On the other hand, $\dot{\epsilon}_c^{-1}$ is the time scale of the stretching from the coiled state, but not necessarily up to the fully stretched state. We can then consider that the abrupt decay of $\dot{\epsilon}$ corresponds to a partial stretching of the chains. At $t = t_c$, the chains are stretched just enough, so the viscosity of the solution rises significantly, inhibiting the liquid inertia. As the concentration, the molecular weight, or the solvent viscosity is increased, the relative stretching required to stop the thinning decreases: the polymer chains need to stretch less to cause the same change in the rheology of the solution.

This hypothesis is supported by Fig. 2.11. Indeed, for a low viscosity of the solvent (75/25 wt% water/glycerol), a low polymer concentration ($c < 0.05\%$) and a low molecular weight (300K PEO), $\dot{\epsilon}_c$ and $\dot{\epsilon}_R$ have comparable values around 3 ms^{-1} . Moreover, the actual break-up of the filament occurs shortly after the transition [see Fig. 2.6(a)]. This suggests that the chains fully stretch at the transition. On the other hand, for a more viscous solvent (50/50 wt% water/glycerol), a higher polymer concentration ($c = 1\%$) and higher molecular weight (4000K), $\dot{\epsilon}_c$ is ten times larger than $\dot{\epsilon}_R$. In this case, the chains are only partially stretched after the transition, and it takes much longer (about the longest relaxation time λ_R) to fully stretch them.

2.5 Conclusion

In this chapter, we investigated the capillary flows of polymer solutions. The initial thinning dynamics are Newtonian for both configurations, followed by a viscoelastic regime characterized by elastic stresses. We characterized the transition between the Newtonian regime and the viscoelastic regime in the pinch-off of a drop of dilute polymer solution. Macroscopically, this transition corresponds to the transformation of the liquid neck that binds the drop to the nozzle into a long filament. Microscopically, the transition corresponds to the coil-stretch transition of the polymer chains. Rather than the thickness of the neck, the relevant quantity to describe the thinning dynamics are the instantaneous strain rate $\dot{\epsilon}$. We have shown that in terms of strain rate, the transition follows a universal self-similar dynamics that is only controlled by the critical strain rate $\dot{\epsilon}_c$. The quantity $\dot{\epsilon}_c$ represents the ease with which the polymer chains unwind: the smaller $\dot{\epsilon}_c$ is, the less external deformation is required to trigger the transition. We have shown that a more viscous solvent, a higher molecular weight of the polymer, or a stronger external stress reduces $\dot{\epsilon}_c$ and facilitates the transition to the viscoelastic regime. Moreover, it appears that a higher polymer concentration also facilitates the transition, independently of the viscosity increase that it causes. The typical time scale of the transition $\dot{\epsilon}_c^{-1}$, and therefore the time scale at which viscoelasticity appears, can be much shorter than the longest relaxation time of the polymer λ_R . A better understanding of the transition between the Newtonian and the viscoelastic regimes could be beneficial to applications that require the break-up of ligament of polymer solutions [28], and the atomization into droplets [87, 88, 89, 163]. The work presented here has been published [144]. In Chapter 3, we investigate the symmetrical opposite situation of a droplet pinch-off, where we look at the break-up dynamics of an air bubble in a polymer solution.

2.6 Supplementary Materials

Influence of the flow rate on the thinning dynamics

To ensure that the thinning of the polymer solutions is not influenced by the flow rate set by the syringe pump, the pinch-off experiments were carried out at different flow rates. We show an example in Fig. 2.12 for the thinning of a 4000K PEO of concentration $c = 0.5\%$ in a 75/25 wt% water/glycerol. The flow rates used are $Q = 0.01, 0.02, 0.05, 0.1, \text{ and } 0.2 \text{ mL/min}$. We observe that the thinning dynamics at those different flow rates collapse on the same master curve, thus ensuring that in this range of flow rate, the thinning occurs in a quasi-static regime.

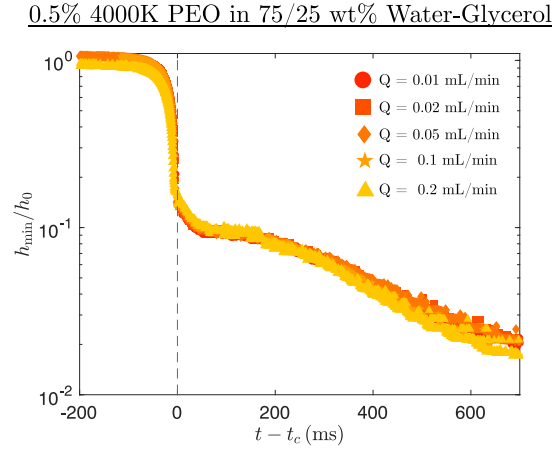


FIGURE 2.12: Thinning dynamics of polymer solutions of 4000K PEO with $c = 0.5\%$ in a 75/25 wt% water/glycerol solvent. The flow rates varies from $Q = 0.01$ to 0.2 mL/min .

Influence of the frame rate on the critical strain rate

For the experiments involving the 4000K PEO in 75/25 wt% water/glycerol solvent, the frame rates were varied from 500 FPS to 10000 FPS depending on the concentration of polymer to account for the large range of relaxation times λ_R obtained. For example, we

estimated the influence of the frame rate from 5000 FPS to 50000 FPS for the 4000K PEO at $c = 0.005\%$ in 75/25 wt% water/glycerol solvent to ensure that the frame rate does not influence the measurement of $\dot{\epsilon}_c$ obtained at the transition. The concentration $c = 0.005\%$ was considered since this concentration led to the shortest relaxation time for this molecular weight. We also consistently increased the size of the window over which $\dot{\epsilon}_c$ was averaged with the frame rate. The mean strain rates over different frame rates is $\dot{\epsilon}_c = 1.1 \text{ ms}^{-1}$ with less than 5% deviation around this value.

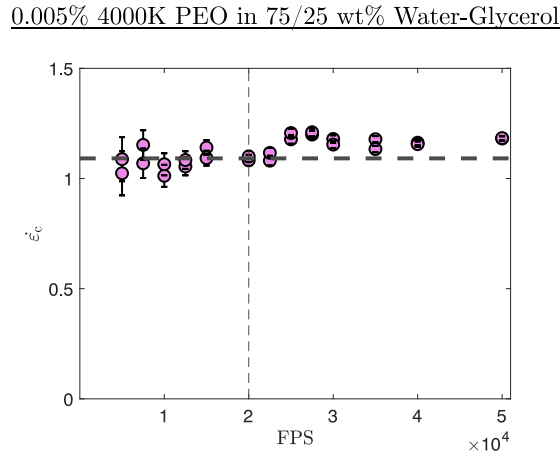


FIGURE 2.13: Evolution of $\dot{\epsilon}_c$ obtained experimentally when varying the frame rate per second (fps) for 4000K PEO at $c = 0.005\%$ in a 75/25 wt% water/glycerol solvent.

Rheology of 300K and 4000K PEO in 75/25 wt% water/glycerol solvent

We measured the shear viscosity η of the solution of 300K and 4000K PEO in a 75/25 wt% water/glycerol solvent. We measured the viscosity of each solution using a rheometer (Anton Paar MCR 92) with a 50 mm-wide 1° cone-plate geometry. For the 300K PEO, the shear viscosity remains constant with the shear rate $\dot{\gamma}$ for $c = 0.01\%$ to 0.5% , and shows a weak shear-thinning at $c = 1\%$. The 4000K PEO the shear viscosity remains nearly constant between $c = 0.005\%$ and 0.02% , and then a shear-thinning is observed for $c = 0.05\%$ to 1% .

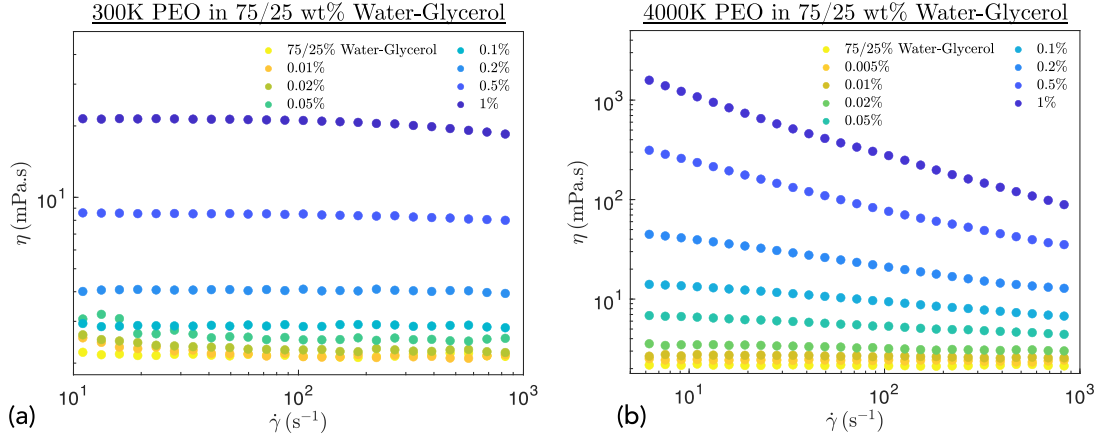


FIGURE 2.14: Evolution of the shear viscosity η with the shear rate $\dot{\gamma}$ for polymer solutions prepared with different mass concentrations of (a) 300K PEO and (b) 4000K PEO in a 75/25 wt% water/glycerol solvent.

Influence of the nozzle diameter on the thinning dynamics and the strain rate

To elucidate the influence of weight of the drop on the thinning and the pinch-off, we considered nozzles of different diameters $h_0 = 0.4, 0.9, 1.6$, and 2.75 mm. Here, we show the results for the 300K PEO at $c = 0.5\%$ in a 75/25 wt% water/glycerol solvent. The corresponding thinning $h(t)$ and $\dot{\epsilon}(t)$ are shown in Fig. 2.15(a) and 2.15(b), respectively.

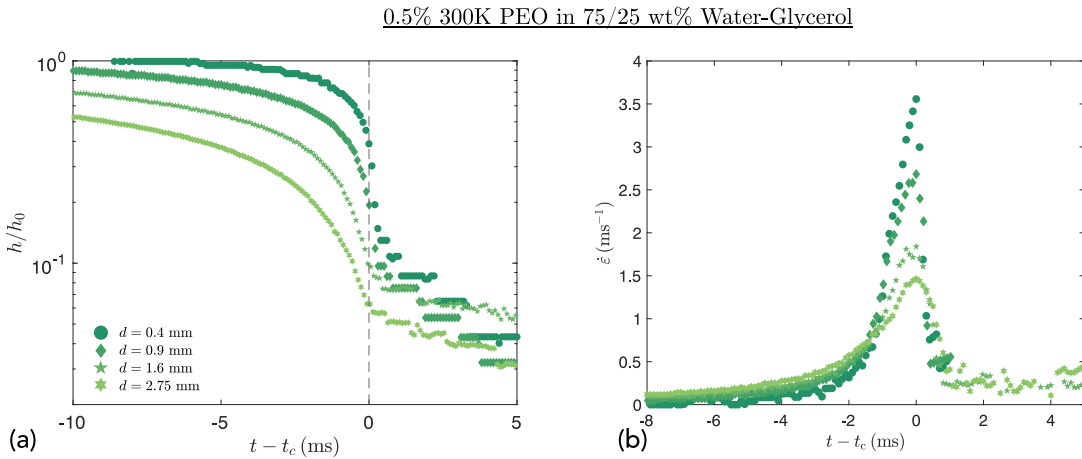


FIGURE 2.15: (a) Thinning dynamics $h(t)/h_0$ and (b) evolution of the strain rate $\dot{\epsilon}(t)$ of a 300K PEO solution at $c = 0.5\%$ in 75/25 wt% water/glycerol solvent for different nozzle diameters $h_0 = 0.4, 0.9, 1.6$ & 2.75 mm.

Chapter 3

Bubble pinch-off in polymer solutions

The pinch-off of an air bubble in a liquid medium is a fundamental problem in fluid mechanics that serves as a geometric and dynamical inverse to the droplet pinch-off process investigated in Chapter 2. In Newtonian fluids, both configurations are characterized by a finite-time singularity where the strain rate diverges as the neck thickness vanishes [47]. This phenomenon has been extensively explored in the context of bubbles by researchers such as Burton *et al.* [21] and Thoroddsen *et al.* [176]. Specifically, it has been established that the bubble neck undergoes power-law thinning, similar to the Newtonian droplet dynamics discussed in Chapter 2, albeit with a modified scaling exponent.

While the Newtonian case is well-understood, the introduction of polymers adds a layer of complexity due to the onset of elastic stresses. Previous studies by Jiang *et al.* [82] reported a modified pinch-off behavior in polymeric solutions, noting deviations from Newtonian scaling. However, the full physical picture remained incomplete. Our work, presented in this chapter, demonstrates that bubble pinch-off in high-concentration polymer solutions can be clearly demarcated into two distinct regimes: an initial Newtonian regime followed

by a viscoelastic regime. This behavior mirrors the bifurcated dynamics observed in droplet pinch-off, but within an inverse geometric framework. By rescaling the evolution of the minimum neck thickness, $h_{\min}$, we provide the first quantitative indication of coil-stretch transition in the regions surrounding the bubble neck due to high localized strain rate, and subsequent elasto-capillary thinning in this configuration – which can be directly observed in solutions of higher concentrations due to a lower ε_c needed for their onset.

This phenomenon was recently investigated further by Verschuur *et al.* [182], who utilized both experimental and numerical methods to identify the role of macroscopic boundary conditions on the transition. Notably, they found that the nozzle geometry significantly influences the onset and duration of the viscoelastic regime, with larger nozzles promoting the formation of longer-lived viscoelastic threads.

3.1 Relevance of Polymer Additives for Industrial Bubbly Flow

The ability to control bubble dynamics via polymer additives has profound implications for particle technology and process engineering. In the mining industry, particularly in froth flotation, the stability and attachment of bubbles to mineral particles are critical to separation efficiency; adding trace amounts of polymers can retard bubble coalescence and stabilize the froth, thereby improving mineral recovery rates. Similarly, in the food industry, the aeration of viscoelastic matrices—such as doughs, foams, or protein-rich solutions—relies on understanding how polymeric stress prevents the premature rupture of liquid films between bubbles. This stabilization is essential for controlling texture,

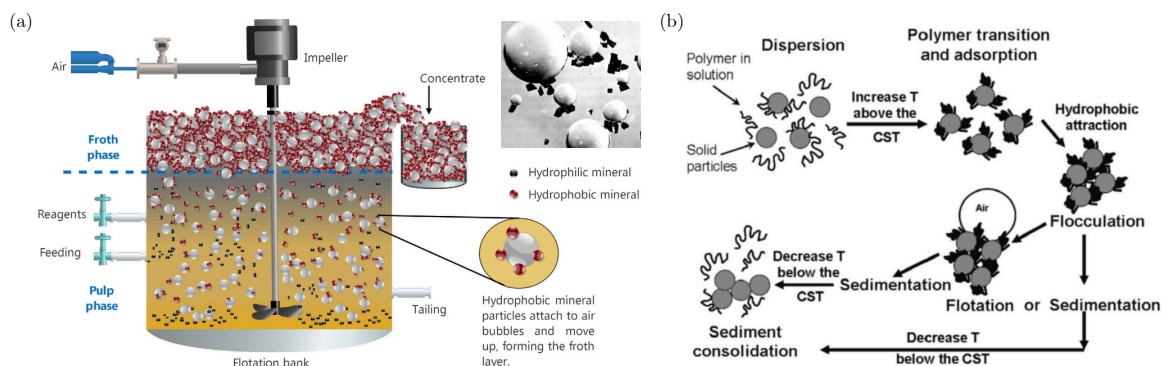


FIGURE 3.1: **Froth Flotation** (a) Cutaway view of a cubic mechanical flotation cell showing the production of bubbles and the gathering of froth (Li *et al.* [102]) [Reproduced with permission from Publisher]. Right inset: photograph of water-repellent mineral particles attached to rising bubbles. The input bubbles in industrial flotation are ~ 1 mm in diameter, about the size of the largest bubble in this photograph [Photograph by H. Rush Spedden, reproduced with permission]. (b) Schematic illustration of the interactions between particles and polymers (N-isopropyl acrylamide) in each step of the process, comprising steps of dispersion, flocculation, flotation, sedimentation, and sediment consolidation (Franks *et al.* [57]) [Reproduced with permission from Publisher].

porosity, and shelf stability of aerated food products. By bridging the gap between molecular-scale polymer dynamics and macroscopic bubble pinch-off, the work in this chapter provides a framework for optimizing these industrial multiphase flows.

In the mining industry, polymers are critical for the froth flotation process, where they act as selective reagents to optimize mineral recovery. For instance, natural polysaccharides such as guar gum and starch are widely used as eco-friendly depressants to inhibit the flotation of unwanted minerals, such as silicates and pyrite [10]. Similarly, high-molecular-weight synthetic polymers such as polyethylene oxide (PEO) or polyacrylamide (PAM) are used to induce flocculation, thereby reducing mechanical entrainment of fine waste particles into the froth phase. Furthermore, polyglycol-based polymers function as effective frothers, stabilizing the bubble-particle aggregates as they rise, which prevents premature collapse of the foam layer [55, 134].

In the food industry, the emphasis shifts toward foam stabilization to control the texture and shelf life of aerated products. Biopolymers, particularly proteins and polysaccharides, are added to viscoelastic matrices like doughs and ice cream to prevent the drainage and rupture of the liquid films between bubbles [75]. Specialized surface-active polymers, such as hydrophobins, create highly elastic interfaces that offer exceptional resistance to bubble coalescence [131]. These additives are also vital in the production of solid foams, such as bread, where the rheology of the polymer matrix prevents bubble rupture during thermal processing [168]. By governing the transition from Newtonian to viscoelastic thinning, these polymers ensure the structural integrity of multiphase systems in both natural and industrial environments.

Pinch-off of bubbles in a polymer solution

The work summarized here has been published as S. Rajesh, S. Peddada, V. Thiévenaz, and A. Sauret (2022). "Pinch-off of bubbles in a polymer solution". Journal of Non-Newtonian Fluid Mechanics, 104921.

3.2 Introduction

Bubbles are encountered in a wide range of situations such as industrial processes [32], biological systems [180], and geological studies [130]. In the medical industry, bubbles have been used as contrast agents for ultrasound scans [16]. Compound bubbles formed by water contaminated with harmful substances due to the possible aerosolization are of concern to our health [81]. Preventing cavitation bubbles is of crucial importance in biological

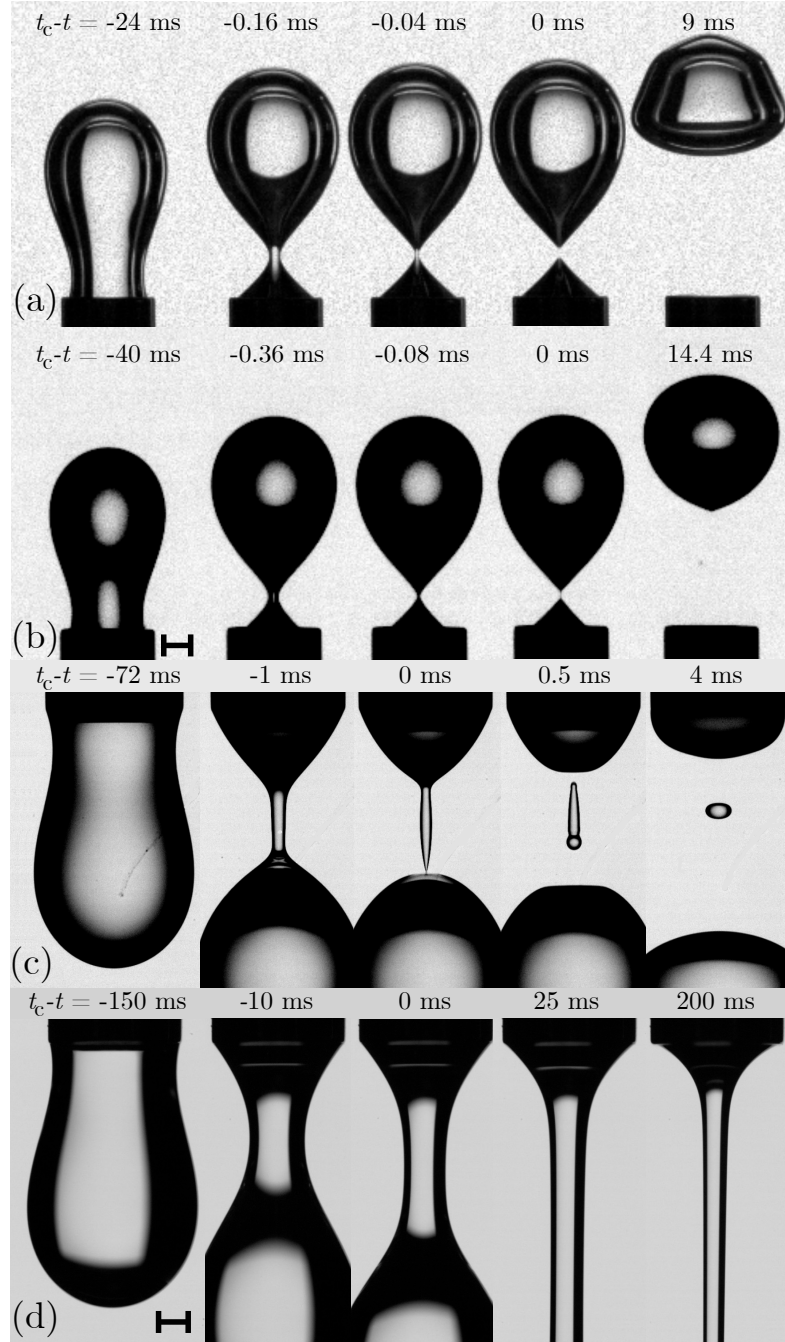


FIGURE 3.2: [Symmetry in droplet / bubble pinch-off] Examples of a gas bubble pinch-off in a quiescent liquid of (a) 75/25% by weight water/glycerol, and (b) a polymer solution (0.5% mass concentration of 4000K PEO in 75/25% by weight water/glycerol). Examples of pinch-off in air of a liquid droplet of (c) 75/25% by weight water/glycerol ($\eta_s = 2.14$ mPa.s), and (d) a polymer solution (0.5% mass concentration of 4000K PEO in a 75/25% by weight water/glycerol). Scale bars are 1 mm.

networks in plants [19], or in the design of underwater turbines and propellers [140]. The formation of bubbles are also of particular interest in microfluidic devices [74], microcapillary tubes [128], as well as in turbulent flows [154]. In many applications, the liquids involved have a more complex rheology. For instance, the presence of cells, particles, or polymeric substances dispersed in the liquid modifies their rheology [58, 84, 109, 110, 132, 174, 175]. The modified rheology of polymer solutions has been exploited to achieve drag reduction in flow [171], and suppress the effect of cavitation [20]. It is known that the presence of polymers modifies the pinch-off of a liquid droplet in air [3, 177]. The inverse problem of pinch-off of an air bubble in a polymer solution has received less attention.

The pinch-off of a gas bubble in a Newtonian liquid, shown in Fig. 3.2(a), is usually quantified through the time evolution of the minimum thickness $h_{\min}$ of the neck that connects the bubble with the nozzle. The moment the bubble detaches from the nozzle in a Newtonian fluid is a singularity in time t_c . For a short duration before the pinch-off, the minimum thickness follows a power law, $h_{\min}(t) \propto (t_c - t)^\alpha$. Burton *et al.* [21] have shown that the exponent α is a function of the external liquid viscosity for a Newtonian liquid. For inviscid liquids ($\eta \lesssim 10$ mPas), the exponent is around 0.5 and for viscous liquids ($\eta \gtrsim 100$ mPas), it is approximately 1. For liquids of intermediate viscosities, the exponent was reported in the range 0.5 to 1. A follow-up work by Thoroddsen *et al.* [176] at a higher spatial and temporal resolution reported an exponent of 0.57 for inviscid Newtonian liquids. This slightly larger exponent was theoretically derived by Eggers *et al.* as $\alpha = 1/2 + 1/[4\sqrt{-\ln(t_c - t)}]$ for the collapse of an axisymmetric cavity [46]. The exponents are hence non-universal, and depend on the initial condition of the system and the experimental resolution. In this study, we do not focus on the influence of the initial condition. Instead, we use a spatial and temporal resolution similar to Burton *et al.*,

which is sufficient to examine the moment leading up to the bubble pinch-off in polymer solutions. An example of thinning and pinch-off of a bubble in a polymer solution is shown in Fig. 3.2(b).

In the opposite configuration, *i.e.*, when a drop of inviscid liquid thins in air, the minimum thickness is described by the power-law $h_{\min}(t) \propto (t_c - t)^{2/3}$ [86]. Here, the time t_c describes the moment the drop separates from the liquid attached to the nozzle, as shown in Fig. 3.2(c). Until a time t_c , the thinning of polymer solution, shown in Fig. 3.2(d), is also captured by a power law [144]. At t_c , while the drop breaks off for a Newtonian liquid, adding even a small amount of polymer results in a transition to a viscoelastic thinning [3]. At the transition, the polymers, which are initially coiled, begin to unwind and interact with the flow [63, 144]. A macroscopic manifestation of this interaction is the formation of a long and slender liquid thread, which persists for a long time. A further consequence of polymer uncoiling is the increase in the flow resistance. When the polymers are coiled, their hydrodynamic interaction with the solvent is minimized. As the polymer unwinds, more regions of the chain are exposed to the solvent. This results in an increase in the viscosity of the solution, *i.e.*, an extensional thickening effect [3, 43, 44]. In this regime, the slender filament thins exponentially following $h_{\min}(t) \propto \exp[-t/(3\lambda_R)]$, where λ_R is the longest relaxation time of the polymer [5]. The exponential thinning is followed by either a beads-on-a-string (BOAS) instability [31] or a blistering instability [36].

