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ÉCOULEMENTS CAPILLAIRES DE SUSPENSIONS GRANULAIRES

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Thèse de doctorat de Physique

Dirigée par Élisabeth GUAZZELLI & Matthieu ROCHÉ

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Capillary flows of granular suspensions

by

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Abstract

Keywords: Suspensions, capillarity, interfaces, confinement

This work focuses on the capillary flow of granular suspensions. Suspensions, heterogeneous mixtures of particles in a fluid, are ubiquitous in our environment and in the industry (blood, avalanches, cosmetics, cement). Granular suspensions are used when particle agitation is negligible.

Unlike most studies dealing with large volumes of surface-air suspensions, my research focuses on millimeter flows of suspensions coupled to a dynamic interface. These flows are then called capillary flows because they are dominated by capillary forces at the interface. The suspended particles then interact with an interface that confines them more or less according to their size. My approach, based on experience, is deepened by theoretical reflections on the key ingredients of modeling these systems.

First, I studied how these suspensions spread over a surface and showed that particles can be used as probes to understand how energy dissipation occurs in the liquid by cleverly playing with their size. Thus, my work enriches our knowledge of granular suspensions, but also of dynamic anchoring in general. In particular, I have shown experimentally that the classical laws of Tanner and Cox-Voinov still hold provided one uses effective viscosities that can depend on different parameters.

My second project investigates the effect of particles in gravitationally unstable thin films. This Rayleigh-Taylor instability selects a more unstable hexagonal pattern for a continuous fluid characterized by wavelength and growth time. With the addition of particles, the instability is found to exhibit two regimes: for small particles, the instability differs from the simple fluid only in its growth rate. For larger particles, the instability is inhibited. In addition to deepening our understanding of these phenomena, these results pave the way for stabilizing thin films by adding particles.

Résumé

Mot-clés: Suspensions, interfaces, capillarité, confinement

Cette thèse porte sur les écoulements capillaires de suspensions granulaires. Les suspensions, mélanges hétérogènes de particules dans un fluide, sont omniprésentes dans notre environnement et dans l'industrie (sang, avalanches, cosmétiques, ciment). On parle de suspensions granulaires lorsque l'agitation des particules est négligeable.

Contrairement à la plupart des études qui traitent des cas de grands volumes de suspensions sans surface avec l'air, mes travaux de recherche portent sur les écoulements millimétriques de suspensions couplés avec une interface dynamique. Ces écoulements sont alors qualifiés de capillaires puisque dominés par les forces de capillarité au niveau de l'interface. Les particules en suspensions interagissent alors avec une interface qui les confine plus ou moins selon leur taille. Mon approche, basée sur les expériences, est approfondie par des réflexions théoriques sur les ingrédients-clé de la modélisation de ces systèmes.

J'ai d'abord étudié la façon dont ces suspensions s'étalent sur une surface et montré que les particules peuvent être utilisées comme sondes pour comprendre comment la dissipation d'énergie se produit dans le liquide en jouant astucieusement sur leur taille. Ainsi, mon travail enrichit nos connaissances sur les suspensions granulaires, mais aussi celles sur le mouillage dynamique en général. En particulier, j'ai montré expérimentalement que les lois classiques de Tanner et Cox-Voinov s'appliquent toujours avec des viscosités effectives qui peuvent dépendre de différents paramètres.

Mon deuxième projet explore l'effet des particules dans des films minces instables sous l'effet de la gravité. Cette instabilité de Rayleigh-Taylor sélectionne un motif hexagonal plus instable pour un fluide continu, caractérisé par une longueur d'onde et un temps de croissance. Lors de l'ajout de particules, l'instabilité semble présenter deux régimes : pour des petites particules, l'instabilité ne diffère du fluide simple que par sa vitesse de croissance. Pour les plus grosses particules, l'instabilité est inhibée. En plus d'étoffer notre compréhension de ces phénomènes, ces résultats ouvrent la voie à la stabilisation de films minces par ajout de particules.