While the pinch-off of bubbles in Newtonian liquids is well characterized [128, 12], there is a dearth of the literature on bubble pinch-off in viscoelastic liquids. At a larger scale, notable differences exist for bubbles in viscoelastic liquids, such as the negative wake reported by Hassager [71]. The problem of discontinuity of the terminal velocity with respect to the bubble volume in polymer solutions has also been of long-standing interest [97, 18]. The scales associated with the pinch-off are more challenging to capture

Chapter 3. *Bubble pinch-off in polymer solutions*

and require a spatio-temporal resolution of a few microns over a few microseconds. A recent work by Jiang *et al.* [82] has reported the existence of two distinct regimes during the final stages of the bubble pinch-off in polymer solutions of higher concentrations. At lower polymer concentrations, the thinning is a power-law, with the exponent $0.5 < \alpha < 1$. This value is larger than the thinning exponent for the solvent, which is $\alpha = 0.5$. At higher concentrations, there is no clear description for the thinning.

Yet, a recent study on the coalescence of two drops of liquid, which is another example of singular behavior [133], has shown that the minimum thickness of the coalescing polymer solutions is also described by a power-law and with the same exponent as the solvent [38]. The polymer solutions used in the coalescence study exhibit weak shear thinning and strong elasticity, *i.e.* a sufficiently large relaxation time. In contrast, the solutions used by Jiang *et al.* for their pinch-off experiments have strong shear thinning and elasticity for all the concentrations studied, with relaxation times of the order of a few seconds. In particular, the change in exponent observed by Jiang *et al.* [82] could be induced by the strong shear thinning of their solutions or the elastic effects, or by both.

To elucidate the influence of elastic stresses, we use polymer solutions that are weakly shear-thinning, except at large concentrations but with large enough relaxation times for all concentrations studied. The chapter is organized as follows: in § 3.3, we describe the experimental methods and the rheology of the polymer solutions used. We characterize the shear thinning and the relaxation time of the polymer solutions. In § 3.4, we compare our results with Newtonian fluids to the results previously reported in the literature. We then present the thinning obtained for the polymer solutions. We observe that different concentrations of polymers lead to different pinch-off dynamics. We discuss our results in § 3.5, where we describe the influence of elastic forces on the shape of the bubble near

the pinch-off. We further highlight this by presenting the contours of the bubble in the polymer solution as it breaks off.

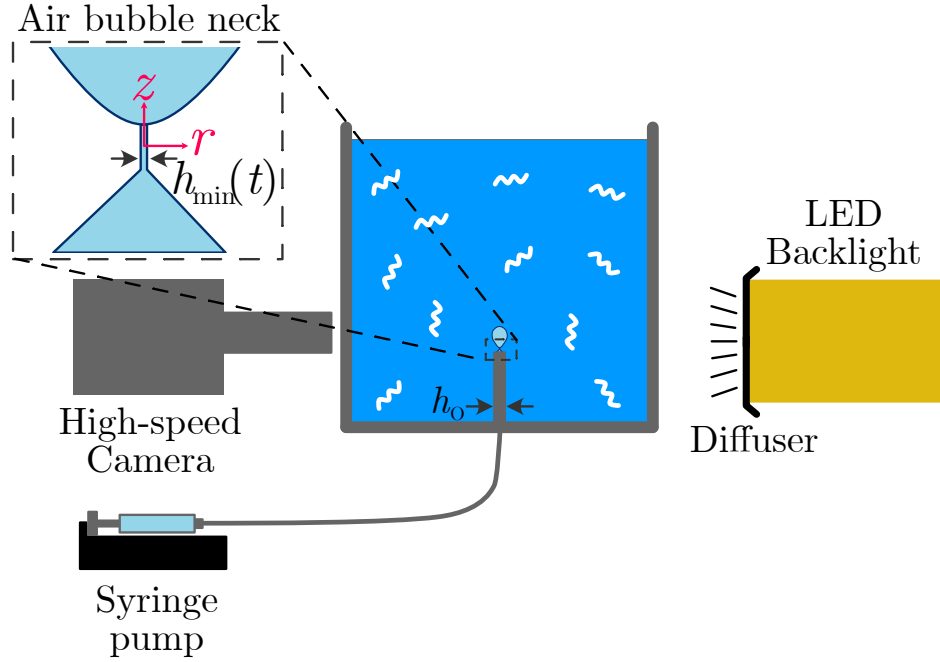


FIGURE 3.3: Schematic of the experimental setup. A needle of internal diameter $h_0 = 2.31$ mm is set at the bottom of a tank filled with the liquid and connected to a syringe filled with air. A syringe pump is used to generate a bubble from the nozzle. The length $h_{\min}$ corresponds to the minimal thickness at the neck of the bubble. The z -axis corresponds to the axis of symmetry at the neck. The system is backlit with an LED (Light Emitting Diode) and a diffuser; the dynamics are recorded with a high-speed camera.

3.3 Experimental Methods

The bubble pinch-off experiments are performed in a $50 \times 50 \times 50$ mm³ transparent tank that contains the liquid (Fig. 3.3). A syringe pump (KDS Legato 110) extrudes air bubbles through a stainless-steel nozzle (inner diameter $h_0 = 2.31$ mm) at a controlled flow rate Q . The vertical alignment of the needle is obtained by using a custom 3D-printed

c	c/c^*	σ [mN/m]	λ_R [s]	η_0 [mPa.s]	η_∞ [mPa.s]	λ [s]	n_{cf}
0%	0	72.7	-	-	-	-	-
0.01%	0.37	62.3	0.023	2.7	1	0.041	1
0.02%	0.74	63.8	0.043	3.7	2.89	0.23	0.7
0.05%	1.85	63.8	0.074	7.2	3.02	0.2	0.8
0.1%	3.71	64.0	0.11	15.4	2.61	0.19	0.79
0.2%	7.41	63.8	0.16	57.9	0.52	0.36	0.72
0.5%	18.52	63.6	0.26	1150	0.1	2.63	0.54
1%	37.04	63.5	0.51	20000	18.5	6.78	0.32

TABLE 3.1: Rheological properties and surface tension σ of the 75/25% by weight water/glycerol solvent, and PEO solutions of various mass concentrations ($c = 0.01\%$ to $c = 1\%$). $c^* = 0.291\text{kg/m}^3$ or 0.027% is the critical overlap mass concentration. λ_R is the longest relaxation time of the polymer. η_0 , η_∞ , λ , and n_{cf} are the parameters obtained from the Carreau fit shown in Fig. 3.4(a).

setup to place the needle in the tank. The tip of the needle is at least 10 mm below the air/liquid interface, ensuring that the free surface has no effect on the pinch-off dynamics. We use flow rates in the range $Q = 0.02\text{ mL min}^{-1}$ to 0.2 mL min^{-1} depending on the viscosity of the liquid. The flow rate is well below the critical flow rate where the flow transitions to jetting and allows us to generate a single bubble of constant volume in a quasi-static regime [125]. We ensure that changing the flow rate in this range does not influence the results, which confirms that we remain in the quasi-static regime (see supplementary materials 3.7).

The liquids consist of mixtures of deionized (DI) water and glycerol (Sigma-Aldrich) for the solvent and the polymer solutions are prepared using Polyethylene oxide (PEO) of molecular weight $M_w = 4000\text{ kg/mol}$ (Sigma Aldrich). We tune the viscosity of the solvent η_s by varying the weight fraction of glycerol from $\eta_s = 1\text{ mPa.s}$ (0% glycerol), to $\eta_s = 213.3\text{ mPa.s}$ (90% glycerol by weight). The change in the fraction of glycerol

has minimal influence on the surface tension σ [173]. We prepare the polymer solutions by adding the polymer powder to a 75/25% by weight water/glycerol mixture, slowly mixing them on a roller mixer for 24-48 hours, and we ensure that the polymer solutions are homogeneous at the end of the preparation. We use PEO of mass concentrations between $c = 0.01\%$ and $c = 1\%$. The surface tension, measured using the pendant drop method, does not vary significantly in this range of concentrations. The measurements are summarized in Tab. 3.1. An increase in the polymer concentration results in large variations of the shear viscosity η and the relaxation time λ_R . The shear viscosity is measured using a 50 mm 1° smooth cone and plate geometry on an MCR 302 rheometer (Anton Paar). We report the evolution of the shear viscosity with shear rate $\dot{\gamma}$ in Fig. 3.4(a). We observe that up to a polymer concentration of approximately $c = 0.1\%$, the viscosity remains more or less constant, whereas the largest concentrations exhibit shear-thinning similar to observations reported in past studies [37]. The shear viscosity $\eta(\dot{\gamma})$ can be fitted using a Carreau model defined as $\eta = \eta_\infty + (\eta_0 - \eta_\infty)(1 + (\lambda\dot{\gamma})^2)^{\frac{n-1}{2}}$ [14]. The fitting parameters η_0 , η_∞ , λ , and n are the zero-shear viscosity, infinite shear viscosity, a time constant, and the power-law index, respectively. Their values are summarized in Table 3.1. The Carreau model was used to fit the viscosities instead of the Carreau-Yasuda model since it provided a more robust fit for all concentrations of polymer solutions used in the present study. While the Carreau-Yasuda model also fits the data well, it yields a larger error for $c = 1\%$ concentration due to a bias of the fitting model for the large viscosities measured at lower shear rates. In Fig. 3.4(b), we show the longest relaxation times λ_R of the polymer solutions, obtained from droplet pinch-off experiments [35, 144]. We measure this relaxation time by fitting the rescaled minimum thickness $h_{\min}/h_0$ during the formation of a liquid droplet in the viscoelastic regime ($t - t_c > 0$) with an exponential thinning model $h_{\min} \propto e^{-(t-t_c)/3\lambda_R}$, as shown in the inset of Fig. 3.4(b) [5]. The relaxation time varies from $\lambda_R = 0.02$ s to $\lambda_R = 0.5$ s when increasing the PEO concentration from

$c = 0.01\%$ to $c = 1\%$. The relaxation time was also measured from the relaxation modulus of the polymer solution for $c = 1\%$ concentration. The measured relaxation time was found to be comparable to the λ_R measured from droplet pinch-off [181] (see supplementary material 3.7). The evolution of the relaxation time with c is well captured by the empirical law $\lambda_R \propto (c/c^*)^{0.66}$ [177, 35]. Here c^* is the critical overlap concentration above which the polymer coils start to overlap. For the solutions used here, we calculate $c^* = 0.027\%$ [67].

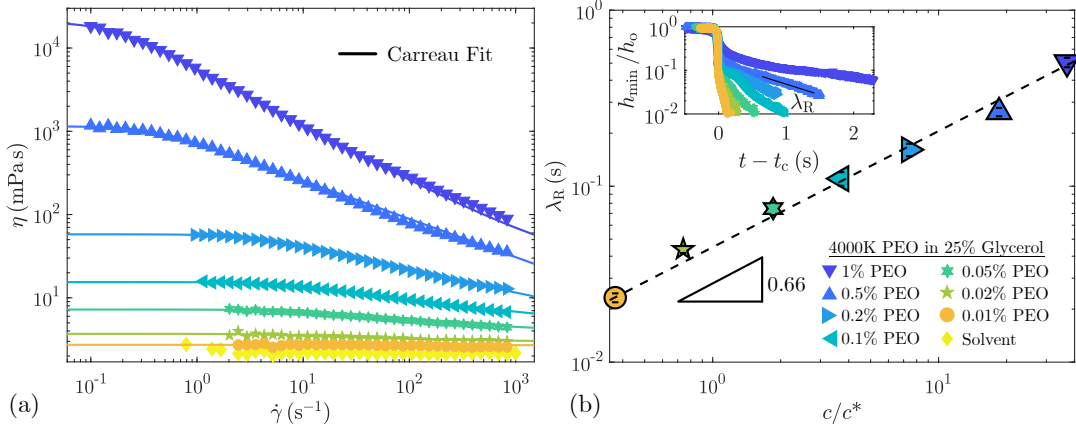


FIGURE 3.4: Physical properties of the 4000K PEO polymer solutions with mass concentration between $c = 0.01\%$ and $c = 1\%$ prepared in a 75/25% by weight water/glycerol solvent. (a) Shear viscosity η of the solutions as a function of the shear rate $\dot{\gamma}$. (b) Relaxation time λ_R of the solutions measured from the droplet thinning experiments. The increase in the relaxation times with the concentration follows a power-law with an exponent 0.66. Inset: Thinning dynamics of PEO solutions. We extract the rescaled minimum thickness $h_{\min}/h_0$ as a function of time. The relaxation time λ_R is obtained from the slope when $t - t_c > 0$, *i.e.*, after the transition to the viscoelastic regime.

We record the bubble pinch-off using a high-speed camera (Phantom VEO 710) equipped with a macro lens (Nikon Micro-NIKKOR 200 mm f/4 AI-s) and a microscope lens (Mitutoyo X2). The spatial resolution is about $10\ \mu\text{m}$ per pixel. The recordings are typically made at 100,000 frames per second or higher, and the setup is back-lit with an LED panel (GSVitec) with a diffuser. Most of the results reported here are obtained at

100,000 frames per second. We ensured that the power-law exponents are independent of the frame rates within the experimental resolution (see supplementary materials 3.7). We then process the recordings using custom ImageJ macros and python routines to extract the temporal evolution of the minimum thickness $h_{\min}$ and outline of the bubble.

3.4 Results

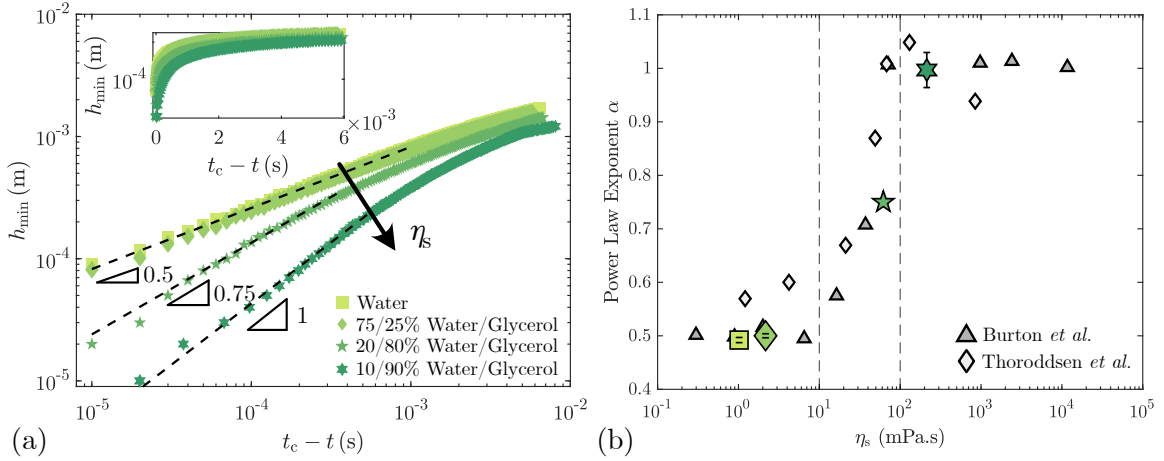


FIGURE 3.5: Bubble pinch-off in Newtonian liquids. (a) Thinning dynamics for different Newtonian liquids: water ($\eta_s = 1$ mPa.s) and mixtures of water/glycerol at 75/25% by weight ($\eta_s = 2.14$ mPa.s), 20/80% by weight ($\eta_s = 62.1$ mPa.s), and 10/90% by weight ($\eta_s = 213.3$ mPa.s). The pinch-off occurs at $t = t_c$, and the time goes from right to left. All experiments exhibit a power-law before the pinch-off given by $h_{\min} = A(t_c - t)^\alpha$. Inset: Semi-log plot of the temporal evolution of the minimum thickness for the same liquids. (b) Evolution of the power-law exponent for air bubbles generated in Newtonian liquids of different shear viscosity. The viscosity is tuned by using water/glycerol mixtures with different compositions by weight of glycerol (between 0% and 90%). The exponents compare well with values previously reported in the literature (grey symbols) [21, 176]. The two vertical lines delimit the regime at low viscosity ($\eta_s \leq 10$ mPa.s) where $\alpha \simeq 0.5$ and at large viscosity where $\alpha \simeq 1$ ($\eta_s \geq 100$ mPa.s).

3.4.1 Bubble pinch-off in Newtonian fluids

Because of the short time scales involved in the pinch-off, finding the exact value of t_c is experimentally challenging. We can detect the last frame where the bubble is still connected to the nozzle and the first frame after the pinch-off, but cannot describe the thinning in between due to the limit of our temporal resolution ($10\ \mu\text{s}$). We numerically improve this accuracy by searching for a best-fit power law in a narrow time range near t_c (see supplementary materials 3.7 for more details) [38]. We test this method by comparing our measurements to the values in the literature for Newtonian solvents of different viscosities [21, 176].

In Fig. 3.5(a), we report the time evolution of the minimum thickness $h_{\min}$ for the bubble in solvents with increasing fractions of glycerol, and hence, increasing viscosity. Because of the short timescale of the pinch-off, it is necessary to appropriately define t_c to recover the correct power-law exponent. Our experiments show that for all the viscosities, the resulting thinning dynamics are well-fitted with the equation $h_{\min} = A(t_c - t)^\alpha$. For pure water and the 75/25% by weight water/glycerol solvent, which are in the inviscid limit ($\eta_s < 10\ \text{mPa}\cdot\text{s}$), the fitting parameters $\alpha \simeq 0.5$ and $A \simeq 0.025$ matches the results of Burton *et al.* [21] In the viscous limit ($\eta_s > 100\ \text{mPa}\cdot\text{s}$), the minimum thickness follows $h_{\min} = (\sigma/\eta_s)(t_c - t)$ [45]. The experimental fit leads to $\alpha \simeq 1$, similar to exponents observed in previous studies [21, 176]. For the prefactor, we recover $A \simeq 0.4$, which is slightly larger than $\sigma/\eta_s = 0.34$ for the viscous solvent we use. We note a similar discrepancy in the data reported by Burton *et al.* [21]. For the 20/80% by weight water/glycerol solvent, which has an intermediate viscosity $10\ \text{mPa}\cdot\text{s} < \eta_s < 100\ \text{mPa}\cdot\text{s}$, the fitting parameters are $\alpha \simeq 0.75$, and $A \simeq 0.135$. In Fig. 3.5(b), we summarize α and compare them with the exponents reported by Burton *et al.* [21] and Thoroddsen

et al.[176]. The exponents we recover from our experimental method for the Newtonian solvents (mixtures of water and glycerol) match the results observed in the literature. In the following, we consider the influence of viscoelasticity by adding polymers (PEO) to the solvent, and in particular, on the evolution of the thinning dynamics with the polymer concentration.

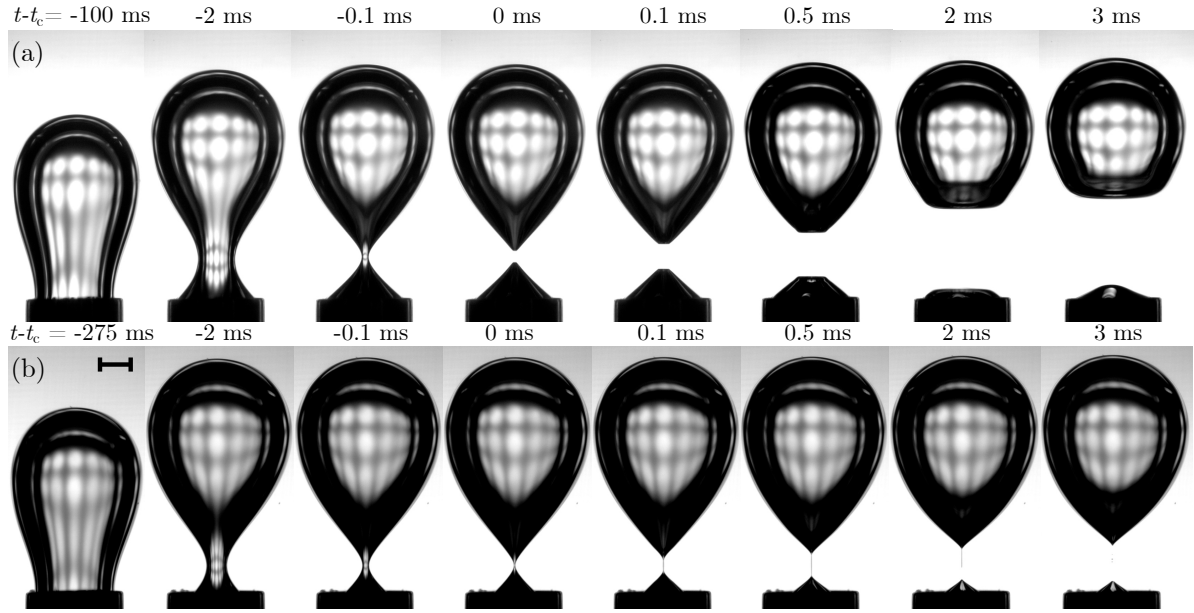


FIGURE 3.6: Time sequence of bubble pinch-off in polymer solutions (a) in a $c = 0.01\%$ mass concentration of 4000K PEO in a 75/25% weight water/glycerol solvent and (b) in a $c = 1\%$ mass concentration of 4000K PEO in a 75/25% weight water/glycerol solvent. The scale bar is 1 mm.

3.4.2 Bubble pinch-off in polymer solution

We now consider the formation of an air bubble in a viscoelastic solution of polymers. As shown in Figs. 3.2(c) and 3.2(d), the pinch-off of a drop of Newtonian liquid and a polymer solution in air is drastically different. Indeed, the thinning and pinch-off of a polymer solution droplet in air exhibits two successive regimes [144]. First, a Newtonian

regime where the thinning of the solution is similar to the solvent in which it was prepared, captured by $h_{\min} \propto [\sigma(t_c - t)^2/\rho]^{1/3}$. Here t_c is the time at which the drop would have broken if there were no polymers dissolved [175, 144]. The presence of polymers results in an increase in the extensional viscosity as the liquid thins, and delays the pinch-off [3]. Around $t = t_c$, the thinning slows down due to the coil-stretch transition of the polymers, and becomes viscoelastic [175, 144]. The viscoelastic regime is characterized by a thread connecting the drop to the nozzle. This ligament thins exponentially as $h_{\min} \propto e^{-t/(3\lambda_R)}$ where λ_R is the longest relaxation time of the polymer in the solvent [5].

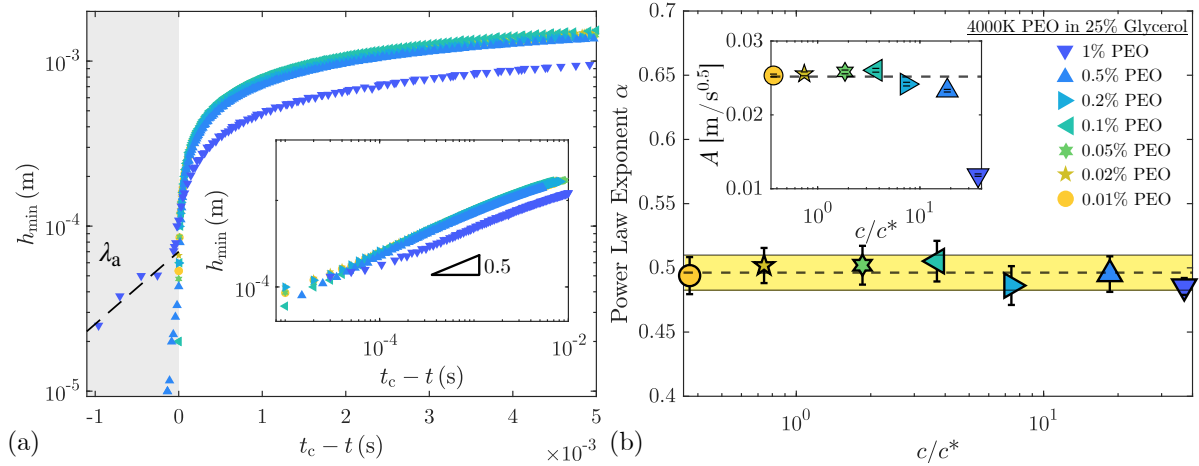


FIGURE 3.7: Evolution of the minimum thickness $h_{\min}$ of an air bubble in a 4000K PEO solution at different concentrations c in a 75/25% by weight water/glycerol solvent. Note here that for solutions with a well-defined viscoelastic regime, t_c corresponds to the moment where the pinch-off would have occurred if there were no polymer in the solution. For $t_c - t < 0$, the thinning is fitted with an exponential thinning model with a fitting parameter λ_a . Inset: Log-log evolution of $h_{\min}$ for solutions of different concentrations. (b) Exponents α extracted from the power-law $h_{\min} = A(t_c - t)^\alpha$ for the experiments performed in the polymers solution of rescaled concentrations $c/c^* = 0.37$ to $c/c^* = 37$, corresponding to $c = 0.01\%$ to $c = 1\%$. The horizontal dashed line indicates the exponent $\alpha = 0.496 \pm 0.01$. The yellow shaded region is the standard deviation of the measured exponents. Inset: Evolution of the prefactor $A(\eta)$ with the polymer concentration.

For droplet pinch-off, the presence of polymer is felt even at very low concentrations, such as 0.001% or 10 parts per million by weight for solutions of a 4000K PEO [35]. Bubble

pinch-off in polymer solution is different. In Figs. 3.6(a)-(b), we illustrate the thinning of an air bubble in polymer solutions of two different concentrations. Fig. 3.6(a) illustrates the formation of an air bubble in a solution of 4000K PEO at $c = 0.01\%$ and Fig. 3.6(b) at $c = 1\%$ mass concentration prepared in a 75/25% by weight water/glycerol solvent. For a certain duration of time, the thinning of the bubble appears similar in solutions of both low and high concentrations. At low polymer concentrations ($c \leq 0.02\%$), the bubble pinch-off is similar to the inviscid solvent. Following the definition for the solvents, the bubble detaches at time $t = t_c$. Above a certain concentration ($c \geq 0.05\%$), the pinch-off is modified; an air thread appears that binds the bubble to the nozzle (see supplementary materials 3.7). For bubbles in polymer solutions of concentration $c \geq 0.05\%$, we define $t = t_c$ as the moment when the thin and slender air thread first appears. This structure lasts for a very short time before the pinch-off. The thickness and lifetime of this structure increase with concentration, similar to the viscoelastic thinning of a drop in air. At the highest concentrations considered here ($c = 0.5\%$ and $c = 1\%$), we have sufficient spatial and temporal resolutions to quantify this thinning, as shown in Fig. 3.7(a).

Similarly to the Newtonian liquid, we extract the time evolution of the minimum neck thickness $h_{\min}$ for polymer solutions of 4000K PEO of mass concentration 0.01% to 1% in Fig. 3.7(a). As noted before, and similar to the case of the pinch-off of polymer solutions droplet in air [144], when the air thread appears, we define t_c as the time of its appearance, rather than the pinch-off time. While the difference is not strongly noticeable for dilute polymer solutions, the distinction must be made for larger concentrations (for solutions of $c \geq 0.05\%$). Indeed, for instance, for $c \geq 0.5\%$ of PEO, the pinch-off of the bubble only happens a few ms after the thread-like structure first appears. This is visible as a new regime of thinning in Fig. 3.7(a) when $t_c - t < 0$. Using the above criteria to select t_c , we report the time evolution of $h_{\min}$ in log-log scale in the inset of Fig. 3.7(a).

Interestingly, all the polymer solutions considered in this study follows the same power law, $h_{\min} = A(t_c - t)^\alpha$ with $\alpha = 0.496 \pm 0.01$. This result is remarkable, especially for solutions of higher concentrations, since the zero-shear viscosity of solutions spans over four orders of magnitude. We further note that the prefactor $A \simeq 0.025$ remains equal to that of the solvent, up to a concentration $c = 0.1\%$, and then decreases. This captures the slowing down of the thinning of the higher concentration solutions. We also draw attention to the thinning of the air thread when $t_c - t < 0$. At the highest concentrations we study ($c = 0.5\%$ and $c = 1\%$ mass concentration in 4000K PEO in 75/25% by weight water/glycerol solvent), we characterize the thinning using an exponential thinning model [5]. When $t_c - t < 0$, we define the minimum thickness as $h_{\min} \propto e^{-(t_c - t)/(3\lambda_a)}$. Here, λ_a is a fitting parameter for the thinning of the air thread surrounded by a polymer solution, and is different from the relaxation time λ_R of the polymer solution. We estimate the values of this parameter as $\lambda_a \sim 0.027$ ms and $\lambda_a \sim 0.33$ ms for $c = 0.5\%$ and $c = 1\%$ concentrations, respectively. We note that the values are at least three orders of magnitude smaller than the relaxation times λ_R . This suggests that the pinch-off of a polymer drop in air and a gas bubble in a polymer solution, although qualitatively similar, have notable differences.

3.5 Discussion

The thinning of a bubble in a polymer solution has different behaviors depending on the solution concentration. However, by appropriately selecting t_c , we can extract the value of the power-law exponent α in the Newtonian regime. The log-log inset in Fig. 3.7(a) shows the evolution in the power-law regime for $c = 0.01\%$ to $c = 1\%$ mass concentration. We summarize the value of the exponent α when varying c in Fig. 3.7(b) and obtain

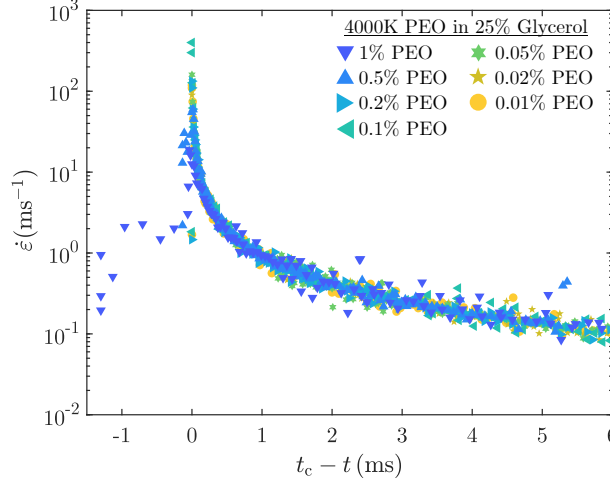


FIGURE 3.8: Evolution of the strain rate $\dot{\epsilon}$ of the thinning for polymer solutions at different concentrations c . The strain rate reaches a maximum $\dot{\epsilon}_{\max}$ when the flow transitions from the Newtonian to the viscoelastic regime.

$\alpha = 0.496 \pm 0.01$ for all polymer concentrations considered here. The results we report here, where the power-law exponent is independent of the polymer concentration, are similar to a recent study on the singular coalescence of polymer solutions [38]. For solutions that show weak shear thinning and strong viscoelasticity, similar to the solutions we use, the elastic coalescence also modifies the interface shape. As discussed later, we see a similar strong modification of the bubble interface near the pinch-off. Furthermore, the result is similar to the droplet pinch-off of polymer solutions, where the Newtonian regime of the thinning has an exponent $\alpha = 2/3$ independent of the concentration [175, 144]. We discuss two possible flow behaviors of the external liquid during the bubble pinch-off to qualitatively rationalize why the exponent remains independent of the concentration. We assume that during the thinning, the liquid viscosity is either purely shear-thinning, or extensional thickening. In the inset of Fig. 3.7(b), we observe that the prefactor A , obtained from the best fit of a power-law, decreases with the polymer concentration, and has a sharp drop for $c = 1\%$ concentration. Similar observations have been made during

the droplet thinning of solvents and suspensions of increasing viscosity [175]. Therefore, the prefactor can hence be considered as an amplitude of the second-order effect of viscosity on the thinning. This decrease in A , and the observed slowing down of the thinning with increase in concentration suggests that the extensional thickening is a more likely mechanism at play here.

For the thinning shown in Fig. 3.7(a), we show the strain rate $\dot{\epsilon}$ near the liquid/air interface in Fig. 3.8. The strain rate scales as $\dot{\epsilon} \sim \dot{h}_{\min}/h_{\min}$ [3]. For the solvent and low concentration solutions, $\dot{\epsilon}$ diverges near t_c . At larger concentrations corresponding to the formation of the air thread, $\dot{\epsilon}$ reaches a maximal value near t_c and decreases when $t_c - t < 0$. This decrease is clearly visible for polymer concentrations of $c = 0.5\%$ and $c = 1\%$, where the experimental resolution allows us to track the thin air thread. In a shear flow, the polymer solutions are shear thinning, as shown in Fig. 3.4(a). If the solution shear thins, the thinning near the pinch-off would become faster. However, the thinning slows down near the pinch-off in polymer solutions. A slower thinning suggests an increase in the flow resistance, similar to an extensional viscosity thickening in droplet pinch-off [3]. The increase in the flow resistance in the droplet pinch-off arises due to a coil-stretch transition when the flow reaches a critical strain rate [63]. Near $t \rightarrow t_c$, the strain rate increases sharply, as shown in Fig. 3.8. Hence, it is likely that $\dot{\epsilon}(t_c - t \rightarrow 0)$ is large enough to uncoil the polymers in the vicinity of the liquid-air interface due to the local elongational flow. A macroscopic manifestation of the elastic interaction of the uncoiled polymers with the solvent is the modified interface shape we observe at larger concentrations, as can be seen when $t - t_c > 0$ in Fig. 3.6(b). When $t_c - t > 0$, far from the pinch-off, $\dot{\epsilon}$ is below the coil-stretch transition limit and the polymers do not interact with the flow [144, 175]. The thinning depends only on the solvent, as suggested by Fig. 3.7(a) where the evolution of $h_{\min}$ for different polymer concentrations overlaps. This

is further confirmed by the recovered exponents, which are independent of the polymer concentration. The slight difference observed at the highest concentration is associated with the increased viscosity due to the spherical polymer coils, which follows Einstein's law [108].

When the strain rate $\dot{\epsilon}$ of the flow reaches its maximal value near $t = t_c$, the polymers likely start to uncoil locally near the interface. Further, the maximum coil-stretch transition strain rate $\dot{\epsilon}_{\max}$ decreases with the polymer concentration [144]. There are two possible explanations for why we see the air thread only above a threshold concentration. Indeed, it is likely that $\dot{\epsilon}_{\max}$ for the low concentration solutions ($c = 0.01\%$ and $c = 0.02\%$) is larger than the time resolution of our experiments, and the air thread thickness smaller than the lowest pixel length. Alternatively, the time scale of the singularity may be larger than the time scale of the coil-stretch transition strain rate ($1/\dot{\epsilon}_{\max}$) of the solution, hence the bubble pinches off before it enters the viscoelastic regime.

The droplet and bubble pinch-off have similar features, such as a period of Newtonian power-law thinning, which is independent of the concentration, followed by a transition to a viscoelastic regime. However, we highlight certain key differences in the thinning, particularly during the viscoelastic regime. Although the air thread in the bubble pinch-off in polymer solutions resembles the viscoelastic filament in the droplet pinch-off, the thread itself has no polymers. The thinning of this thread is likely governed by the stretching of the polymers in the vicinity of the liquid/air interface. We recall that the air threads in the solutions with mass concentrations $c = 0.5\%$ and $c = 1\%$ have sufficient thickness to characterize their thinning. Although λ_a , the fitting parameter we obtain from the exponential thinning [5], resembles the relaxation time λ_R of the droplet thinning, it is at least three orders magnitude smaller. Further, the prefactor of the thinning, $A(\eta)$, decreases with increasing concentration. This suggests a slower thinning of the higher

concentration solutions during the pinch-off. We also estimate the time-scale of the stretching of the $c = 0.5\%$ and 1% polymer solutions during the bubble pinch-off as $1/\dot{\epsilon}_{\max} \sim 0.03$ ms. This gives an order of magnitude estimate of the extensional viscosity as $\eta = 2\sigma/(h_{\min} \dot{\epsilon}_{\max}) \sim 80$ mPa.s. It is also interesting to note that by rearranging the expression for the extensional viscosity $\eta = 2\sigma/(h_{\min} \dot{\epsilon}_{\max})$ [3], we obtain $\tau_{\eta,c} \sim 1/\dot{\epsilon}_{\max}$, the visco-capillary time scale. The observations here are an apparent paradox; even though the higher concentration solutions are more viscous, the exponent we recover is that of an inviscid pinch-off.

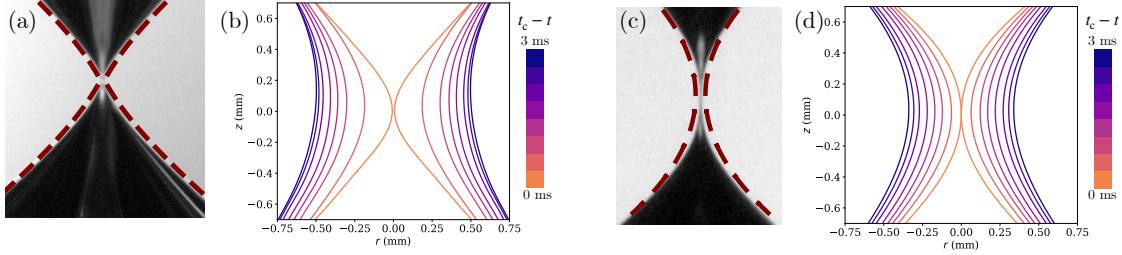


FIGURE 3.9: Bubble neck profile and spatial evolution for Newtonian liquids. (a) A close-up view of the neck near the pinch-off in a 75/25% by weight water/glycerol (inviscid) solvent. The dotted lines at the liquid/air interface are a hyperbolic fit. (b) Polynomial-fitted spatial evolution of the bubble in the corresponding solvent. (c) The bubble near the pinch-off in a 10/90% water/glycerol (viscous) solvent. The dotted line is a parabolic fit. (d) Polynomial fitted spatial evolution of the neck of a viscous solvent.

Singularities in the bubble pinch-off are regions of topological transitions, where the initial bubble separates to form a main bubble and micron-sized satellite bubbles [65]. The differences in the topology arise either as a function of viscosity, illustrated in Figs. 3.9(a)-(d) or elasticity, which is the case in polymer solutions shown in Figs. 3.10(a)-(h). In Fig. 3.9(a), we show the bubble neck in a 75/25% by weight water/glycerol solvent before the pinch-off. The neck is fitted with a hyperbola of the form $r = R_1 \sqrt{1 + z^2}$, where r and z are the neck radius and the width, respectively, and R_1 is a fitting parameter. Similar fits have been considered for a bubble neck in an inviscid liquid in past studies [176]. Fig.

3.9(b) reports the spatial evolution of the neck for the time $t_c - t = -3$ to 0 ms using a polynomial fit. As the thinning approaches the singularity, we see the neck evolving from a smooth profile to a sharp corner before the pinch-off. When the bubble thins in a more viscous solvent, like the 10/90% water/glycerol shown in Fig. 3.9(c), the neck is modified. Viscosity has a smoothing effect on the neck, which is fitted with a parabola $r = az^2 + bz + c$, with a , b , and c as the fitting parameters. The parabolic neck has also been observed in previous studies [17]. Fig. 3.9(d) shows the polynomial fitted spatial neck profile for a viscous liquid for $t_c - t = -3$ to 0 ms. In a viscous liquid, the neck has a smooth profile as it approaches the singularity.

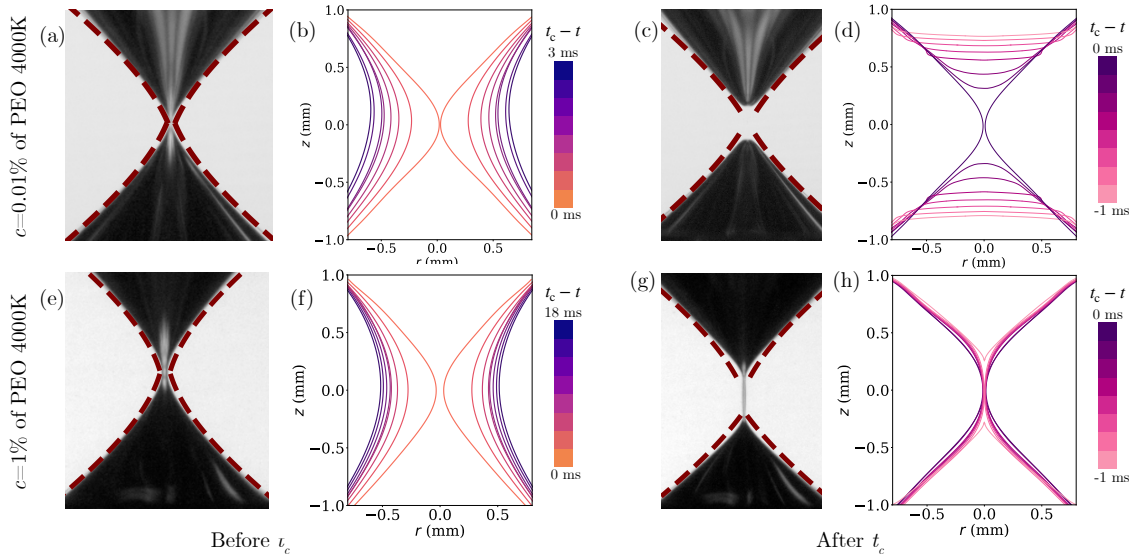


FIGURE 3.10: Bubble neck profile and spatial evolution of the neck in 4000K PEO solution in a 75/25% by weight water/glycerol solvent and (a)-(d) $c = 0.01\%$, (e)-(h) $c = 1\%$. (a) The bubble neck near the pinch-off with a hyperbola fit. (b) Polynomial-fitted spatial evolution of the neck near the pinch-off (c) The neck a few μ s after the pinch-off, with a hyperbolic fit. (d) Polynomial-fitted spatial evolution of the neck after the pinch-off. (e) The bubble neck a few μ s before the air thread forms at $t_c - t = 0$, fitted with a hyperbola. (f) Polynomial-fitted spatial evolution of the neck before the air thread forms. (g) The bubble neck a μ s after the pinch-off. The ends of the air thread are fitted with a hyperbola. (h) Polynomial-fitted spatial evolution of the air thread.

Chapter 3. *Bubble pinch-off in polymer solutions*

For a bubble in polymer solutions, stretching of the polymers in the vicinity of the liquid/air interface results in an elastic contribution. At low concentrations, this contribution is likely beyond the limits of what we observe. Hence, the bubble neck profile for low polymer concentrations is similar to the bubble neck in the solvent. For a 0.01% mass concentration, we fit the neck near the pinch-off with a hyperbola as illustrated in Fig. 3.10(a). As reported in Fig. 3.10(b), the spatial evolution of the neck for the time $t_c - t = -3$ to 0 ms is also comparable to the solvent, which evolves at a similar rate. After the pinch-off, the hyperbolic neck in Fig. 3.10(c) destabilizes within a few milliseconds. We show this decay in Fig. 3.10(d). At a higher concentration, the local Deborah number $De \sim \lambda_R \dot{\epsilon}_{\max}$ is of the order of 10^4 . Thus, we expect the elastic forces to influence the bubble neck near the pinch-off. The solution is also more viscous due to a larger concentration of polymers. From a viscosity-based argument alone, we expect a smoother neck near the pinch-off for higher polymer concentration. However, the neck remains hyperbolic, as seen in a solution of 1% concentration in Fig. 3.10(e). We also note that as $t \rightarrow t_c$, the neck profiles are similar to the solvent and 0.01% solution. However, because of a larger viscosity of the solution, the neck evolves over a time $t_c - t = -18$ ms to 0 ms, as reported in Fig. 3.10(f). As discussed earlier, the dissolved polymers influence the thinning only when the strain rate is sufficiently high. For $t_c - t < 0$, the elastic contribution modifies the neck to form the air thread visible in Fig. 3.10(g). Interestingly, we note that the neck, which connects the air thread, remains a hyperbola as the thread thins. Fig. 3.10(h) reports the fitted thinning of the neck. For $t_c - t < 0$, the solution elasticity strongly modifies the neck profile of the bubble. Hence, up to the point when the neck profile approaches $t = t_c$, the thinning depends only on the viscosity of the solvent. Elasticity begins to influence the thinning around $t = t_c$, which results in a unique bubble neck, different from the neck profiles reported for a bubble in inviscid and viscous liquids.

3.6 Conclusion

The pinch-off of a bubble is a classic example of singularities in fluids. As the bubble approaches pinch-off, the minimum thickness of the bubble neck follows a power-law. For a bubble in a Newtonian liquid, the power-law exponent α is a function of liquid viscosity; it takes a value $\alpha = 0.5$ for low viscosity liquids and $\alpha = 1$ for high viscosity liquids. For a narrow range of viscosities in between, the exponent lies in the range $0.5 < \alpha < 1$. In this study, we consider the pinch-off of bubbles in polymer solutions of different concentrations. The polymer solutions are almost Newtonian except at the highest concentrations but produce strong viscoelastic effects in extensional flows at all concentrations. Further, the solutions have zero-shear viscosities varying over four orders of magnitude, and higher than that of the solvent. Thinning of the bubbles in low concentration polymer solutions (up to $c = 0.02\%$) is similar to that of the solvent. But for sufficiently high concentrations ($c \geq 0.05\%$), an air thread appears for a short time before the pinch-off. By defining an appropriate t_c , solutions of all concentrations follow a power-law thinning with exponent $\alpha \simeq 0.5$. Above a large enough concentration ($c > 0.5\%$ here), the spatio-temporal resolution of our experiments allows us to quantify the minimum thickness of the air thread. The thinning here indicates the existence of two distinct regimes before the pinch-off. Similar to the droplet pinch-off of polymer solutions in air [144], we define t_c not as the time when the bubble separates, but rather as when the thinning transitions from one regime to another. This approach allows us to show that the thinning of a bubble in polymer solutions also follows a power-law with an exponent $\alpha \simeq 0.5$. This result is of notable interest as the solutions at larger concentrations are more viscous. We attempted to rationalize this result by noting that near $t = t_c$, the thinning slows down. This suggests that the viscosity of the solution increases, similar to the extensional thickening observed during the droplet pinch-off of a polymer solution [3,

144]. The increase in the viscosity is likely due to the unwinding of the polymers near the liquid/air interface at a critical strain rate [63]. Until the point of coil-stretch transition, the polymer remains coiled and does not interact with the flow. This could explain why the exponent observed for the solutions remains similar to the solvent. The uncoiling and interaction of the polymers with the flow is seen as the unique structure formed by the bubble before it pinches off. The exponent observed also echoes the recent results obtained for the singular coalescence of polymer solution droplets, where a single exponent characterizes the power-law thinning independent of the concentration [38].

The strong elastic effects due to the high polymer concentrations also lead to a change in the topology of the bubble near the pinch-off. For pinch-off in low viscosity Newtonian liquids, the neck of the bubble has a hyperbolic shape. Unlike the high viscosity solvents, which exhibit a parabolic neck, the polymer solutions retain the hyperbolic shape as they approach $t = t_c$. At sufficiently large concentration, a thread-like structure becomes barely visible for a short time as a result of strong elastic forces experienced by the solution at high strain rates. At even higher concentrations, the effect on the topology of the air-liquid interface is evident. After a period of thinning during which the bubble has a hyperbolic shape and power-law thinning, it transitions to a regime with an elongated thread appearing, analogous to the cylindrical structure in the pinch-off of polymer drops.

3.7 Supplementary Materials

Defining the moment of Pinch-off

Due to the nature of the experiments, defining the exact moment of pinch-off t_c is challenging. Indeed, we use image processing routines to extract the minimum thickness

of the neck connecting the air bubble and the nozzle and are thus limited by this spatial resolution. Besides, we are able to detect the neck up to the last frame before the bubble separates. These spatial and temporal uncertainties introduce some variation on the exact value of t_c . We use a Python routine to manually select a region close to the last data point (which corresponds to the smallest minimum thickness measured before pinch-off). For polymer solutions with $c \geq 0.05\%$, a filament appears between the bubble and the nozzle for a short time before pinch-off. In this case, the routine is slightly modified and will be discussed in the next section. We adopt an approach similar to the one used recently for the coalescence of liquid droplets [38]. For the processing, the time of the smallest minimum thickness measured is defined as a temporary value of $t = t_c$. We then vary this value $t_c - t$ in a narrow time range Δt and perform a best fit routine of this time axis with the minimum thickness. The exponent corresponding to the lowest value of the residual obtained from this best fit is the exponent associated with the thinning, which is reported in this study.

Modified definition for t_c in polymer solutions

For solutions of 4000K PEO at concentration $c \geq 0.05\%$, our experiments show that the filament shape is modified before pinch-off. The initial thinning exhibits a Newtonian-like dynamics. At later time, an air thread forms, connecting the bubble to the nozzle. The thinning of this air thread follows a different dynamics. This dynamics is visible in Fig. 3.11(a), which is obtained by using the definition of t_c used for Newtonian fluids (shown in pink). We modify the definition of t_c by selecting the moment the thread-like structure first appears as the new value of t_c . A similar approach has been successfully used for the pinch-off of droplets of polymers (see *e.g.*, [144]).

This modified evolution of the thinning is shown in Fig. 3.11(b). Using this rescaling of

time leads to a power-law evolution of the thinning dynamics in the Newtonian regime. The best fit of the data with the equation $(t_c - t)^\alpha$ shows here that we obtain an exponent close to 0.5. Note that such a power law is not recovered if we consider t_c as the final time of pinch-off. The power-law evolution is only valid for $t < t_c$, *i.e.*, in the Newtonian-like regime.