Résumé long

Introduction - Chapitre 1

Les contextes industriels (cosmétiques, peinture, ciment) comme naturels (sang, avalanches, coulées de boue) regorgent de dispersions de particules dans un liquide, appelées suspensions. Plus spécifiquement, pour des particules de plus d'un micron avec une agitation thermique imperceptible, on parle de suspensions granulaires. Ces fluides font partie de la famille des fluides complexes et ils peuvent être décrits à grande échelle grâce à l'utilisation de propriétés macroscopiques effectives, comme par exemple une viscosité dite de volume, qui quantifie la dissipation générée par l'écoulement. Ces propriétés aux grandes échelles sont établies pour des systèmes supposés infinis et sans interface avec l'air. Cependant, de nombreux écoulements, industriels ou encore biologiques, présentent des surfaces libres au niveau desquelles s'exercent des contraintes de tension de surface, dont l'importance est d'autant plus grande que la taille caractéristique de l'écoulement est petite. L'étude de ces systèmes pour des suspensions manque, théoriquement, numériquement et expérimentalement. Ma thèse est précisément consacrée à l'exploration expérimentale et théorique d'écoulements de suspensions granulaires concentrées avec interfaces libres. En particulier, j'étudie les cas canoniques de l'avancée d'une ligne de contact lors de l'étalement d'une goutte et la déstabilisation de l'interface d'un film mince sous l'effet de la gravité pour des suspensions granulaires concentrées. Mon travail, qui s'adresse de prime abord à la communauté des suspensions, offre également des réponses aux communautés du mouillage ou des interfaces et peut aussi trouver résonnance chez d'autres types écoulements multiphasiques avec interface libre.

Caractérisation des suspensions - Chapitre 2

Les particules utilisées, de 10 à 500 microns de diamètre, sont en polystyrène ou en poly méthacrylate, ces dernières pouvant avoir le même indice optique que le fluide suspendant afin d'obtenir un mélange transparent, même à haute concentration. Des images en microscopie électronique et optique ont permis de caractériser la forme et la surface des particules ainsi que leur distribution en taille. Dans le fluide suspendant choisi, les particules représentent 30 à 40% du volume total, on parle alors de régime de suspensions concentrées ou denses. Elles ont de plus la même densité que le fluide suspendant, de manière à ne pas avoir de sédimentation. Les suspensions sont dites iso-denses. Une caractérisation rhéologique minutieuse et systématique des suspensions a été menée pour mesurer la viscosité du mélange en particulier. Pour des suspensions monodisperses, c'est-à-dire avec une seule taille de particules, il est important de savoir que leur viscosité est multiple de celle du liquide suspendant, avec un facteur indépendant du diamètre des particules. Pour des suspensions polydisperses, la viscosité est plus complexe et dépend également des proportions relatives des différentes tailles.

Etalement de gouttes de suspensions granulaires - Chapitres 3, 4 et 5

Deux points de vue peuvent être adoptés pour étudier l'étalement de gouttes de suspensions granulaires. Une approche locale, qui se concentre sur le bord de la goutte, repose sur la compétition entre les forces visqueuses et capillaires et mène à la loi de Cox-Voinov. Á l'échelle globale de la goutte, la compétition entre la gravité et les forces visqueuses mène à la loi de Tanner.

Théorie - Chapitres 3

La dérivation de ces lois et des discussions sur leur domaine de validité sont présentés dans le chapitre 3. Une échelle caractéristique de cut-off visqueux est également dérivée dans ce chapitre à partir de l'équation de l'interface et en utilisant des arguments d'autosimilarité.

Dans les chapitres 4 et 5, l'étalement de goutte est étudié expérimentalement selon les deux approches évoquées précédemment. Les gouttes sont formées en déposant un volume de suspension sur une surface très régulière, appelée wafer, nettoyée avec précaution afin de ne pas gêner l'étalement du fluide au niveau de la ligne de contact. Les visualisations de dessus et de côté permettent d'extraire, avec des programmes d'analyse numérique que j'ai développés, profil de la goutte, angle de contact, rayon, distance des particules à la ligne de contact ...

Approche locale - Chapitre 4

Les vues du dessus révèlent une région de liquide pur près de la ligne de contact, d'autant plus large que les particules sont grandes. Les particules ne peuvent ainsi pas introduire de dissipation quand l'épaisseur du liquide est inférieure à leur taille. Quand l'épaisseur de la goutte devient de l'ordre d'un diamètre, une monocouche cristallisée de particules est observée, conséquence connue du confinement par l'interface. Suit une région désordonnée, lorsque le confinement par l'interface devient moins important.

Malgré cette structure complexe et hétérogène, j'ai montré expérimentalement que la relation classique entre angle de contact et vitesse d'étalement (loi de Cox-Voinov) reste valable à condition de remplacer la viscosité de volume par une viscosité de mouillage moindre. La viscosité effective est d'autant plus faible que le diamètre des particules est grand, elle dépend donc de la taille des particules, contrairement à la viscosité de volume. Pour des diamètres de plus de 100 microns, la viscosité de mouillage se réduit à celle du fluide pur, ce qui correspond à un dixième de la viscosité de volume.