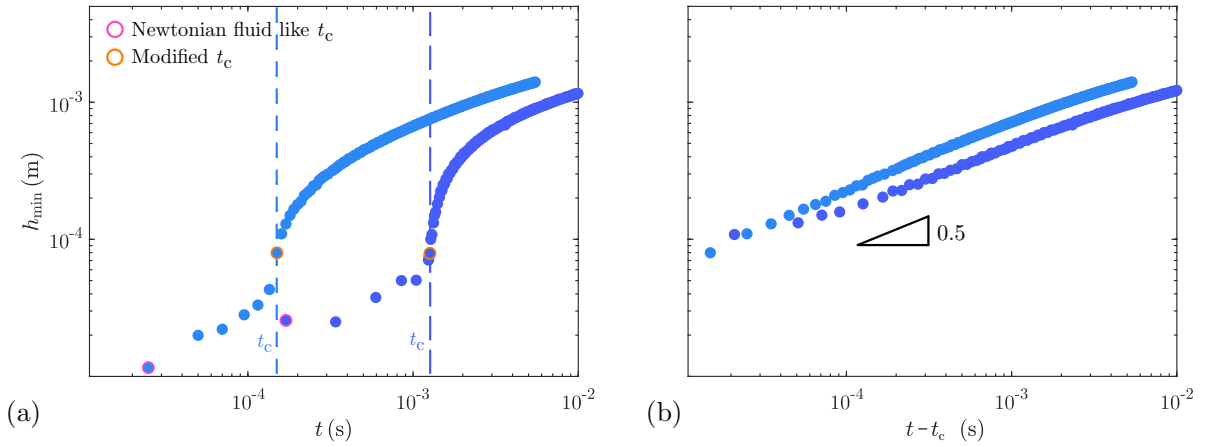


FIGURE 3.11: Thinning of a bubble in polymer solutions of 4000K PEO with mass concentration $c = 0.5\%$ (light blue) and $c = 1\%$ (dark blue) in a 75/25 wt% water/glycerol solvent at a flow rate $Q = 0.02 \text{ mL min}^{-1}$. (a) Evolution of the thinning dynamics without applying any time shift. (b) Log-log scale evolution after selecting t_c as the instant where the neck transition to an elongated thread.

Influence of the flow rate and the frame rate on the measured thinning dynamics

To ensure that the results reported in this study are not dependent on the experimental conditions, we vary the following experimental parameters: 1) the flow rate Q of the syringe pump used to generate the air bubble and 2) the frame rate of the recordings.

We set the syringe pump to the following flow rates $Q = 0.02, 0.05, 0.1, 0.2$ and 0.5 mL min^{-1} . The resulting thinning dynamics for the different flow rates are reported in Fig. 3.12(a). After selecting appropriate values of t_c , the thinning at different flow rates

overlaps well to reveal an exponent $\alpha \simeq 0.5$. Further, we extract the exponents with best fit power-laws and report the values in the inset of Fig. 3.12(a). For the range of flow rate Q considered, the variations in the exponent is within the accuracy of the experiment, here $\alpha = 0.5094 \pm 0.0129$. These experiments confirmed that the results reported in this study do not depend on the flow rate in the range $Q \leq 0.5 \text{ mL min}^{-1}$ considered here.

We also show in Fig. 3.12(b) the thinning dynamics extracted from movies recorded at frame rates of 75,000, 100,000, 150,000, and 200,000 frames per second. After shifting the thinning with appropriate t_c using the method described in the previous section, we observe that the thinning of the neck follows power-law evolution with best fit exponents $\alpha = 0.5023 \pm 0.023$, with no particular trend observed [see inset of Fig. 3.12(b)]. The value of the exponent of the power law does not depend on the frame rate of the recordings for the experimental conditions investigated in the main article, providing that the frame rate used is large enough.

Thinning in Newtonian solvents

The thinning dynamics in Newtonian fluids depends on the solvent viscosity, leading to power-law evolutions differing for inviscid and viscous solvents. This is shown in the main article, where the exponent $\alpha \simeq 0.5$ for inviscid solvents and $\alpha \simeq 1$ for viscous solvents is recovered [21]. The difference in thinning is also qualitatively visible at the bubble neck, which has a more conical or hyperbolic shape in the inviscid solvent. However, when the viscous forces are dominant, the thinning is slowed down, and the resulting neck can be fitted with a parabola.

Thinning in increasing concentrations of polymer solutions

We show in Fig. 3.14 the thinning in polymer solutions when time $t > t_c$. For low concentrations of 4000K PEO ($c \leq 0.02\%$), this time corresponds to when the bubble

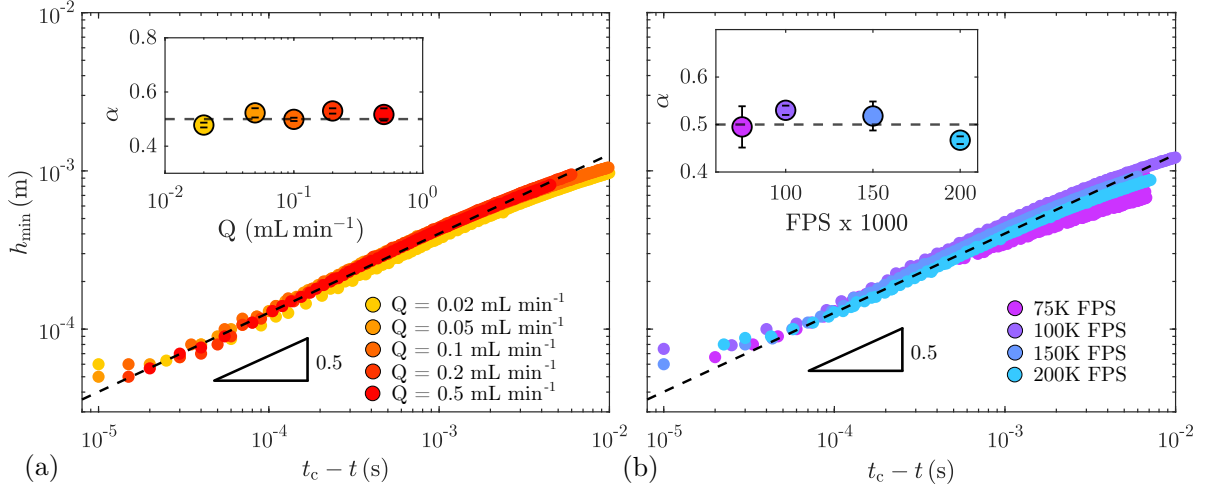


FIGURE 3.12: Thinning dynamics of air bubbles in polymer solutions of 4000K PEO with $c = 1\%$ mass concentration in a 75/25 wt% water/glycerol solvent. (a) Thinning dynamics for different flow rates Q between 0.02 mL/min and 0.5 mL/min. (b) Thinning dynamics recorded at different frame rates between 75,000 and 200,000 frames per second. The insets in both figures show the exponents obtained by the best-fit power law $(t_c - t)^\alpha$.

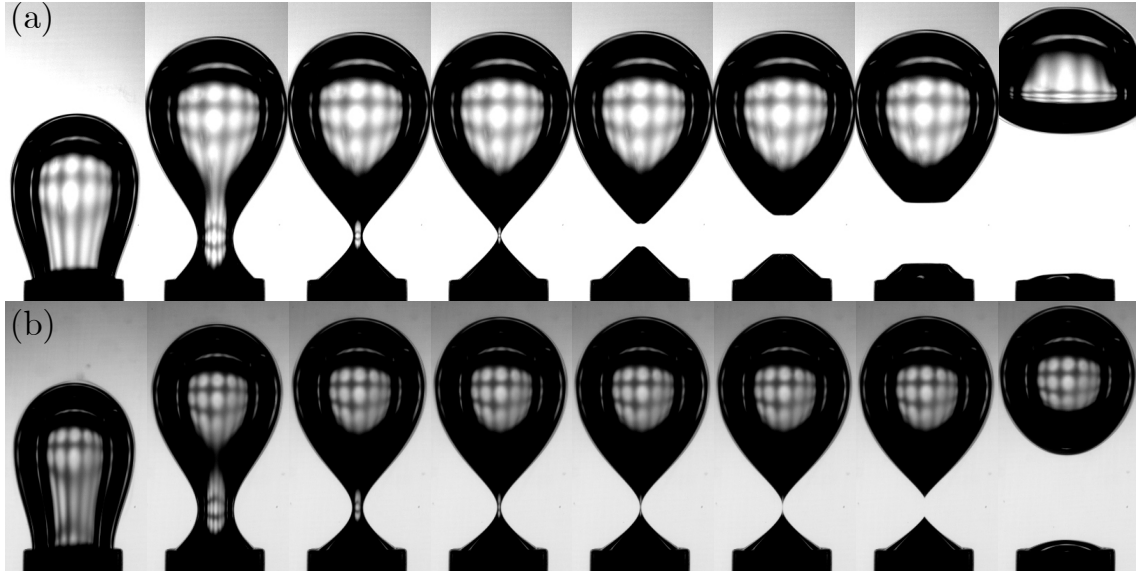


FIGURE 3.13: (a) Thinning of a bubble in a 75/25 wt% water/glycerol solvent of viscosity $\eta_s = 2.14$ mPa.s and (b) in a 10/90 wt% water/glycerol solvent of viscosity $\eta_s = 213$ mPa.s.

Chapter 3. *Bubble pinch-off in polymer solutions*

has already separated. However, for $c \geq 0.05\%$, the air filament is visible. The initial thickness of this filament increases with the polymer concentration, as illustrated in Fig. 3.14.

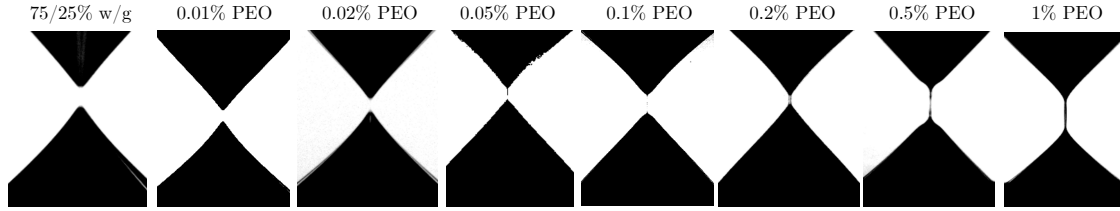


FIGURE 3.14: Profiles observed during the thinning of air bubbles in polymer solutions of 4000K PEO with mass concentrations from $c = 0\%$ to $c = 1\%$, prepared in a 75/25 wt% water/glycerol solvent. The pictures are taken slightly after t_c .

Chapter 4

Building a Capillary Bridge

Rheometer for particle-particle liquid bridges

The evolution of our understanding of capillary bridges—a field spanning more than two centuries—is a story of moving from static descriptions of liquid films to the complex, high-speed dynamics of polymeric systems. This chapter reviews the historical development of capillary force measurements and describes the construction of the "Capillary Bridge Rheometer," which formed a major part of my PhD work.

4.1 Historical Context

4.1.1 Young-Laplace and the birth of capillary cohesion measurements

The history of capillarity began with Thomas Young’s 1805 essay, which described the characteristic contact angle of a liquid on a substrate and identified how meniscus shape dictates the attractive or repulsive nature of the interaction [195]. Pierre-Simon Laplace mathematically derived the laws of fluid equilibrium in his *Mécanique Céleste* using ”corpuscular attraction” to establish the curvature-dependent pressure difference now known as the Young-Laplace equation [95]. While these foundational works focused on determining fluid elevation and meniscus profiles between solid objects, they did not yet utilize the modern term ”surface tension.” This terminology evolved throughout the 19th century alongside the development of precision measurement devices, such as the thin-plate method introduced by Ludwig Wilhelmy [193]. Further refinements in surface science were made through the experimental observations of Agnes Pockels and Lord Rayleigh regarding surface contaminants [141]. The field was later revolutionized by Irving Langmuir’s development of the surface balance in the early 20th century, which allowed for the study of monomolecular films and the precise quantification of surface pressure [94].

The early 20th century saw scientific work apply the concept of capillarity to the cohesion of Newtonian liquids in granular materials. This era was notably marked by the debate between Fisher (1926) [56], who correctly identified the contribution of surface tension alongside Laplace pressure in determining the total static cohesive force in granular assemblies, and Haines (1925) [70]. While Haines initially utilized a simplified toroidal

approximation to evaluate soil suction and moisture distribution, Fisher refined this model by demonstrating that the surface tension acting along the three-phase contact line must be included to accurately predict how cohesive stresses vary with moisture content. This critical exchange established the rigorous mathematical foundation for interparticle capillary forces, leading to the development of modern "regime maps" and numerical solutions that characterize the stability of wet granular matter.

4.1.2 Early developments in particle scale force measurements

A significant development in measuring capillary forces between individual particles was achieved by Mason and Clark (1965) [111], who conducted pioneering experiments using buoyancy-matched liquids. By suspending a liquid mixture in water to eliminate gravitational effects, they accurately measured rupture distances and forces as a function of separation distance and bridge volume, providing high-fidelity data that validated Fisher's original calculations. The measurements of Mason and Clark were further validated by Lian *et al.* (1993) [103], who developed exact numerical solutions for liquid bridges with zero and non-zero contact angles. They also derived analytical solutions based on the toroidal approximation considered by Fisher, assuming a constant curvature of the liquid bridge. In addition to achieving good agreement between numerical solutions and the measurements by Mason & Clark, this work was notable for establishing that the rupture distance of a liquid bridge scales with the cube root of its volume.

Willett, Adams, and Seville (2000, 2002) [2, 194] brought the focus back to experimental investigations of the forces exerted on particles. They developed closed-form approximations and regime maps to calculate capillary forces and rupture distances between equal and unequal spheres. Their work systematically accounted for the influence of gravity (via

the Bond number) and, in particular, quantified the differences in the force experienced by particles at different positions in a gravitational field—specifically, the distinction between the lower and upper particles.

4.1.3 Viscous dissipation in liquid bridges

Around the same time, Pitois *et al.* (2000) [139] proposed a simplified approximation to describe the dynamic force between spherical particles connected by a perfectly wetting fluid. This approximation accounted for the volume of the liquid bridge and, by including a viscous dissipation term derived from a lubrication approximation and a correction factor, incorporated viscous effects for high-viscosity oils. The effect of viscosity in liquid bridges was investigated in detail earlier by Ennis *et al.* (1990) [50], who measured the dynamic axial force of liquid bridges using various viscous fluids by imposing oscillations at a fixed frequency. Ennis defined the strength of the liquid bridge as the peak force measured as the particles are separated and derived an expression to rescale this peak force as a function of the system’s capillary number.

Much of this earlier work on liquid bridges focused on perfectly wetting Newtonian fluids, where the solid-liquid wetting angle was close to 0° . More recent research has focused on real fluids such as water, notably the work by Kruyt *et al.* (2017) [93] and Mielniczuk *et al.* (2018) [118]. Kruyt *et al.* developed an analytical description to quantify capillary forces based on the shape of the liquid bridge—a significant development, as it required accounting for the non-constant curvature of the bridge interface in contrast to the toroidal approximation. Mielniczuk made precise experimental measurements of capillary forces in aqueous systems, tracking their evolution under both terrestrial gravity and microgravity

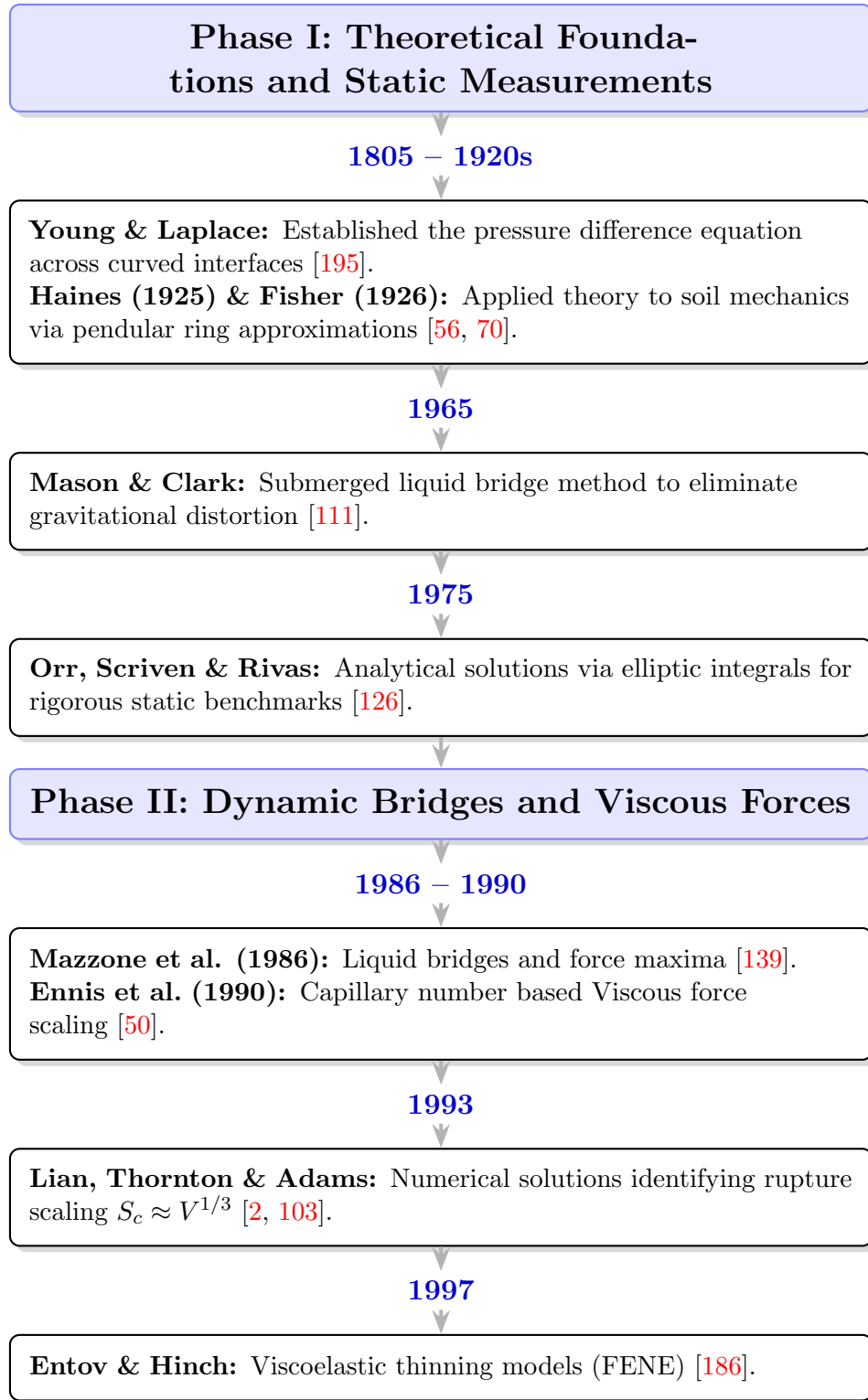


FIGURE 4.1: Evolution of Capillary Bridge Research (Part 1: 1805–1997)

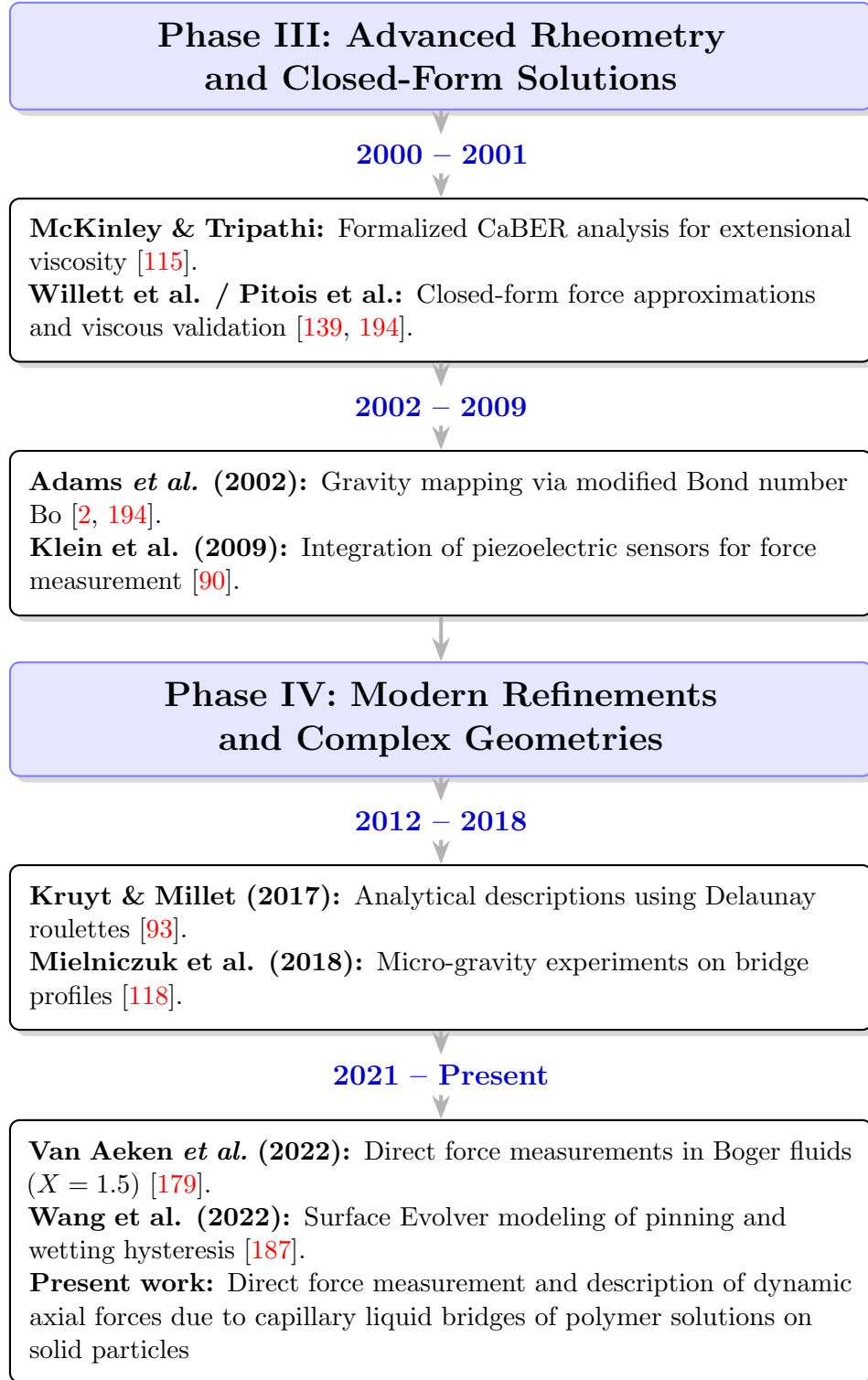


FIGURE 4.2: Evolution of Capillary Bridge Research (Part 2: 2000–Present)

conditions. Furthermore, their work tracks the dynamic evolution of the contact angle, offering a more realistic approach than previous static models.

4.1.4 Extensional rheology of polymer solutions and liquid bridges

In parallel with developments in capillary force measurements, the field of extensional rheology saw significant advances in the late 20th century through the development of devices such as the Filament Stretching Extensional Rheometer (FiSER) and the Capillary Breakup Extensional Rheometer (CaBER). The FiSER, pioneered by Gareth McKinley and colleagues in the 1990s, operates by actively moving two circular end-plates apart using a motor-driven system to impose a spatially uniform, exponentially increasing separation. This active stretch ensures a constant rate of extensional strain, allowing for the direct measurement of transient extensional stress growth from the onset of deformation; however, the device remains mechanically complex and prone to gravitational sagging in low-viscosity fluids [6, 114]. In contrast, the CaBER, introduced by Bazilevskii *et al.* (1997) [8], McKinley and Tripathi (2000) [115], and Rodd *et al.* (2005) [149], utilizes a “step-stretch” followed by a passive thinning phase. In this protocol, the end-plates are separated rapidly to a fixed distance, forming a fluid bridge that subsequently thins and breaks under the sole influence of capillary pressure, balanced by internal viscous and elastic stresses [115, 149]. While the CaBER is simpler to operate and highly effective for mobile, low-viscosity fluids, it does not allow for a pre-prescribed strain rate, requiring researchers to back-calculate rheological properties from the self-selected thinning rate of the mid-filament diameter.

Chapter 4. *Building a capillary rheometer*

As in the work by Kruyt *et al.* [93], there are studies in the literature on indirect stress measurements in liquid bridges of polymer solutions. For example, Van Aeken *et al.* (2022) [179] developed techniques to indirectly determine the axial stresses within a liquid bridge by analyzing its global geometry. Specifically, Van Aeken *et al.* utilized the "tilted CaBER" or horizontal filament method, where the gravitational sagging of a stretching polymer filament is fitted to a catenary function to extract the axial force from the shape of the bridge. The focus of this thesis, however, moves beyond such static, indirect measurements toward the direct, dynamic quantification of axial forces relevant to process modeling in powder technology. This work refocuses the analytical framework on the axial forces acting on the solid boundaries, thereby providing a molecularly informed description of the forces that hold together complex polymeric granular systems. The approach taken in this thesis to build a quantifiable description of capillary liquid bridges in polymer solutions closely resembles these extensional rheometry methods, effectively treating the solid spherical particles as the end-plates of a microscale rheometer.

4.2 Instrumentation for Capillary Bridge Rheometry

In this section, we present a detailed summary of the instrumentation developed for this work, the associated calibrations, and the measurement protocols followed to quantify interparticle capillary forces. We begin by describing the initial Stage I iteration, which utilized a precision weighing scale-based approach for static benchmarking. This is followed by a discussion of the Stage II development, which incorporates a high-sensitivity load cell for dynamic testing of viscoelastic fluids.

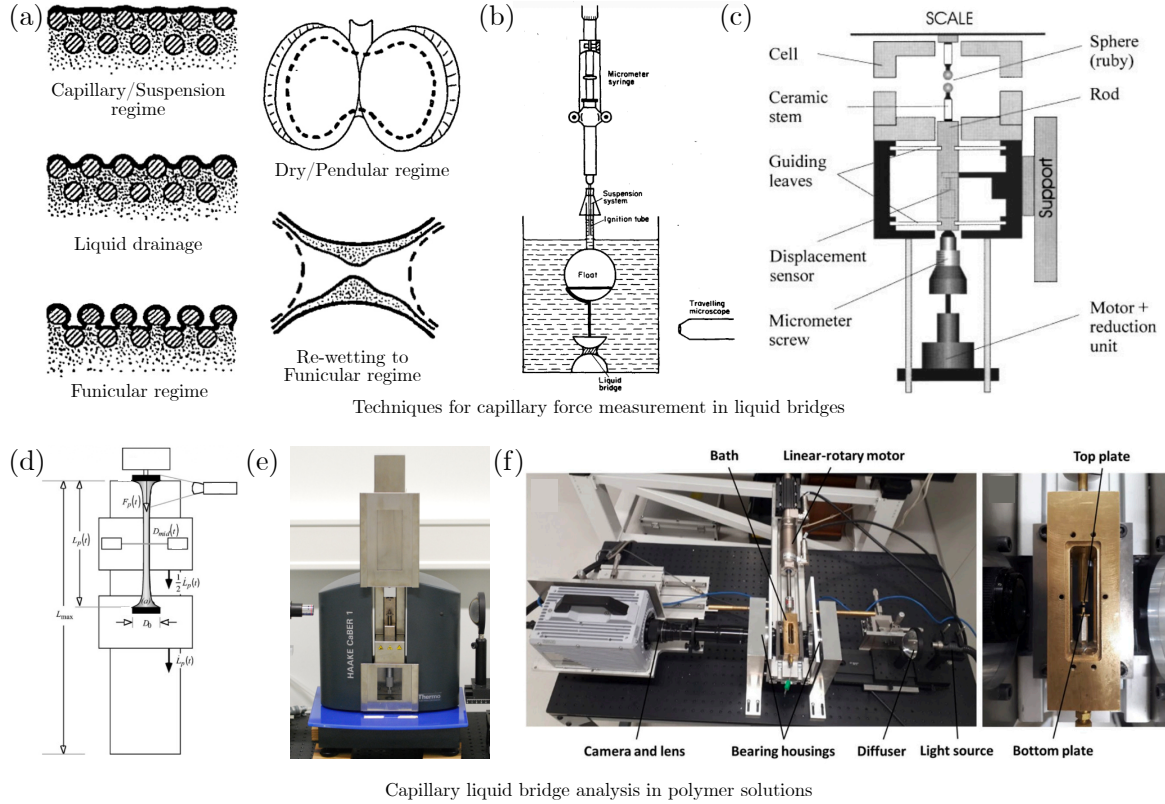


FIGURE 4.3: (a) Schematic provided by Haines (1930) [69] of various regimes of capillary liquid bridges of water in a model soil system. On the left is the drying process, and on the right is the re-wetting [Reproduced with permission from Cambridge University Press]. (b) Mason and Clark's (1965) [111] schematic of a buoyancy-matched liquid bridge experiment used to eliminate gravitational distortion in measurements [Reproduced with permission from Elsevier]. (c) Precision force balance setup used by Pitois *et al.* (2000) [139] for measuring interparticle forces, featuring a micrometric stage for particle-particle gap control [Reproduced with permission from Elsevier]. (d) FiSER device used for measuring filament shape and end-plate forces in a viscoelastic fluid [Reproduced with permission from AIP Publishing]. (e) A commercial CaBER device. [Wikipedia] (f) Modified horizontal CaBER built by Van Aeken *et al.* (2022) [179] for measuring the stress in a horizontal liquid bridge of polymer solution [Reproduced with permission from Springer Nature].

4.2.1 Stage I: Benchmarking and validation with precision scale

The primary objective of Stage I was to benchmark the working principles of the custom-built device and provide experimental validation of foundational capillary models. For this purpose, we measured the capillary forces of a $100 \text{ mPa} \cdot \text{s}$ silicone oil—the exact formulation utilized in the seminal studies by Pitois *et al.* [139].

The experimental setup, illustrated in Fig. 4.4, consisted of a precision weighing scale (OHAUS Pioneer) fitted with a custom 3D-printed mounting assembly. Following the methodology of Pitois *et al.*, ruby spherical lenses were employed as model particles. The lower particle was secured to the 3D-printed base on the scale, while the upper particle was mounted to a connecting rod attached to a linear translation stage (Thorlabs). This rod was interfaced with the stage via two perpendicular micrometric translation stages, enabling precise alignment of the particle pair along the x , y , and z axes. To mitigate environmental noise, the entire system was mounted on a Thorlabs optical breadboard, supported by passive vibration-isolation pads. A CMOS camera equipped with a Nikon macro lens was positioned to record the liquid bridge profile for shape analysis and volume quantification.

For this benchmarking phase, AP100 silicone oil (Sigma-Aldrich) was used. At 20°C , this oil has a viscosity of approximately $100 \text{ mPa} \cdot \text{s}$, closely matching the fluid properties reported by Pitois. A small volume of the oil was gently loaded between the particles using a micropipette. The upper particle was oscillated vertically to ensure the resulting bridge was perfectly axisymmetric before initiating the measurement protocol. To simulate a quasi-static regime and minimize viscous contributions, the particles were separated at the minimum possible velocity allowed by the translation stage ($v = 0.01 \text{ mm/s}$). The force

data were continuously recorded and streamed to a computer at a fixed sampling rate, enabling precise mapping of axial force as a function of the interparticle gap distance, D .

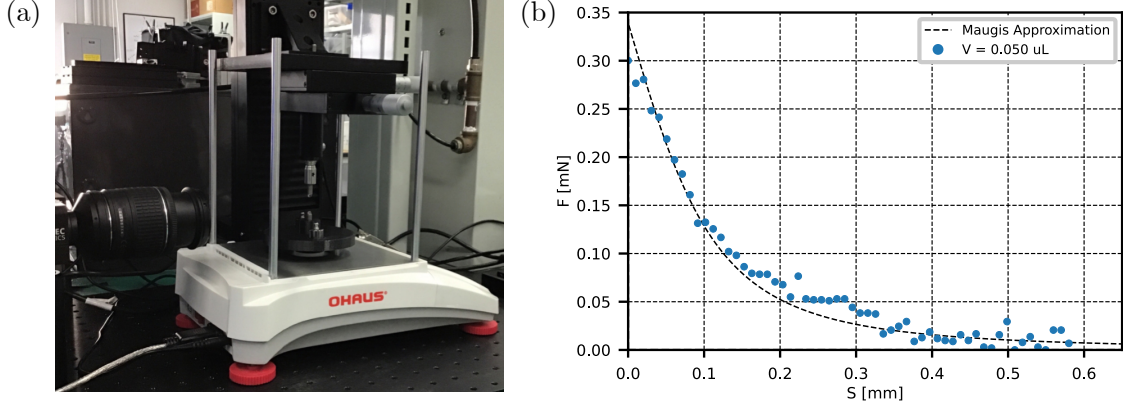


FIGURE 4.4: (a) Experimental setup for Stage I development, utilizing a precision weighing scale for quasi-static force measurements between a ruby sphere and a stationary base. (b) Axial force due to a liquid bridge of AP100 silicone oil between 4 mm spherical particles measured with the precision force setup.

To validate the experimental results, the measured forces were compared against the "Gorge method" approximation as shown by Pitois *et al.* [139] and derived by Maugis [112]:

$$F_{\text{Cap}} \approx 2\pi R\gamma \cos \theta \left[1 - \frac{1}{\sqrt{1 + \frac{2V}{\pi R S^2}}} \right] \quad (4.1)$$

where R is the particle radius, γ is the surface tension of the liquid, θ is the contact angle, V is the liquid bridge volume, and S is the separation distance. This expression is derived from the toroidal approximation, which assumes a constant curvature of the liquid meniscus. For silicone oil on a ruby surface, the contact angle is assumed to be perfectly wetting ($\theta \approx 0^\circ$).

A significant challenge in these measurements is the precise determination of the bridge volume V . Standard pipetting procedures are challenging to execute at the specific loading angles required by the particle geometry, leading to discrepancies between the nominal

and actual bridge volumes. To ensure the system remained in the gravity-free regime defined by Adams *et al.* [2], we targeted a small volume of $V = 0.05 \mu\text{L}$. This corresponds to a dimensionless volume $V^* = V/R^3 \simeq 0.00625$ and a Bond number ($\text{Bo} = \rho g R^2 / \gamma$) of approximately 1.74, where ρ is the liquid density and g is the gravitational constant.

4.2.2 Volume measurement with image analysis

To overcome the uncertainties of manual pipetting, we developed a custom image analysis pipeline in Python to calculate the volume post-experiment. The liquid bridge was treated as a solid of revolution by binarizing the two-dimensional profile captured by the CMOS camera (see Fig. 4.5). Assuming axisymmetry about the vertical axis, the total volume V is defined by the integral:

$$V = \int_{z_{\min}}^{z_{\max}} A(z) dz = \int_{z_{\min}}^{z_{\max}} \frac{\pi [D(z)]^2}{4} dz \quad (4.2)$$

where $D(z)$ is the local bridge diameter at height z . To compute this numerically, the bridge domain was discretized into N horizontal slices corresponding to pixel rows. The volume was then calculated as a discrete sum:

$$V \approx \sum_{i=1}^N \frac{\pi d_i^2}{4} \Delta z \quad (4.3)$$

In this expression, d_i is the physical diameter calculated by dividing the pixel width of the bridge at row i by the spatial scaling factor S , and $\Delta z = 1/S$ represents the physical height of a single pixel row. This summation provides the total volume in mm^3 , which is equivalent to microliters (μL).

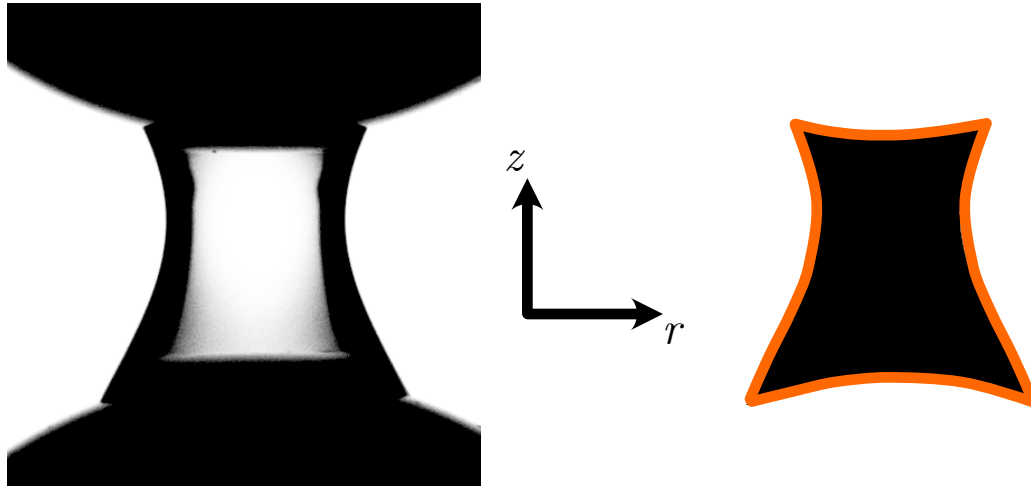


FIGURE 4.5: Processed image showing the detected contour and discretized horizontal slices used for calculating the liquid bridge volume via a solid-of-revolution approximation.

4.2.3 Stage II: High-frequency measurements with precision Load Cells

Once we established a working protocol for force measurements using the precision balance scale, we replaced the scale with a load cell to enable high-frequency data acquisition. The pre-calibrated load cell, whose specifications are discussed below, directly acquires force data and transmits it in real time to the computer.

The experimental methods and setup used for the capillary force measurements, shown in Fig. 4.6, were custom-built in-house. The core of the setup consists of a Futek force

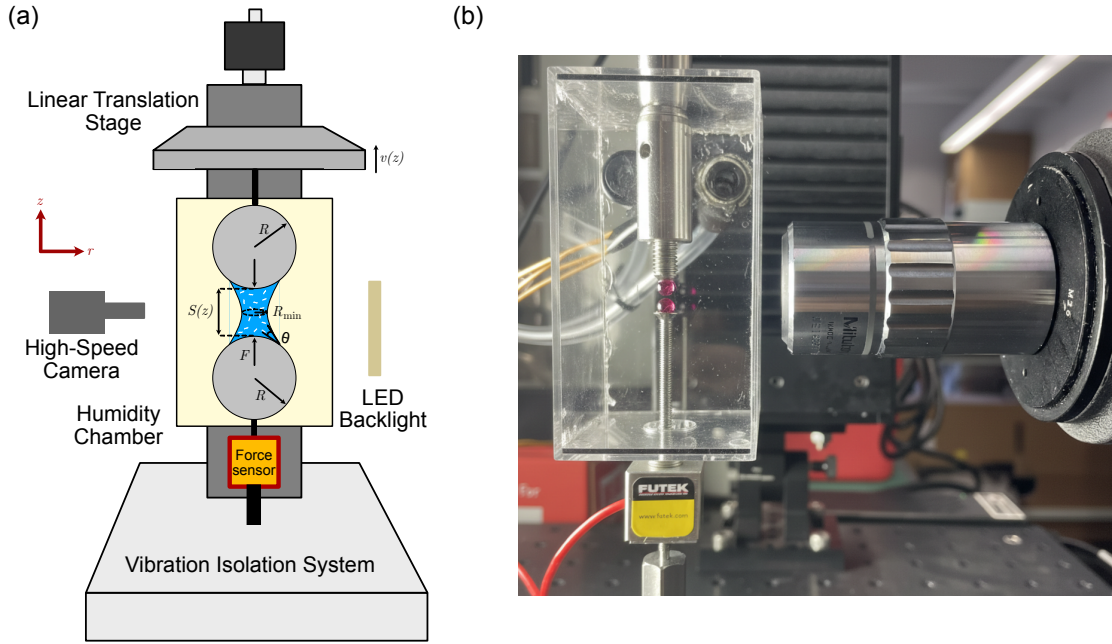


FIGURE 4.6: Schematic of the experimental setup

sensor equipped with a 10-gram load cell (LSB 200), providing a measurement accuracy of $\pm 10 \mu\text{N}$. The load cell has a resonant frequency of 140 Hz; however, data acquisition was performed at 100 Hz, well below this resonant frequency. To ensure accurate measurements, data were also acquired at multiple frequencies to verify that the values obtained were unaffected by resonant-frequency noise. To minimize noise from external vibrations, the force sensor was mounted on an active vibration-isolation system (Nexus, Thorlabs). This pad effectively damps noise originating from ground vibrations or environmental disturbances. The lower bead, part of the experimental setup, was mounted on the force sensor. Both the lower and upper beads used here have the same radius, $R = 2 \text{ mm}$. The beads used were acquired from Edmund Optics (Ruby Doped Sapphire Ball Lens) and feature a surface roughness on the order of a few microns.

The polymer solution used in the experiments has a relaxation time on the order of

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100 ms or larger. This ensures that the chosen data acquisition frequency is sufficient to resolve the axial forces generated by the polymers within the droplets used in the study. The upper bead used in the experiments was attached to a linear translation stage from Thorlabs. This translation stage offers precise control over position, velocity, and acceleration with a resolution of $1\text{ }\mu\text{m}$. In addition, we also maintain a constant humidity of 80% within the experimental setup and prevent evaporation of the polymer solution during the experiment using an in-house custom humidity chamber. This level of humidity, as confirmed by previous studies, is sufficient to prevent evaporation of the polymer solution during the experimental timescales [76], of the order of 10 to 100 s. In addition to data acquisition from the force sensor, the droplet’s extensional dynamics were recorded simultaneously using a high-speed camera (VEO Phantom 710). Data was acquired at frame rates ranging from 100 to 1000 frames per second, depending on the polymer concentration and corresponding relaxation time of interest.

The procedure for measuring capillary forces in polymer solutions is as follows: the solution droplet is first deposited onto the lower bead, which is positioned at a sufficient distance from the upper bead to allow easy sample loading. The sample is deposited using an Eppendorf pipette, with volume ranging from 0.5 to $1\text{ }\mu\text{L}$. This volume range was selected to ensure sufficient sample is available for the measurements. However, due to the high viscosity of polymer solutions, accurately dispensing a known volume directly from the pipette is challenging. To address this, an independent image analysis is developed to estimate the sample volume with precision and is described in the previous section. Once the sample is loaded onto the lower bead, the upper bead is carefully lowered to contact the polymer solution. To ensure an axially symmetric initial liquid-bridge configuration, the upper bead is oscillated by a few micrometers at sufficiently low rates to avoid disrupting the polymer microstructure. Following this, the gap between the

two beads is reduced to near-zero separation. The starting position of the upper bead is determined before loading the liquid by monitoring the live force readings, which become negative upon contact between the two beads.

Data acquisition is initiated after the beads make contact and is started simultaneously with the movement of the translation stage, which controls the separation of the beads at a set velocity. This allows us to track the Force F as a function of the gap S between the beads for a given velocity. The velocity range used in the study spans 0.01 to 10 mm/s. The rupture distance of the liquid bridge varies with polymer concentration and separation velocity, but remains within the maximum separation distance of 30 mm permitted by the current design. The data from the force sensor and high-speed camera are post-processed using custom routines in ImageJ and Python.

4.2.4 Validating the experimental setup with silicone oil

In Fig. 4.7, we show the capillary liquid bridge formed by AP100 silicone oil (by Sigma-Aldrich). AP100 has very low viscosity ($\eta \simeq 100$ mPa.s) and surface tension ($\gamma = 24$ mN/m, as provided by the supplier), which also results in a small contact angle ($\theta = 0^\circ$). For the validation test, the volume of silicone oil is also kept very low to avoid any perturbation from gravity. We measure the volume $V = 0.036 \mu\text{L}$ from the image analysis described in 4.2.2.

The particles shown in Fig. 4.7 are separated quasi-statically. In the present work, the quasi-static condition is defined as $v = 0.01$ mm/s. We show the capillary force (F) measured as the gap (S) increases in Fig. 4.8. The measured force is compared with the approximation derived from the Gorge method by Pitois *et al.* [139](Eqn. 4.1). The experimental measurements agree well with this approximate equation, which is only

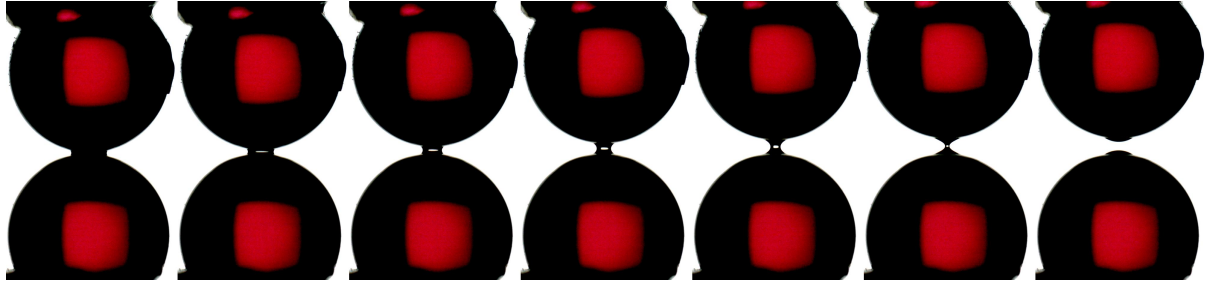


FIGURE 4.7: Capillary liquid bridge formed by $0.036 \mu\text{L}$ of AP100 silicone oil between $R = 2 \text{ mm}$ particles separated quasi-statically ($v = 0.01 \text{ mm/s}$).

valid for liquids with small contact angle ($\theta \simeq 0 - 10^\circ$). Notably, for $V = 0.036 \mu\text{L}$, the experimental measurements follow the expected curve very closely. Furthermore, the measured rupture distance $S_{\text{rup}} = 0.345 \text{ mm}$ is close to the value estimated from the expression provided by Lian *et al.* [103] $(1 + 0.5\theta)V^{1/3} \simeq 0.33 \text{ mm}$.

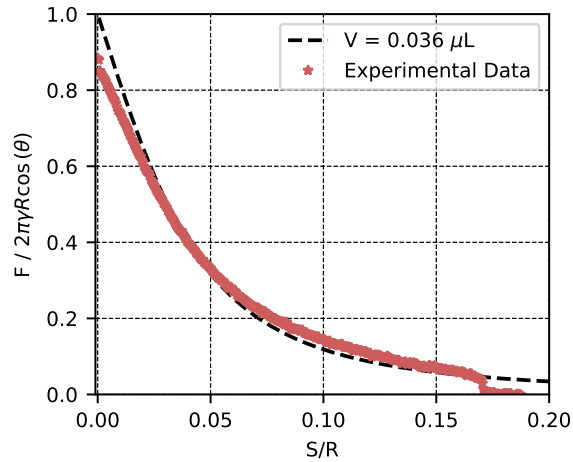


FIGURE 4.8: Axial force due to AP100 silicone oil of $V = 0.036 \mu\text{L}$ on spherical particles measured using the force sensor-based setup described in 4.2.3. The measured forces agree well with the Maugis approximation based on the Gorge method, thereby validating the experimental setup.

4.3 Conclusion

We presented a brief historical overview of developments in capillary force measurement devices and the experimental protocol used to obtain the results discussed in Chapter 5. Historically, these devices have focused either on liquid bridges of Newtonian fluids—measuring the force exerted by the fluid on connecting particles—or on the extensional viscosity of polymer threads, aiming to resolve axial stresses in cylindrical ligaments formed during uniaxial extension. This thesis bridges these two related fields by quantifying the role of polymer rheology in the axial forces exerted on particles. We present an experimental protocol to measure axial stresses directly using a force sensor and validate this technique with a Newtonian liquid (AP 100). In the subsequent chapter, we systematically vary polymer concentrations to establish a framework for incorporating polymer rheology into axial force measurements.

Chapter 5

Axial forces in capillary liquid bridges of polymer solutions

This chapter investigates direct force measurements of capillary liquid bridges in polymer solutions. Liquid bridges form between particles during wet mixing with binders or via condensation from ambient humidity, inducing macroscopic cohesion that drives the formation of particulate agglomerates and stabilizes structures like sandcastles. Because bulk cohesive properties arise from these microscopic interactions, particle-scale measurements are essential for developing predictive models. While most existing studies assume Newtonian liquids, many industrial and environmental binders exhibit viscoelastic behavior.

In this chapter, we measure the axial force generated by viscoelastic polymer solution bridges between two spherical beads during controlled uniaxial separation. By varying the polymer concentration, separation velocity, and particle size, we track the evolution of the force as the bridge thins and ruptures. At quasi-static extension rates, polymer rheology

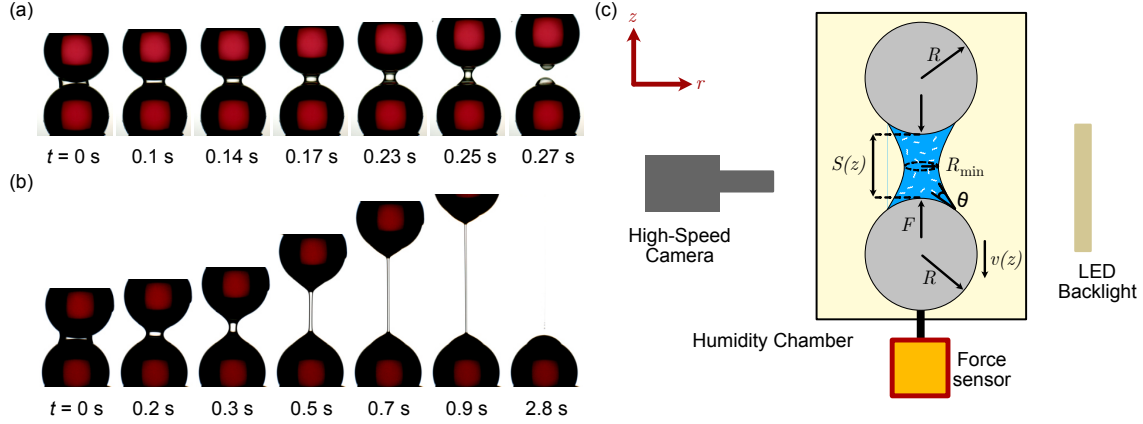


FIGURE 5.1: Thinning of a liquid bridge of (a) Water, and (b) 4M PEO with 1% by mass concentration prepared in water. The liquid bridge is positioned between two beads of radius $R = 2$ mm and separated with a velocity $v = 10$ mm/s. (c) Schematic of the experimental setup.

does not significantly affect the capillary force. However, increasing the stretching rate increases the peak force through viscous dissipation and promotes the formation of a viscoelastic filament, delaying rupture. Rupture is preceded by elasto-capillary thinning of the filament. This dynamics differs notably from observations under exponential separation (CaBER) or gravity-driven thinning (droplet pinch-off, Chapter 2); the constant separation velocity induces partial stretching of the polymer chains, resulting in a shorter characteristic relaxation time. Finally, we show that peak capillary forces collapse when rescaled by the capillary number and particle size, while the rupture distances scale with the Weissenberg number. These results ultimately provide a simple particle-scale force law for polymeric binders.

5.1 Introduction

Liquid bridges between solid particles are ubiquitous, appearing in contexts ranging from soil moisture [11, 26, 70] to industrial granules [23, 146]. Many natural and industrial

solids are heterogeneous—for instance, due to extracellular polymeric substances (EPS) in moisture trapped between soil particles [106] or the use of polymeric binders in industrial slurries [15, 98, 146, 199]. In high-intensity erosion and debris flows, rapid deformations with large localized strain rates at particle scales can trigger microscale polymeric cohesion [85, 92, 127, 196]. Similarly, precise modeling of particle-scale interactions with binders is critical for industrial granulation, fluidization, and asphalt pavement design [9, 51, 200]. However, direct measurements of polymeric axial forces between individual particles are lacking in the literature.

Particle-scale axial forces in Newtonian liquid bridges, shown in Fig. 5.1(a), are well-established [111, 139, 194]. Early investigations focused on theoretical descriptions of capillary cohesion in soil [56, 70] and submerged, gravity-free measurements of inter-particle adhesion [111]. Lian *et al.* [103] later provided numerical solutions for capillary force and rupture distance, which were validated experimentally using silicone oil by Willet *et al.* [194] and Pitois *et al.* [139]. Pitois *et al.* and Ennis *et al.* [50] extended these measurements to fully wetting viscous fluids. Force measurements in industrially relevant water-based solutions add challenges involving evaporation, contact angle hysteresis [167], gravitational effects [113, 118, 190], and three-body interactions [187]. The present work extends these investigations to include the impact of polymeric viscoelasticity.

Inter-particle axial forces are primarily controlled by capillarity. The capillary thinning dynamics of Newtonian and non-Newtonian liquid bridges are well established [6, 7, 38, 42, 53, 60, 61, 115, 114, 144, 150]. Previous investigations have shown that polymers modify capillary flow in uniaxial extension, where the thinning dynamics are demarcated by distinct Newtonian and viscoelastic regimes, introducing new length scales to the flow [3, 24, 52, 144, 177]. Techniques such as FISER [6, 114], CaBER [115, 150], droplet pinch-off [38, 144, 145], Dripping-onto-Substrate (DoS) [43, 42], and the Slow Retraction

Chapter 5. *Axial forces in polymer solutions*

Method (SRM) [60, 61] have established that polymeric axial flows exhibit an initial Newtonian regime, followed by a sharp coil-stretch transition to a viscoelastic regime characterized by cylindrical ligaments. We show this for a capillary liquid bridge between spherical particles in Fig. 5.1(b). Recent studies indicate a smoother transition at semi-dilute entangled concentrations due to lower critical coil-stretch strain rates [61, 144]. In the Newtonian regime, coiled polymers contribute to viscous dissipation that scales with concentration, generating larger axial forces than the solvent. Consequently, the combined effects of increased force and delayed rupture distinguish polymeric bridges from Newtonian ones, requiring modified bulk descriptions for granular-polymer mixtures.

This chapter investigates the axial forces in polymeric liquid bridges across a range of polymer concentrations and separation velocities, v , spanning four orders of magnitude. We specifically use a constant separation velocity, contrasting with the exponential or gravity-driven profiles in previous studies, [115, 144] due to the relevance of grain kinematics in Discrete Element Method (DEM) models. Experimental methods and polymer rheology characterization are detailed in § 2. Section 3 examines these forces under quasi-static conditions ($v = 0.01$ mm/s), where thinning is strictly controlled by capillarity, as well as under dynamic separations, where viscoelastic effects become prominent. We then present a first-order analytical framework to describe the evolution of the force across both regimes. In § 4, we develop dimensionless scaling laws: we collapse the peak force—which governs the bridge’s adhesive strength—using the Capillary number, confirm its linear scaling with particle size, and rescale the extended rupture distance using the Weissenberg number. Finally, § 5 provides our concluding remarks.

5.2 Experimental Methods

The experimental setup and methodology used in the following have been discussed in Chapter 4, subsection 4.2.3. All the measurements and results presented here were obtained using a high-precision load cell. In the following section, we discuss in more detail the rheology and interfacial properties of the solutions used.

5.2.1 Rheology of the Polymers

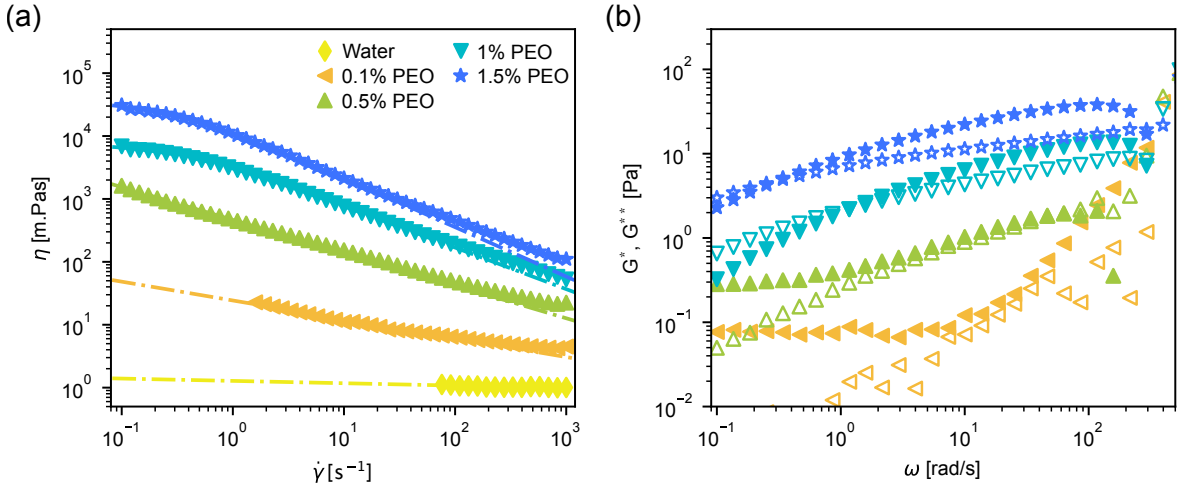


FIGURE 5.2: (a) Evolution of the shear viscosity η with the shear rate $\dot{\gamma}$ as well as (b) storage and loss modulus at different angular frequency ω for polymer solutions prepared with different concentrations of 4M PEO in water.

Polymer solutions are prepared by dissolving polyethylene oxide (PEO, Sigma-Aldrich) powder with molecular weight $M_w = 4000$ kg/mol in deionized (DI) water; these are hereafter referred to as 4M PEO. Mixtures are homogenized on a roller (ThermoFisher ScientificTM) at 40 RPM for 24 hours prior to use. The intrinsic viscosity is $[\eta] = 0.072M_w^{0.65} = 1.41$ m³/kg, yielding an overlap concentration $c^* = 0.77/[\eta] = 0.055\%$ [177]. We test concentrations $c = 0, 0.1, 0.5, 1$, and 1.5% , spanning the semi-dilute to dense

regimes ($2 \leq c/c^* \leq 30$). To minimize chain degradation, solutions of each concentration are prepared individually rather than by diluting a stock. The shear rheology for the solutions, summarized in Fig. 5.2(a), exhibits strong shear-thinning behavior fitted by the Carreau-Yasuda model. Fig. 5.2(b) details the corresponding viscous and elastic moduli.

5.2.2 Extensional Rheology

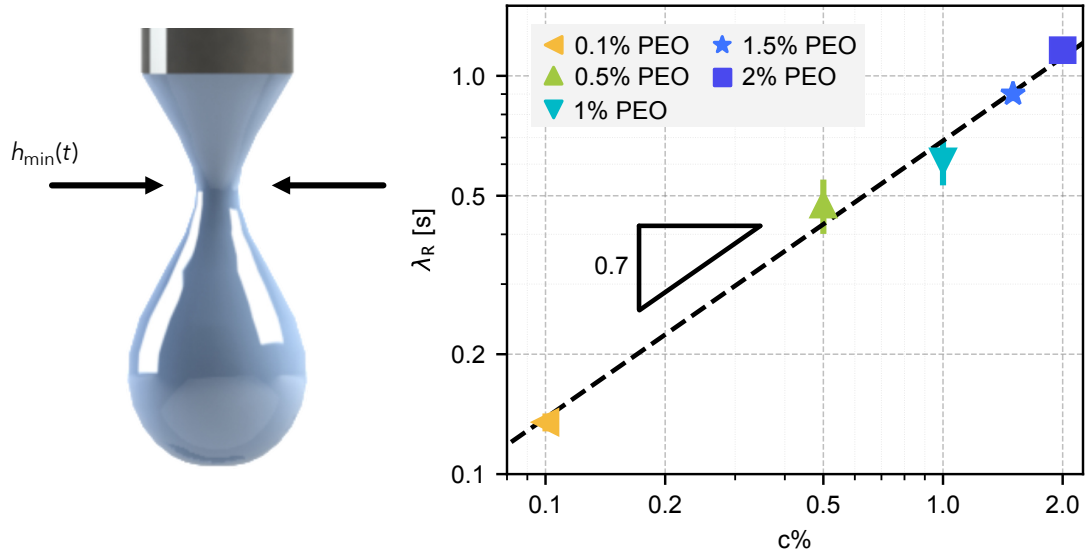


FIGURE 5.3: (a) Schematic of a droplet indicating how the minimum thickness of the thinning droplet is measured (b) Relaxation time (λ_R) of a 4M PEO solution at $c = 0.1 - 2\%$ in water. The nozzle diameter used to measure λ_R is $h_0 = 2.75$ mm.

The extensional rheology of the polymer solutions is summarized in Fig. 5.3. To measure the relaxation time, we quantify the evolution of the minimum thickness of the neck in a droplet pinch-off, $h_{\min}(t)$. As noted in numerous previous studies [144, 177], the droplet pinch-off in the viscoelastic regime follows an exponential thinning characterized as: $h_{\min}(t) \propto e^{-t/3\lambda_R}$. By fitting the thinning dynamics in the exponential regime, we extract the relaxation time (λ_R) for the polymer solutions, summarized in Fig. 5.3. As

noted in previous works, the relaxation time scales with the concentration of the polymer solution as

$$\lambda_R \propto c^{0.7} \quad (5.1)$$

where the exponent of 0.7 is similar to values previously reported by Tirtaatmadja *et al.* [177] and Rajesh *et al.* [144]. From Fig. 5.3, we observe that λ_R increases with concentration with an exponent of 0.7, consistent with previous observations [144, 177]. The relaxation time provides a timescale for analyzing the axial force measurements and rupture distance of the liquid bridge, as discussed later in the chapter.

5.2.3 Interfacial Properties

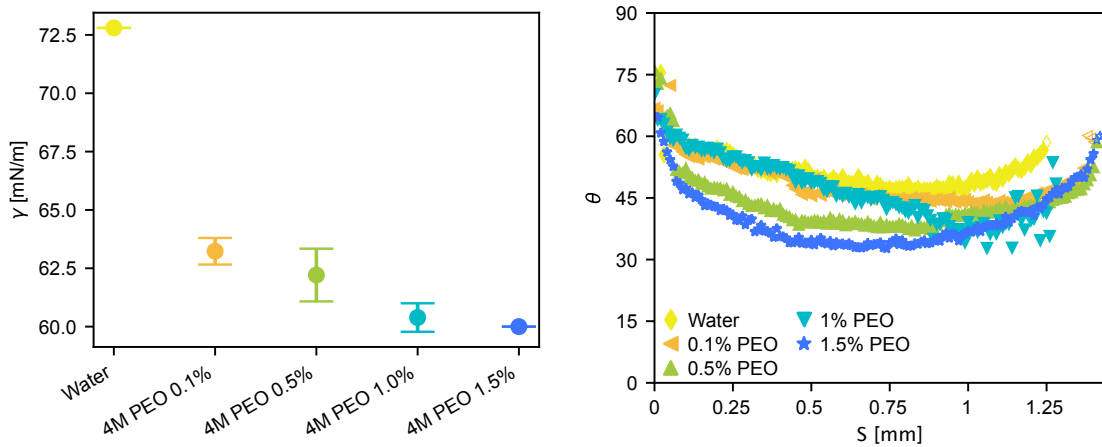


FIGURE 5.4: (a) Surface tension and (b) evolution of the contact angle (θ) as a function of the gap (S) between the particles for water and 4M PEO solutions of $c = 0.1 - 1.5$ %.

Interfacial properties are summarized in Fig. 5.4. Fig. 5.4(a) shows that adding 0.1% polymer reduces the surface tension from $\gamma = 72.8$ mN/m for water to ≈ 63 mN/m. Subsequent concentration increases yield negligible changes, as measured by an Attension

Tensiometer. While direct measurement at $c = 1.5\%$ proved difficult, we assume $\gamma = 60$ mN/m consistent with high-molecular-weight solutions [25]. The solid-liquid contact angle θ in Fig. 5.4(b) is extracted via custom Python image processing as a function of separation distance S . At small S , θ drops sharply due to the concave interface formed by initial capillary repulsion, before equilibrating. Although θ varies slightly with concentration and volume, it stabilizes beyond initial gaps to $\theta \in [30^\circ, 50^\circ]$ for all c .

5.3 Results

5.3.1 Quasistatic Capillary Bridges

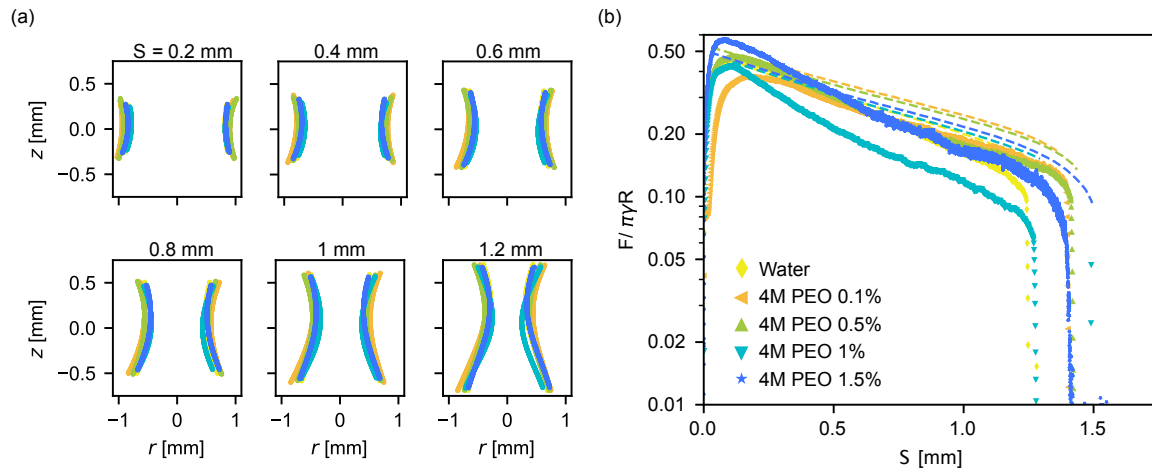


FIGURE 5.5: (a) Contours of a quasi-static liquid bridge of $c = 0$ – 1.5% 4M PEO in water for $S = 0.2$ to $S = 1.2$ mm at separation velocity $v = 0.01$ mm/s for various gaps S between the particles. (b) Quasi-static axial force as a function of the gap S . The dashed lines are fits based on Eqn. 5.4.

In this subsection, we present axial forces measured under quasi-static conditions. For the volumes used here, achieving a true static condition is challenging as the liquid eventually drains due to gravity. However, a velocity of $v = 0.01$ mm/s approximates this regime

satisfactorily. Figure 5.5(a) illustrates the evolution of liquid bridge contours for 4M PEO solutions ($c = 0\text{--}1.5\%$) at separation distances $S = 0.2\text{--}1.2$ mm with $v = 0.01$ mm/s. Although the measured liquid bridge volume varies slightly across concentrations ($V = 0.6\text{--}0.9$ μL), it does not significantly influence the observed curvature. Direct measurements also confirm that surface tension and the dynamic solid-liquid contact angle (see Fig. 5.4) vary only slightly across concentrations. Consequently, capillarity dominates, and we expect similar axial forces for $c = 0\text{--}1.5\%$. Therefore, under quasi-static conditions, capillary forces can be estimated by quantifying the liquid bridge shape, as the primary difference between solutions is merely surface tension, analogous to water [93].

Deriving an exact analytical solution for the capillary force between particles requires solving the Young-Laplace equation, which is generally intractable [126]. Existing work relies on numerical solutions [54, 103, 126] or approximations from assumptions of perfect wetting for the liquid (the Gorge method) [103, 139]. For water, which typically has larger contact angles, accurate descriptions require either numerical integration [103] or cumbersome tracking of bridge geometry [118]. Here, we propose a simplified framework based on the evolution of the minimum neck radius of the liquid meniscus, $R_{\min}$. Such descriptions have been widely used for extensional flows of inviscid, viscous, and viscoelastic liquids [47, 115, 114], and provide a robust framework for quasi-static and dynamic conditions.

To describe the capillarity-dominated axial force on the lower bead, we consider the liquid volume below the minimum meniscus radius $R_{\min}$, as shown in Fig. 5.1(c):

$$F = 2\pi\gamma R_{\min} - \pi R_{\min}^2 \Delta P - V_s \rho g \quad (5.2)$$

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The first term represents the axial contribution of surface tension along the perimeter $2\pi R_{\min}$. The second term accounts for the Laplace pressure difference across the curved interface, while the third term corrects for gravitational distortions [194]. The pressure difference ΔP is given by the Young-Laplace equation:

$$\Delta P = \gamma \left[\frac{1}{R_1} + \frac{1}{R_2} \right] \quad (5.3)$$

where R_1 and R_2 are the principal radii of curvature of the liquid-air interface. We approximate the first principal radius (inside the liquid) as $R_1 \approx R_{\min}$. Image analysis confirms that the local curvature is dominated by the azimuthal component, such that $1/R_1 \gg 1/R_2$. This condition is supported by the relatively large contact angles observed for these water-based solutions [see Fig. 5.4(a)]. Finally, the gravitational volume term V_s exhibits a complex dependence on S . However, for the simplified description sought here, we neglect its influence. These approximations simplify Eqn. 5.2 to:

$$F \simeq \pi\gamma R_{\min} \quad (5.4)$$

Equation (5.4) is plotted against the experimental data as dashed lines in Fig. 5.5(b). Even without accounting for gravitational distortions, it describes the experimental measurements of F reasonably well as the force decays from its maximum, eliminating the need for rigorous modeling of the liquid bridge geometry.

Experimentally, we observe that, consistent with previous work [116, 118, 167, 187], the force initially increases to a peak before decreasing as S increases. This behavior is attributed to the contact angle evolution, θ [Fig. 5.5(b)]: at small gaps, $\theta \geq 90^\circ$ generates a repulsive force due to the convex meniscus. The peak axial force is $F \simeq 0.18 \pm 0.03$ mN

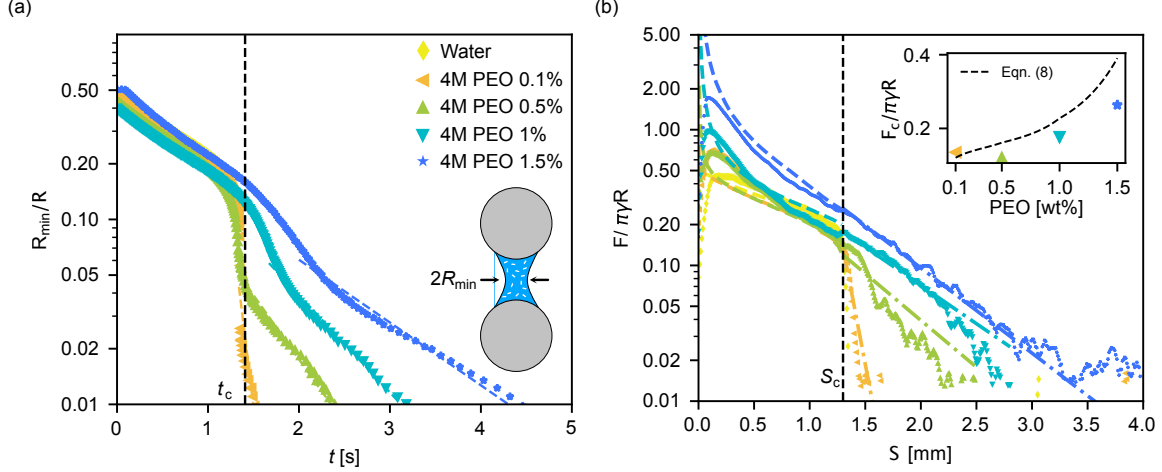


FIGURE 5.6: (a) Time evolution of the rescaled minimum neck radius $R_{\min}(t)/R$ for liquid bridges of 4M PEO in water ($c = 0 - 1.5\%$) separating at $v = 1$ mm/s. The thinning dynamics transition from Newtonian ($t < t_c$) to viscoelastic ($t \geq t_c$). (b) Corresponding rescaled axial force $F/\pi\gamma R$ versus separation gap $S = vt$. Dashed lines correspond to the model predictions in the Newtonian (Eqn. 5.7) and viscoelastic (Eqn. 5.8) regimes. The inset compares the fitted critical force F_c from Eqn. 5.8 with the prediction from Eqn. 5.9.

across all concentrations ($c = 0 - 1.5\%$). Furthermore, the $F(S)$ profile is similar for all solutions. Minor variations, particularly for $c = 1\%$, result from a smaller bridge volume ($V = 0.6 \mu\text{L}$ versus $0.7 - 0.9 \mu\text{L}$ for the other concentrations). A smaller volume leads to faster force decay, as evidenced by the rupture distance scaling $S \propto V^{1/3}$ [103]. Consequently, the measured forces are essentially independent of c . For $c \geq 0.1\%$, weak viscoelastic effects appear only milliseconds before rupture and are negligible.

5.3.2 Dynamic Liquid Bridges: Role of polymer concentration on capillary forces

When the separation velocity $v > 0.01$ mm/s, the viscoelastic regime becomes increasingly relevant. The transition between regimes is triggered by the imposed strain rate, which, when sufficiently large, leads to the onset of viscoelasticity [144]. In velocity-controlled

setups, such as FISER or the present chapter, the strain at a gap S is $\varepsilon_v = S/R$, resulting in an imposed strain rate $\dot{\varepsilon}_v = v/R$. If $\dot{\varepsilon}_v$ is sufficiently large, it triggers the abrupt uncoiling and extension of polymer chains [63], resulting in a viscoelastic regime characterized by cylindrical ligaments.

Figure 5.6(a) shows the time evolution of the rescaled minimum neck radius, $R_{\min}(t)/R$, for 4M PEO solutions at $v = 1$ mm/s. As expected, the initial thinning regime ($t < t_c$) is dominated by Newtonian effects, resulting in similar profiles for all concentrations ($c = 0\text{--}1.5\%$) [144, 150]. At $t \sim t_c$, the dynamics become viscoelastic [dashed lines in Fig. 5.6(a)]. Although t_c varies with concentration, we approximate it as $t_c \simeq 1.3$ s for simplicity. For $t > t_c$, the bridge undergoes exponential thinning:

$$R_{\min} \propto R_c e^{-t/3\lambda_e} \quad (5.5)$$

where R_c is the critical radius at the onset of the viscoelastic regime and λ_e is a characteristic timescale for the relaxation of the stretched polymers in the liquid bridge. In standard Capillary Breakup Extensional Rheometry (CaBER) protocols, an exponential strain-rate profile is imposed on the separating plates. This applied strain rate is deliberately kept larger than the polymer's relaxation strain rate to guarantee fully stretched chains, ensuring the measured timescale reflects the longest relaxation time, λ_R . Similarly, in droplet pinch-off (Chapter 2), the droplet stretches under constant gravity, which drives the polymer extension dynamics to achieve full stretching. Here, however, we employ a constant separation velocity. This approach directly relates the bridge dynamics to the kinematics of interacting grains typical in Discrete Element Method (DEM) modeling of wet granular materials. Because this constant velocity yields only partial chain stretching, we observe $\lambda_e < \lambda_R$, though a detailed investigation of this

discrepancy is beyond the present scope.

The corresponding axial forces are shown in Fig. 5.6(b). In the Newtonian regime, the axial force measured at $v = 1$ mm/s increases with concentration. Furthermore, an increase in concentration sustains the force for a longer duration following the transition to the viscoelastic regime. In summary, both the breakup time and the rupture distance increase with v and c , thereby distinguishing viscoelastic bridges from their Newtonian counterparts under dynamic conditions.

In the Newtonian regime ($t < t_c$), polymer chains in solution remain coiled, and the hydrodynamic interactions between these coils primarily drive viscous dissipation [63]. Assuming shear-thinning effects are negligible in this regime, the viscous contribution to the axial force can be expressed as [122, 139]:

$$F_{\text{visc}} = \frac{3}{2} K \pi \eta R^2 \frac{v}{S} \quad (5.6)$$

We use a prefactor of $3\pi/2$ instead of 6π , as the former derives from the lubrication approximation [139], whereas the latter is associated with Stokes drag. The critical parameter here is the increased solution viscosity η due to the presence of polymers. To determine η for a given separation velocity v , we estimate the local strain rate at the meniscus as $\dot{\epsilon} \simeq v/R_{\text{min}}$ and extract the viscosity at $\dot{\epsilon} \approx \dot{\gamma}$ from shear rheology measurements fitted with the Carreau-Yasuda model [Fig. 5.2(a)]. Additionally, a correction factor $K = 0.5$ accounts for the finite volume of the liquid bridge [139].

The total axial force in the Newtonian regime is the sum of capillary and viscous contributions:

$$F \simeq \pi \gamma R_{\text{min}} + \frac{3}{2} K \pi \eta R^2 \frac{v}{S} \quad (5.7)$$

Equation 5.7, plotted as dashed lines in Fig. 5.6(b), accurately describes the experimental measurements in the Newtonian regime, except as $S \rightarrow 0$, where the modeled force diverges. As noted in § 5.3.1, we attribute this discrepancy to large contact angles that result in particle-particle repulsion. Altogether, we present a first-order approximation that captures the axial force for a given polymer concentration and separation velocity using solely experimentally quantified properties. Crucially, this framework requires no empirical fitting parameters.

5.3.3 Axial Force in the viscoelastic regime

As noted with Eqn. 5.5, the viscoelastic regime ($t \geq t_c$) exhibits exponential thinning characterized by cylindrical ligaments. While previous studies using FISER [6, 114], CaBER [90, 179], and droplet thinning [7], have estimated axial stresses in the ligaments, our focus is on the total force exerted on the particles, relevant to bulk cohesive granular flows [147, 164]. The end geometry of the liquid bridge likely modifies this total force compared to the localized stresses in the cylindrical region.

From Fig. 5.6(b), we observe that for $t > t_c$, the axial force decays exponentially, similar to the thinning dynamics. An Oldroyd-B constitutive model, which predicts this exponential thinning, is therefore suitable to capture the force decay:

$$F = F_c e^{-\frac{S-S_c}{3v\lambda_e}} \quad (5.8)$$

where S_c is the critical gap at the onset of the viscoelastic transition, λ_e is the timescale of polymer relaxation measured from the thinning, and F_c is a fitting parameter. As shown in Fig. 5.6, Eqn. 5.8 provides a good approximation for the axial forces in this regime.

The prefactor F_c is the critical elastic force at this transition ($t = t_c$). At its onset, the critical minimum bridge radius is R_c (see Eqn. 5.8)—the radius at which polymers are sufficiently stretched to dominate the dynamics. By equating the Newtonian force (Eqn. 5.7) to the polymeric force $F \approx \pi R_c^2 \tau_{zz}$ at $S = S_c$, and noting that the elastic stress balances the capillary pressure ($\tau_{zz,c} \approx \gamma/R_c$), we can derive F_c . Balancing this yields:

$$F_c \approx \pi \gamma R_c \left[1 + \frac{3K\eta R^2 v}{2\gamma R_c S_c} \right] \quad (5.9)$$

Previous studies have shown that the critical radius scales with concentration as $R_c \propto c^{0.15}$ [38, 144]. Substituting this scaling into Eqn. 5.9 allows us to compare the model's predictions with the fitted values of F_c , as shown in the inset of Fig. 5.6(b). As Rajesh *et al.* [144] noted, R_c increases more rapidly in the semi-dilute entangled regime, which explains the slight overestimation by Eqn. 5.9. Nevertheless, this approach establishes a framework to describe the viscoelastic axial force using parameters extracted entirely from the thinning dynamics.

In summary, combining Eqn. 5.7 and Eqn. 5.8 yields a first-order model that captures the axial forces across both the Newtonian and viscoelastic regimes in polymeric liquid bridges. The piecewise framework presented here is a simplified study that neglects early elastic contributions at higher concentrations and approximates the elasto-capillary transition as discrete regimes. In the following sections, we further investigate these dynamic liquid bridges by varying the separation velocity v , thereby controlling the imposed strain rate $\dot{\epsilon}$.

5.3.4 Axial Force at different stretching velocities

Figure 5.8 quantifies the evolution of $F(S)$ across separation velocities $v \in [0.01, 10]$ mm/s. The measured forces align well with our qualitative observations: an increase in v prolongs the persistence of the force signal. Quantifying this phenomenon is highly relevant to the bulk transport and advection of cohesive grains—such as in fluidization or silo flows [137, 166]—where large inter-particle distances are typical, and the presence of polymers can

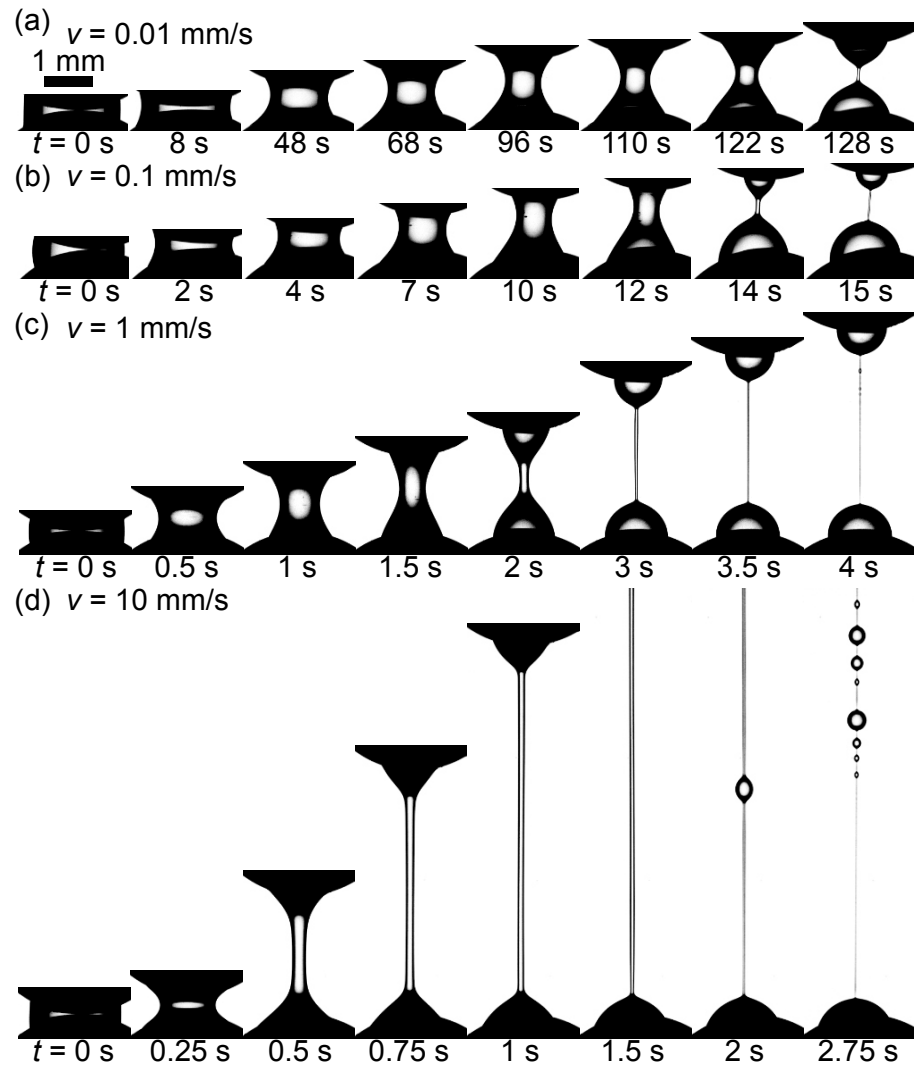


FIGURE 5.7: Temporal evolution of the liquid bridge profile for 1% 4M PEO solution at (a) $v = 0.01$ mm/s, (b) $v = 0.1$ mm/s, (c) $v = 1$ mm/s, and (d) $v = 10$ mm/s.

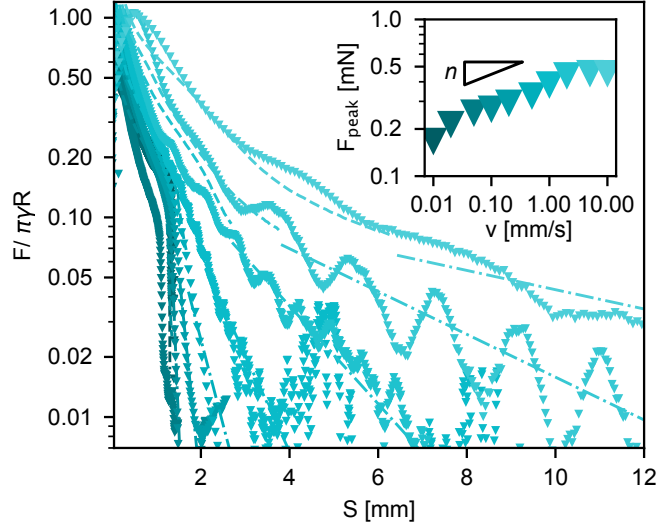


FIGURE 5.8: Axial forces in a 1% 4M poly-ethylene oxide solution prepared in water as a function of velocity in the range $v = 0.01 - 10$ mm/s.

significantly modify particle dynamics. To model the force across these velocities, we apply Eqn. 5.7 in the Newtonian regime and Eqn. 5.8 in the viscoelastic regime. Both equations describe F accurately using parameters extracted directly from shear rheology (η) and thinning dynamics ($R_{\min}$, λ_e).

The inset of Fig. 5.8 shows the peak force, F_{peak} , required to separate the particles, which increases with velocity. This increase in F_{peak} , coupled with the extended duration of the thinning dynamics, is attributed to enhanced viscous dissipation caused by the uncoiling of a larger fraction of polymers at higher imposed strain rates ($\dot{\epsilon}_v$). In the following sections, we further explore the relationship between v and F_{peak} .

5.4 Discussions

5.4.1 Strength of the liquid bridge

Macroscopic cohesive granular flows are typically characterized by their bulk yield stress, τ_z , which is linked to the particle-scale bridge strength via the Rumpf scaling [153]: $\tau_z \propto F_{\text{peak}}/R^2$. Although macroscopic techniques, such as powder shear cells, are commonly used to measure static yield stress, they are often expensive and exhibit high variability. Predicting τ_z directly from particle-scale measurements of F_{peak} provides a robust alternative and establishes a framework for developing structure-property

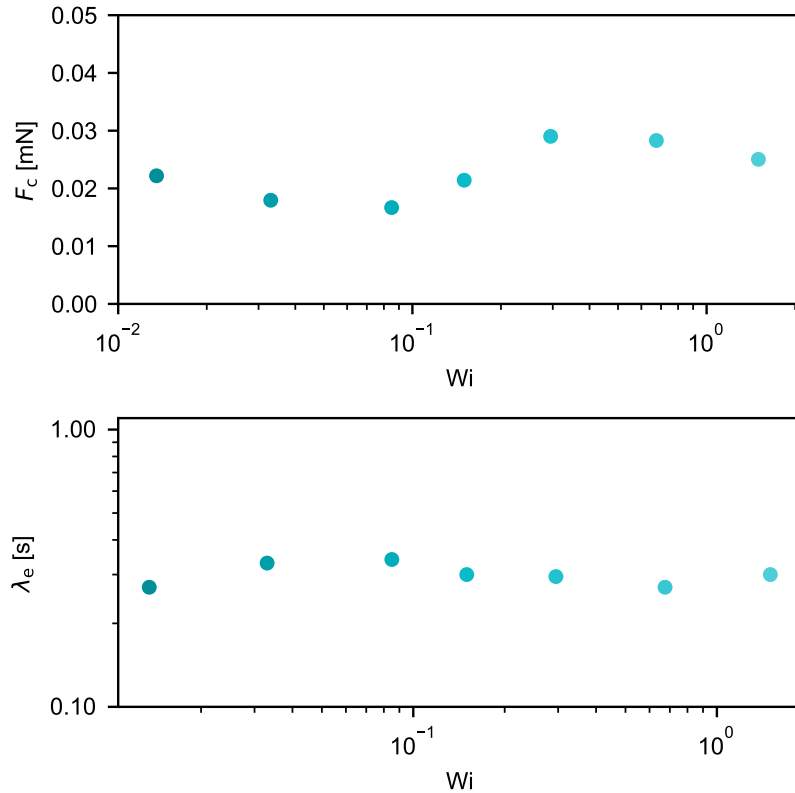


FIGURE 5.9: (a) Elastic Prefactor F_c extracted from the exponential decay of the Force in the viscoelastic regime. (b) Characteristic time λ_e measured from the thinning dynamics of the liquid bridge for various separation velocities v .

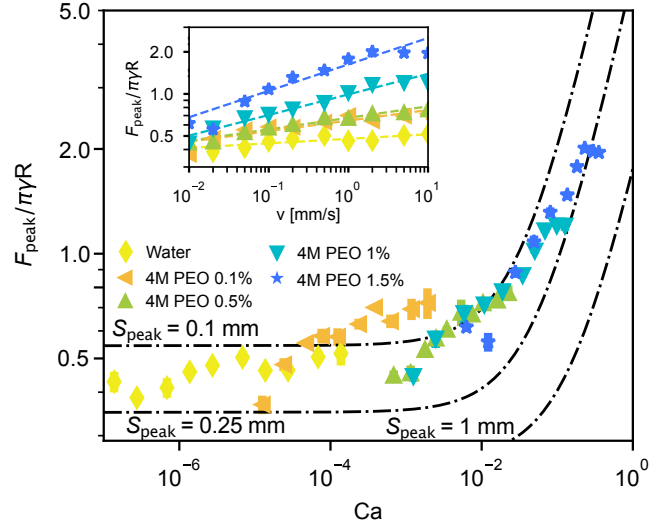


FIGURE 5.10: Bridge strength (F_{peak}) measured for polymer solutions across various concentrations $c = 0 - 1.5\%$ as a function of the capillary number, Ca . Inset: the bridge strength dependence on separation velocities.

relationships [72, 119, 164]. In this section, we characterize the evolution of F_{peak} in polymeric liquid bridges across varying polymer concentrations and separation velocities spanning four orders of magnitude. By rescaling this relationship with the dimensionless Capillary number, Ca , we demonstrate that the scaling framework originally developed for viscous Newtonian liquids [50] can be successfully extended to polymer solutions.

The inset of Fig. 5.10 shows F_{peak} for 4M PEO solutions ($c = 0 - 1.5\%$) across separation velocities $v \in [0.01, 10]$ mm/s. As expected, F_{peak} scales with both velocity and polymer concentration. Because F_{peak} is measured within the Newtonian regime, a Newtonian fluid-based description provides a good starting point, despite polymeric contributions to the viscosity. Motivated by Ennis *et al.* [50], we evaluate Eqn. 5.7 at the gap $S = S_{\text{peak}}$, where the peak force, $F_{\text{peak}} = F(S = S_{\text{peak}})$, occurs. We then rescale this expression using

the Capillary number, $\text{Ca} = \eta v / \gamma$, yielding:

$$\frac{F_{\text{peak}}}{\pi \gamma R} = \frac{R_{\text{min}}}{R} + \frac{3}{2} K \text{Ca} \frac{R}{S_{\text{peak}}} \quad (5.10)$$

To test this model, we plot the experimentally measured F_{peak} rescaled against Ca in Fig. 5.10. The data collapses onto a master curve bounded by Eqn. 5.10 for the experimentally observed gap limits $S_{\text{peak}} \in [0.1, 1]$ mm (see Fig. 5.11). We observe a slight deviation in the rescaled data from $S_{\text{peak}} = 1$ mm. This likely stems from high-velocity polymer solutions (which also exhibit larger S_{peak} gaps) deviating from shear-rheology-based viscosity estimates. Ultimately, however, this data collapse demonstrates that, despite complex polymer-solvent interactions that modify the bulk viscosity, the liquid bridge strength F_{peak} is governed, to first order, entirely by capillary forces and viscous dissipation.

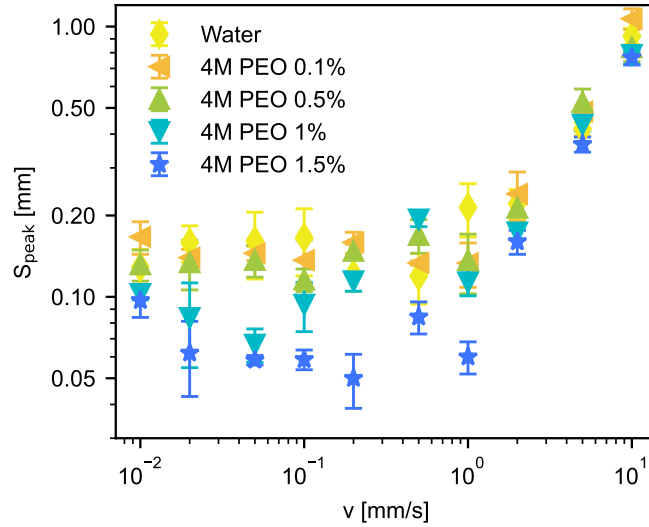


FIGURE 5.11: The gap measured corresponding to the bridge strength (F_{peak}) measured for polymer solutions across various concentrations $c = 0 - 1.5\%$ as a function of velocity $v \in [0.01, 10]$ mm/s.

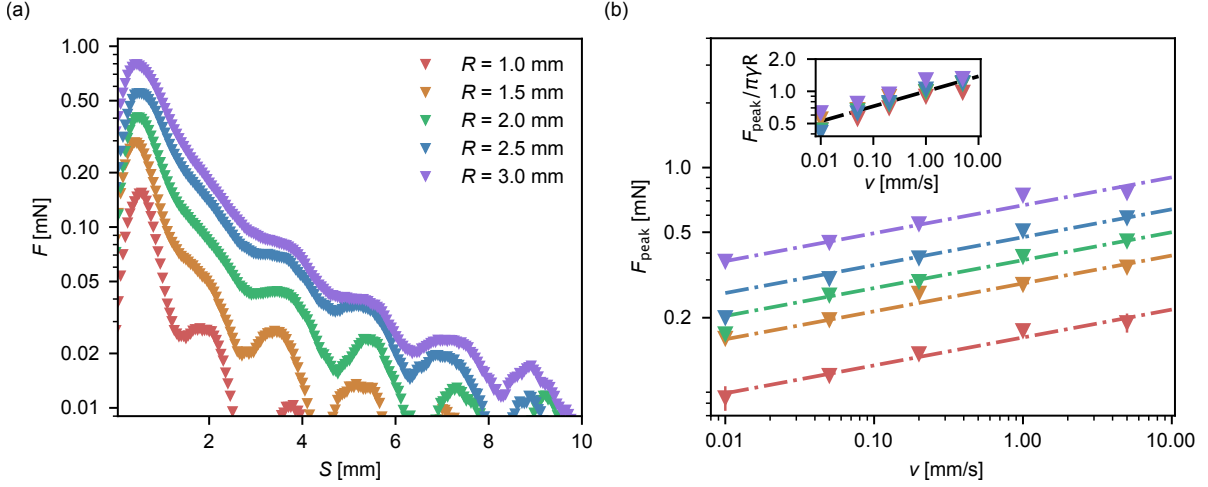


FIGURE 5.12: (a) Evolution of the axial force F with separation distance S for a 1 wt% 4M PEO solution at a fixed velocity $v = 5$ mm/s across varying particle radii R . (b) Dependence of the peak axial force F_{peak} on retraction velocity v . The inset shows the collapse of the peak force data onto a master curve when normalized by the capillary force scale $\pi\gamma R$.

5.4.2 Influence of Particle Size on Axial Forces

To investigate the geometric dependence of the axial force, we performed measurements at a fixed polymer concentration (4M PEO of 1 % concentration) across varying particle radii ($R = 1.0$ to 3.0 mm). Figure 5.12(a) illustrates the evolution of the axial force F as a function of the separation gap S at a constant velocity $v = 5$ mm/s. Across all particle sizes, the force profiles exhibit consistent dynamics: an initial peak characteristic of the Newtonian regime, followed by a transition into a viscoelastic regime marked by filament extension.

In Figure 5.12(b), we analyze the peak axial force, F_{peak} , as a function of retraction velocity. We observe that for a given concentration, F_{peak} increases with velocity following a power-law behavior. Notably, the exponent remains consistent across different particle sizes, described by the relation:

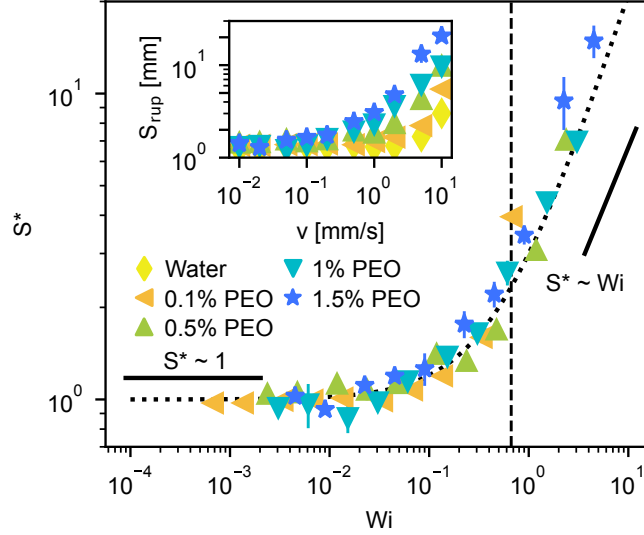


FIGURE 5.13: The rescaled rupture distance $S^* = S_{\text{rup,elast}}/S_{\text{rup,Newt}}$ with respect to the Weissenberg number, Wi , of the polymers. The rescaled S^* collapses onto a curve described by Eqn. 5.13

$$F_{\text{peak}} \propto v^{0.13} \quad (5.11)$$

This consistent scaling suggests that the velocity is independent of particle size. Consequently, we can rescale the peak force with respect to the particle size. As shown in the inset of Figure 5.12(b), normalizing the peak force by the characteristic capillary scale (specifically $F_{\text{peak}}/\pi\gamma R$) collapses the data across the entire range of particle radii onto a single master curve.

5.4.3 Rupture Distance for the Liquid Bridge

For Newtonian fluids, the rupture distance S_{rup} is the maximum gap between the particles at which the liquid bridge remains stable [93, 103]. However, as noted in previous sections,

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the viscoelastic regime in polymer solutions modifies S_{rup} . In these solutions, exponential thinning is typically followed by either satellite drop formation [185] or a blistering instability [36, 156, 157]. The magnitude of the axial force during this instability regime, however, is negligible ($F/\pi\gamma R < 0.01$) and unlikely to influence bulk granular kinematics. Consequently, we adopt this force limit as the threshold for defining the effective rupture distance S_{rup} for the polymeric liquid bridges investigated here.

The rupture distance for a quasi-static Newtonian liquid bridge is a function of bridge volume, V , and contact angle, θ , defined as [103]:

$$S_{\text{rup}} = (1 + 0.5\theta)V^{\frac{1}{3}} \quad (5.12)$$

For the bridge volumes used in the present work ($V \in [0.5, 1] \mu\text{L}$), this yields $S_{\text{rup}} \in [1.14, 1.44] \text{ mm}$, which agrees well with experimental observations of $S_{\text{rup,Newt}} \in [1.25, 1.89] \text{ mm}$ for quasistatic liquid bridges of 4M PEO ($c = 0\text{--}1.5\%$) shown in Fig. 5.5(b). We note a slight increase in S_{rup} with c . In this section, we define the Newtonian rupture distance as $S_{\text{rup}} = S_{\text{rup,Newt}}$.

Equation 5.12 does not hold for dynamic liquid bridges of polymer solutions, where the rupture distance is significantly larger ($S_{\text{rup,elast}} \gg S_{\text{rup,Newt}}$). In Fig. 5.13, we plot the non-dimensionalized rupture distance $S^* = S_{\text{rup,elast}}/S_{\text{rup,Newt}}$, rescaled with respect to the Weissenberg number imposed on the system by the stretching velocity, $\text{Wi} = \lambda_R \dot{\epsilon}_v$. Physically, $S_{\text{rup,Newt}}$ represents the distance at which the bridge would have ruptured in the absence of dynamic polymeric liquid bridges. The relaxation time, λ_R , is obtained from droplet pinch-off measurements, described in 5.2.2. Rescaling S_{rup} for polymer

solutions collapses the data onto the curve:

$$S^* = 1 + 2\text{Wi} \quad (5.13)$$

Equation 5.13 fits the evolution of $S_{\text{rup}}(\text{Wi})$ very well. We highlight that rescaling by Wi rather than Ca is appropriate here, as the elasto-capillary balance dominates the rupture distance in the viscoelastic regime. At small $\dot{\epsilon}_v$ ($\text{Wi} \in [10^{-4}, 10^{-2}]$), we find $S^* \sim 1$, aligning with the Newtonian critical rupture gap $S_{\text{rup,Newt}}$. At larger imposed rates ($\text{Wi} > 10^{-2}$), the scaling shifts to $S^* \sim \text{Wi}$, confirming that elastic effects control liquid bridge rupture.

5.5 Conclusion

Liquid bridges between solid particles are ubiquitous in contexts ranging from soils [11, 26, 70] to industrial granules [98, 146]. In many of these systems, the liquid phase exhibits heterogeneity due to the presence of dissolved polymers. [106] However, the influence of such heterogeneities on liquid bridge dynamics remains poorly understood, as previous studies have predominantly focused on ideal, fully wetting Newtonian fluids like silicone oil [139, 194] or water [93, 187]. In the present work, we investigate polymeric liquid bridges suspended between two solid particles. We quantify the evolution of the axial force as a function of the separation gap across a range of polymer concentrations, separation velocities, and particle sizes.

In the quasi-static regime ($v = 0.01$ mm/s), we demonstrated—both qualitatively through the shape of the liquid bridge meniscus and quantitatively via force measurements and scaling arguments—that the axial forces are dominated by capillarity. Within the range

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of polymer concentrations investigated ($2 < c/c^* < 30$), contributions from viscosity and elastic stresses remain negligible. Under dynamic conditions ($v \geq 0.02$ mm/s), however, we observe and quantify the growing relevance of viscoelastic effects with increasing velocity. To capture this behavior, we divided the axial force evolution into two discrete regimes, Newtonian and viscoelastic, and constructed a first-order approximation using parameters obtained solely from shear rheology and thinning dynamics. We then described the evolution of the peak axial force, F_{peak} , across various velocities and concentrations through a Capillary-number-based rescaling, and confirmed that F_{peak} scales linearly with the particle radius R . Finally, to account for the significantly extended rupture distance in polymer solutions, we introduced a rescaling based on the dimensionless Weissenberg number. This approach allows us to describe the modified rupture distance across a wide range of v and c using a single equation.

This chapter successfully extends capillary force measurements to polymeric liquid bridges, advancing beyond previous research that focused exclusively on fully wetting liquids [50, 139, 194] or water [118, 187]. We note a few limitations in the present work. First, our study focused on purely extensional flows between perfectly spherical particles. In real granular systems, however, liquid bridges experience a combination of extension and shear [169, 170]. While shear contributions can sometimes be approximated using a geometric correction factor [122], the shear-thinning nature of polymer solutions introduces additional complexity that warrants further investigation. Additionally, real granular media consist of irregular particle shapes, which present another necessary avenue for follow-up work [22, 29].

Despite these limitations, our results provide a robust, first-order framework suitable for modeling bulk cohesive granular flows, such as in Discrete Element Method (DEM) simulations [68, 142]. By dividing the axial force into distinct Newtonian and viscoelastic

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regimes, the total force F can be implemented, as discussed in Chapter 6 in brief. Future work could refine this model by developing a continuous, rather than piecewise, description of the transition from the Newtonian to the viscoelastic regime, with a specific focus on the critical force F_c . While Eqn. 5.9 offers a preliminary model for this boundary, a rigorous study of the transition dynamics is needed. Ultimately, by capturing the influence of polymer additives on bridge rupture and cohesive strength, this framework takes a first step towards bridging the gap between micro-scale rheology and the macroscopic mechanics of polymer-based cohesive granular materials.

Chapter 6

Relevance of particle-scale polymeric cohesion in bulk granular flows

6.1 Introduction

In Chapter 5, we developed an experimental approach to quantify cohesion at the scale of individual particles for viscoelastic polymer solutions. In this chapter, we switch gears from particle-scale flows to bulk flows of cohesive granular materials, in which liquid bridges formed by polymer solutions mediate inter-particle cohesion. As discussed in the introduction to this thesis, bulk flows of granular systems frequently involve complex particle-polymer interactions. The results presented in Chapters 2, 3, and 5 offer a quantitative description of how elasto-capillarity emerges in liquid bridges. We observe from these results that at low strain rates, the elastic contributions of polymers are negligible, and the fluid primarily interacts through viscous and capillary forces. However, at higher strain rates and sufficiently large particle-particle separations, elastic

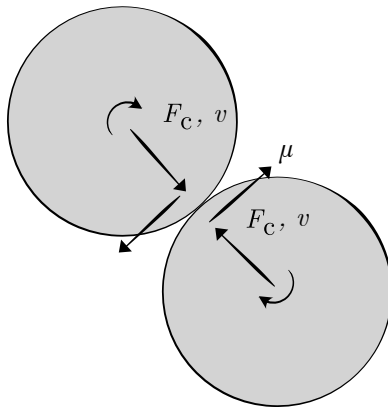


FIGURE 6.1: Schematic illustration of how particle-particle interactions are resolved at the scale of individual grains in a DEM simulation

contributions significantly modify the axial forces in the viscoelastic regime, effectively increasing the length scale over which capillary interactions remain relevant.

In § 6.2, we present a modified capillary force model designed for implementation in Discrete Element Method (DEM) based numerical simulations of cohesive granular materials. In § 6.3, we discuss the relevance of the peak force, F_{peak} , in estimating the bulk yield stress in granular materials. We then present preliminary results on the collapse dynamics of a 2D granular column, where we introduce various binding fluids—such as water, glycerol, and polyethylene oxide solutions—to systematically vary the cohesive properties.

6.2 Discrete Element Method (DEM) and Cohesion Models

The Discrete Element Method (DEM) is a numerical technique used to compute the motion of a large number of interacting particles. Fundamentally, DEM focuses on resolving the velocity and forces acting on individual particles by integrating Newton's laws of motion over small time steps. While originally designed for dry granular flows, DEM allows for the introduction of inter-particle cohesion via contact models (e.g., JKR theory) or non-contact models (e.g., capillary liquid bridges).

6.2.1 Governing Equations and Time Integration

In the Discrete Element Method (DEM), the granular material is modeled as a collection of individual particles, each governed by Newton's laws of motion. The trajectory of each particle i with mass m_i and moment of inertia I_i is resolved by summing all forces and torques acting upon it at every time step. The translational and rotational equations of motion are given by:

$$m_i \frac{d\mathbf{v}_i}{dt} = \sum_j \mathbf{F}_{ij}^c + \mathbf{F}_i^g + \mathbf{F}_i^{\text{ext}} \quad (6.1)$$

$$I_i \frac{d\boldsymbol{\omega}_i}{dt} = \sum_j \mathbf{T}_{ij} \quad (6.2)$$

where $\mathbf{v}_i$ and $\boldsymbol{\omega}_i$ are the translational and angular velocities of particle i . The term $\sum \mathbf{F}_{ij}^c$ represents the summation of contact forces from all neighboring particles j (including

normal and tangential components), $\mathbf{F}_i^g$ is the gravitational force, and $\mathbf{F}_i^{\text{ext}}$ accounts for other external or non-contact forces, such as the capillary bridge forces discussed in § 6.2. Similarly, $\mathbf{T}_{ij}$ represents the torques generated by tangential contact forces or rolling resistance.

The simulation proceeds using an explicit time-integration scheme (typically the Velocity Verlet method). At each time step Δt , the total force is calculated to update the particle's acceleration, which is then used to update its velocity and position. As particle positions are updated, the neighbor lists are refreshed, and new contacts are detected, thereby closing the calculation loop.

6.2.2 Current Newtonian Models

In widely used DEM solvers such as LIGGGHTS, the capillary bridge model is typically restricted to Newtonian liquids. These models generally define the capillary force F_c based on the separation distance δ_n between particles. A standard implementation for Newtonian liquid bridges follows a piecewise function, where the force decays exponentially until a rupture distance is reached:

$$F_c = \begin{cases} -\kappa R e^{-\delta_n/\lambda} - F_{\text{viscous}} & \text{for } 0 \leq \delta_n \leq S_{\text{rupt,Newt}} \\ 0 & \text{for } \delta_n > S_{\text{rupt,Newt}} \end{cases} \quad (6.3)$$

where R is the particle radius, λ is a characteristic length scale, and κ is a pre-factor related to surface tension. The bridge exists only up to a critical rupture distance, $S_{\text{rupt,Newt}}$, which for Newtonian fluids is often approximated as a function of the liquid volume V and the contact angle θ :

$$S_{\text{rupt,Newt}} = (1 + 0.5\theta)V^{1/3} \quad (6.4)$$

6.2.3 Proposed Viscoelastic Model

To the best of our knowledge, current DEM implementations lack a description for the enhanced cohesion provided by viscoelastic fluids. The objective of this thesis, particularly the work detailed in Chapter 5, has been to extend the available models in DEM solvers to account for polymer rheology.

Based on our experimental observations, we propose a modified force law that incorporates a viscoelastic regime. This model extends the interaction range beyond the Newtonian rupture point, accounting for the formation of the stable polymeric filament. The proposed force law is given by:

$$F_c = \begin{cases} -\pi\gamma R_{\min} - F_{\text{viscous}} & \text{for } 0 \leq \delta_n \leq S_{\text{rupt,C}} \\ -F_0 e^{-\frac{\delta_n}{3v\lambda_e}} & \text{for } S_{\text{rupt,C}} \leq \delta_n \leq S_{\text{rupt,elast}} \\ 0 & \text{for } \delta_n > S_{\text{rupt,elast}} \end{cases} \quad (6.5)$$

Here, the force evolution is split into two regimes. The first regime represents the standard capillary and viscous behavior. Post transition at a critical gap, $S_{\text{rupt,C}}$, the second regime captures the exponential decay characteristic of the elasto-capillary thinning of the filament, governed by the relaxation time λ_e and the separation velocity v . Crucially, the presence of polymers delays the breakup of the liquid bridge, leading to a modified rupture distance $S_{\text{rupt,elast}}$ that depends on the Weissenberg number (Wi):

$$S_{\text{rupt,elast}} = S_{\text{rupt,Newt}}(1 + 2\text{Wi}) \quad (6.6)$$

This modification highlights the primary mechanism by which polymers influence bulk flow: by sustaining attractive forces over significantly larger separation distances than their Newtonian counterparts.

6.2.4 Limitations and Future Work

While this proposed model captures the essential physics of the viscoelastic regime, it presents certain limitations that require further attention. First, the transition between the Newtonian-dominated regime and the viscoelastic regime in Equation 6.5 may introduce a discontinuity in the force profile. This continuity issue will be addressed in forthcoming studies, in which we will analyze the thinning dynamics of liquid bridges using the experimental data and methods developed in Chapter 2 to derive a more continuous bridging function.

Second, the current model focuses exclusively on axial (normal) forces. At present, no experimental data is available to accurately quantify the tangential forces exerted by polymer bridges during shear. However, DEM models often use a correction factor to approximate tangential contributions from the normal force, which serves as a reasonable starting point for simulations [122]. Future experimental work is necessary to build a complete particle-scale description that fully couples normal and tangential viscoelastic lubrication forces.

6.3 Relevance of Cohesion in Bulk Granular Transport

While the previous section discussed potential applications of numerical simulations, in this section, we examine the influence of cohesion on bulk transport in granular materials using the canonical 2D granular dam-break configuration. In particular, we discuss the relevance of particle-scale forces, especially the peak force F_{peak} , in describing bulk granular flows.

The collapse of a granular column from an initially confined geometry is illustrated in Fig. 6.2. At $t = 0$ s, the confinement is removed, and the column collapses under its own weight. This gravitational flow is resisted by the material’s yield stress, τ_Y . The yield stress is defined as the minimum stress required for a material to transition from a static equilibrium state to a flowing state. For a dry granular material composed of spherical particles, the macroscopic cohesive yield stress is effectively zero ($\tau_Y \approx 0$), meaning the material flows readily until stabilizing at its angle of repose. However, the introduction of a binding agent—such as a small amount of interstitial liquid—generates a positive yield stress ($\tau_Y > 0$), necessitating an external stress threshold to be overcome for flow to occur.

While various experimental techniques exist to measure yield stress directly, such as the powder shear cell [123, 4, 162], our objective is to link macroscopic behavior to the microscale interactions quantified in Chapter 5. A robust framework for estimating the macroscopic yield stress from particle-scale forces is the Richefeu-Rumpf scaling [153, 148]:

$$\tau_Y \simeq \frac{3\pi\mu\phi}{8} Z \frac{F_{\text{peak}}}{R^2} \quad (6.7)$$

where ϕ is the solid volume fraction, R is the particle radius, μ is the internal friction coefficient, Z is the coordination number, and F_{peak} is the maximum strength of the liquid bridge. This relationship explicitly connects the bulk strength τ_Y to the single-bridge force F_{peak} that we characterized for various polymer concentrations and dynamic conditions in the previous chapter.

6.3.1 Experimental Observations of Column Collapse

To investigate these effects, we performed collapse experiments where cohesion was introduced by adding either water or a polymer solution. Fig. 6.2 compares the final profiles for three cases: (a) dry grains, (b) grains mixed with water ($W = m_{\text{water}}/m_{\text{particles}} = 0.5\%$), and (c) grains mixed with a 0.5 wt% polymer solution (4M PEO in a 50/50 water/glycerol solvent).

The dry granular column (Fig. 6.2(a)) collapses into a smooth, predictable shape where the central height decays gradually and the run-out distance is maximized. In contrast, Fig. 6.2(b) demonstrates that adding a small amount of wetting liquid significantly alters the flow dynamics. The material exhibits enhanced shear strength, resulting in a steeper final pile and a reduced run-out distance. This effect is even more pronounced in Fig. 6.2(c) with the polymer solution, where the run-out distance is further minimized.

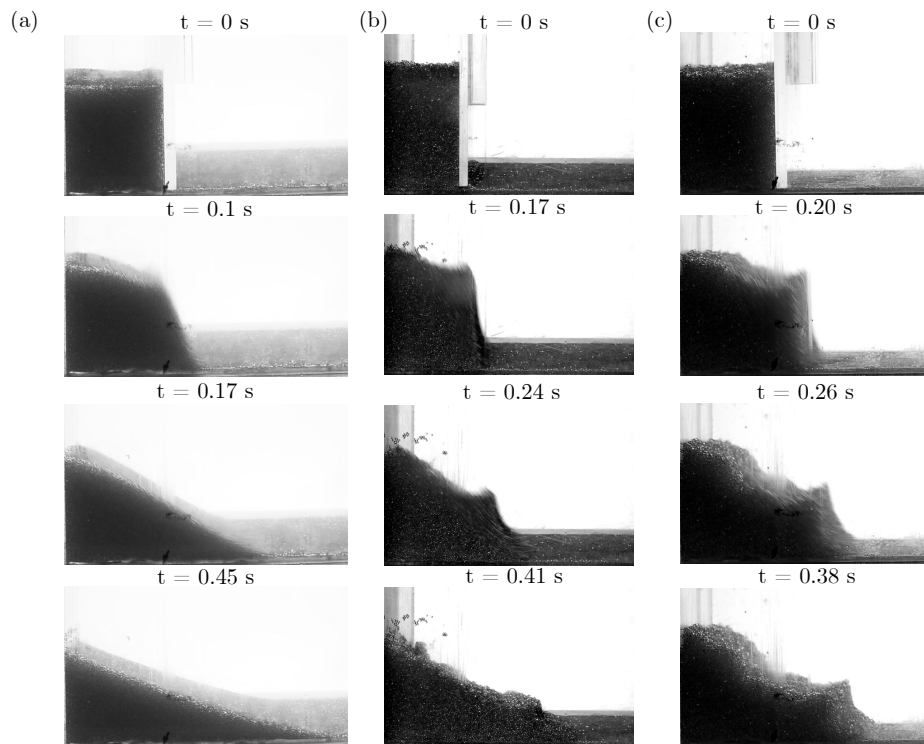


FIGURE 6.2: Evolution of the profile of a cylindrical granular column with aspect ratio $a = 2$ collapsing under its own weight. (a) Cohesionless (dry) grains. (b) Cohesive grains with 0.5 wt% water. (c) Cohesive grains with 0.5 wt% of 4M PEO of $c = 0.5\%$ concentration. Note the significant reduction in run-out distance as cohesion increases from dry to water to polymer.

6.3.2 The Coordination Number Challenge

The reduction in run-out distance observed with the polymer binder can be qualitatively explained by the Richefeu-Rumpf scaling (Eqn. 6.7). Since our Chapter 5 measurements confirm that F_{peak} for polymer solutions is larger than that of water (even at quasi-static rates), the scaling predicts a higher macroscopic yield stress τ_Y , which resists the collapse more effectively.

However, a quantitative prediction remains challenging due to the uncertainty surrounding the coordination number, Z . For a dry packing, Z is simply the average number of physical contacts per particle. In a cohesive wet packing, however, we must distinguish between the

mechanical coordination number and the *liquid coordination number* (Z_{liq})—the average number of liquid bridges per particle. Only contacts possessing a liquid bridge contribute to the cohesive yield stress.

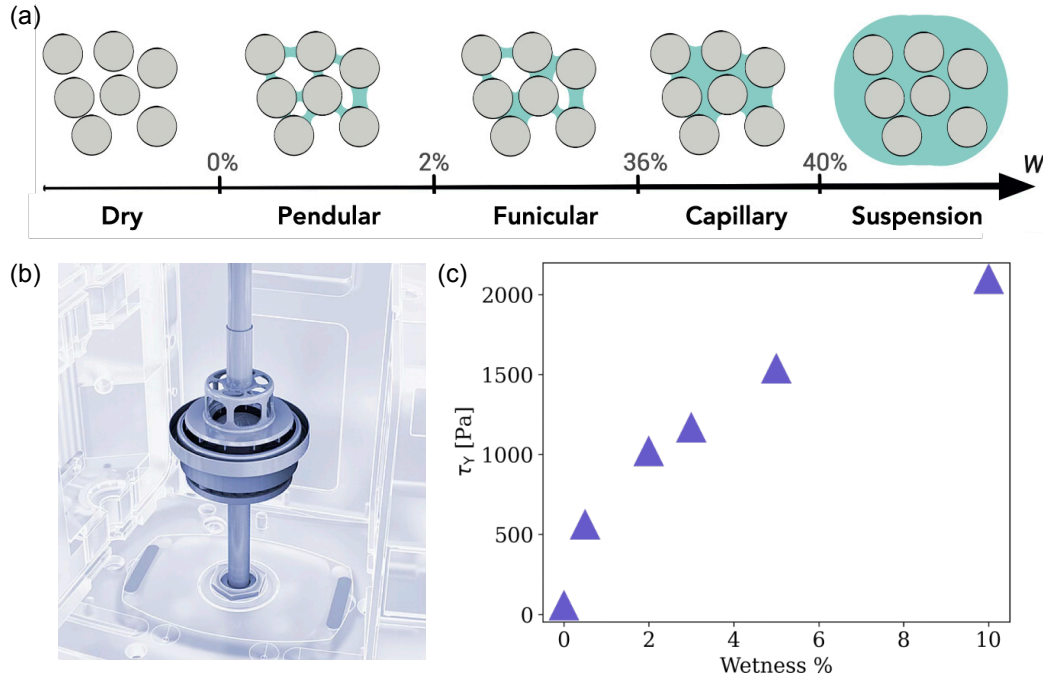


FIGURE 6.3: Regimes of cohesive granular materials as a function of liquid saturation, transitioning from the dry state to the fully immersed suspension state. (c) Shear stress measurements for 45 – 90 μm glass beads at various water saturation levels.

As shown in Fig. 6.3, the mechanical properties of the packing evolve as we transition from the pendular regime (low saturation) to the fully saturated regime. While shear-cell measurements (Fig. 6.3(c)) confirm that yield stress increases with wetness, accurately modeling Z_{liq} for spherical particles remains an open problem. Bridging this gap is essential for using F_{peak} to reliably predict macroscale behavior.

6.4 Conclusion

In this chapter, we extended our investigation from the dynamics of individual liquid bridges to the bulk behavior of cohesive granular materials. We began by addressing the limitations of current Discrete Element Method (DEM) solvers, which typically restrict capillary interactions to Newtonian fluids. Building on the experimental findings of Chapter 5, we proposed a modified contact model that incorporates the effects of polymer viscoelasticity, specifically accounting for enhanced filament lifetime and strain-rate-dependent rupture distance.

Furthermore, we examined the macroscopic implications of this enhanced cohesion through granular column collapse experiments. We observed that polymer-bound granular columns exhibit significantly reduced run-out distances compared to their water-bound counterparts, a result qualitatively consistent with the higher peak forces (F_{peak}) measured at the microscale. By invoking the Richefeu-Rumpf scaling, we established a theoretical link between these single-particle forces and the bulk yield stress. However, we found that quantitative predictions are currently limited by the lack of a robust model for the liquid coordination number (Z) in wet packings. Bridging this gap—coupling the viscoelastic force law with an accurate description of the wetting morphology—remains a critical step toward a fully predictive model for polymer-cohesive granular flows.

Chapter 7

Conclusion

7.1 Summary of Contributions

The primary objective of this thesis was to bridge the gap between the microscopic rheology of complex fluids and the macroscopic behavior of cohesive granular materials. While the role of capillary bridges in wet granular media is well-understood for Newtonian fluids, the introduction of viscoelasticity—common in many industrial and natural settings—fundamentally alters the interaction landscape. By systematically investigating the dynamics of polymer solutions from the scale of a single liquid filament to the bulk flow of a granular assembly, this work provides a comprehensive description of polymer-induced cohesion.

7.1.1 Capillary Dynamics and the Onset of Viscoelasticity

In **Chapters 2 and 3**, we focused on the fundamental fluid mechanics of capillary thinning. Using high-speed imaging, we characterized the extensional flow of polymer solutions using the droplet pinch-off method. A key contribution of this section was the detailed measurement of the thinning dynamics, identifying the distinct transition from a Newtonian (visco-capillary) regime to a viscoelastic (elasto-capillary) regime.

We demonstrated that the onset of the viscoelastic regime—characterized by the formation of a cylindrical filament that thins exponentially—is governed by the relative timescales of fluid relaxation and capillary breakup. By resolving the evolution of the filament diameter over time, we were able to extract the extensional relaxation time, λ_R , for various polymer concentrations and molecular weights. These chapters established the kinematic framework, confirming that even dilute polymer solutions can introduce thinning length scales far longer than their Newtonian counterparts due to significant extensional hardening.

7.1.2 Direct Quantification of Cohesive Forces

Having established the kinematics of thinning, we moved to the dynamics of force generation in **Chapters 4 and 5**. Here, we developed a custom experimental apparatus capable of simultaneously measuring the axial tensile force and the bridge morphology with high temporal resolution. This apparatus allowed us to directly quantify the extensional force exerted by a polymer liquid bridge on solid particles.

The force measurements revealed that polymer bridges exhibit a distinct force signature compared to Newtonian fluids. While Newtonian bridges rupture quickly, polymer

Conclusion

bridges sustain a tensile force over large separation distances due to elasto-capillarity. By decoupling the axial forces into Newtonian and viscoelastic regimes, we proposed independent scaling laws for the force evolution in each regime. Systematically varying the separation velocity and polymer concentration revealed that the peak force, F_{peak} , depends on both variables. We unified these dependencies by defining a capillary number, Ca , which collapsed the data onto a single master curve. This scaling provides a robust predictive tool for estimating the maximum cohesive strength of a polymer bridge based on simple operating parameters. Furthermore, we quantified the increase in rupture distance for polymeric liquid bridges and successfully rescaled these measurements using the Weissenberg number, Wi .

7.1.3 From Microscale to Macroscale

To bridge the gap between single-particle dynamics and bulk flow, we translated our experimental findings into a computational framework suitable for Discrete Element Method (DEM) simulations. Existing DEM contact models typically account only for Newtonian capillary bridges, failing to capture the sustained tensile forces characteristic of polymer solutions. Consequently, in **Chapter 6**, we proposed a modified viscoelastic contact law derived directly from our experimental force profiles. This new model incorporates two critical non-Newtonian features: an exponential decay of the cohesive force governed by the fluid’s relaxation time, and a strain-rate dependent extension of the rupture distance. By implementing this law, we provided a pathway for future simulations to accurately resolve the kinetics of polymer-bound granular flows.

We then extended our investigations to the bulk scale, investigating how these microscopic forces manifest in granular flows. Using the canonical 2D dam-break configuration,

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we compared the collapse of granular columns bound by water versus those bound by polymer solutions. The results provided clear qualitative evidence of enhanced macroscopic cohesion: polymer-bound columns exhibited steeper repose angles and significantly reduced run-out distances.

We proposed a link between the microscale force measurements and the macroscale yield stress using the Richefeu-Rumpf scaling. While this framework qualitatively explains the increased stability of polymer-wetted piles (due to the higher F_{peak}), we identified a critical gap in the quantitative prediction: the wet coordination number, Z_{liq} . The complex morphology of liquid distribution in a dense packing remains the missing link required to fully close the loop between single-particle forces and bulk yield stress.

7.2 Future Outlook

The work presented in this thesis opens several avenues for future research. First, the DEM contact model proposed in Chapter 6 serves as a foundational step. Future numerical studies should focus on implementing this model to explore complex loading geometries, such as mixing or silo discharge, where the strain-rate dependence of the polymer bridge could lead to novel flow instabilities.

Second, the discrepancy regarding the coordination number suggests that further experimental work is needed at the “mesoscale”—clusters of 3 to 10 particles. High-resolution tomography or refractive-index-matched imaging could elucidate how polymer filaments distribute themselves in dense packings, providing the necessary data to refine the Richefeu-Rumpf scaling for viscoelastic materials.

Conclusion

Finally, this thesis focused primarily on axial (normal) forces. However, in shearing granular flows, tangential (lubrication) forces play a significant role. Extending the experimental protocol developed in Chapter 4 to measure tangential forces during shear would provide a complete description of the particle-particle interaction vector, enabling highly accurate predictive modeling of soft matter processing.

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