Approche globale - Chapitre 5

De façon similaire, la loi de Tanner reste valable avec des suspensions granulaires en utilisant une viscosité effective. Etonnement, cette nouvelle viscosité effective ne dépend pas de la taille des particules pour des suspensions denses avec 40% de solide contrairement à la viscosité effective utilisée avec la loi de Cox-Voinov. La viscosité effective est bien moindre que la viscosité de bulk dans les deux cas, sans doute à cause d'important glissement près de la surface solide et de possibles autres phénomènes tels que de la migration de particules, des effets non-newtoniens ou encore de la cristallisation sous confinement. Des visualisations de tranches de suspensions avec une nappe laser sont à l'étude pour quantifier ces différents effets.

Cependant, la loi de Tanner marche jusqu'à une taille critique de goutte qui dépend de la taille des particules. Au-delà, l'étalement ralentit, d'autant plus tôt que les particules sont grosses. Ce ralentissement est expliqué par un confinement critique des particules qui ne peuvent plus se réorganiser lorsque la hauteur de l'interface atteint typiquement un diamètre de particule. Par la suite, un nouveau régime d'étalement est observé, lors duquel le fluide draine hors d'une matrice de particules confinées et immobilisées par l'interface libre. Un modèle théorique permet de prévoir la transition entre le régime de Tanner et le régime de drainage hors du poreux granulaire.

Instabilité de Rayleigh-Taylor - Chapitre 6

Le troisième projet de cette thèse porte sur l'instabilité de Rayleigh-Taylor de films minces de suspensions granulaires. Cette instabilité est rencontrée à l'interface entre deux fluides si le fluide du dessus est plus dense par exemple. Expérimentalement, un volume connu d'une suspension isoindice est versé dans un cadre d'épaisseur connue, fixé à une plaque en verre afin de le remplir à ras. Après plusieurs heures, la plaque est retournée et le film dans le cadre se déstabilise sous l'effet de la gravité, comme sa densité est supérieure à celle de l'air, c'est l'instabilité de Rayleigh-Taylor. Les variations d'épaisseur de fluide sont mesurées grâce à une technique optique qui repose sur la relation entre la déformation d'un motif à l'arrière de la plaque et le profil d'épaisseur de fluide. Je peux ainsi reconstruire la surface et suivre la croissance de l'instabilité de façon non intrusive. Sous l'effet de la gravité, un film mince de liquide au-dessus de l'air se déstabilise. Des dômes se développent, arrangés en réseau hexagonal et lorsque l'un d'eux atteint une épaisseur suffisante, une goutte se détache. Dans mon projet, le fluide est une suspension concentrée de particules de 10 à 300 microns formant un film de 750 microns d'épaisseur. Dans les cas du liquide pur ou pour des suspensions de particules de moins de 100 microns, j'ai montré que les motifs hexagonaux se développent de façon identique mais que la dissipation ajoutée par les particules ralentit la croissance de l'instabilité. La viscosité effective à utiliser pour prédire la croissance des dômes est la viscosité de volume mesuré avec un rhéomètre. En revanche, un régime différent apparait pour des particules de plus de 200 microns, où des dômes apparaissent sans qu'aucune goutte ne tombe. Ils se déplacent sur le film, parfois fusionnent mais l'instabilité est bloquée du fait de la présence des grosses particules. La longueur d'onde sélectionnée par l'instabilité, c'est-à-dire la distance entre deux dômes à un facteur près, n'est pas sensiblement affectée par l'ajout de particules. Ce résultat peut être attendu puisque l'ajout de particules ne modifie que la viscosité du mélange qui n'est pas censé affecter la sélection du mode le plus instable.

Discussions & conclusion - Chapitre 7

L'ajout de particules dans les deux systèmes étudiés questionne quant à l'évolution d'une interface devant composer avec un écoulement biphasique. Mon travail montre que pour de petites particules, les modèles classiques peuvent être étendus en utilisant des viscosités effectives qui diffèrent de celles de volume, mesurées au rhéomètre. En revanche, les situations sont plus complexes avec des particules de grande taille. La dissipation supplémentaire introduite par des particules de plus de 100 microns n'affecte pas l'interface, qui n'est sensible à la dissipation visqueuse qu'à petite échelle. Par des raisonnements sur les équations d'étalement, j'ai abouti à une loi d'échelle pour prédire la taille caractéristique au-delà de laquelle les effets dissipatifs deviennent négligeables. Ce diamètre correspond au seuil critique de 100 microns obtenu expérimentalement. Il est intéressant de comprendre qu'ici, les particules permettent de sonder les zones de dissipation de façon astucieuse en contrôlant sa localisation au travers de la taille des objets à l'origine de la dissipation additionnelle. Ce travail répond donc à des questions relatives au mouillage en général, pour des fluides simples ou complexes. L'étude de systèmes bidisperses permet de confirmer les effets de taille et d'ordre des particules à proximité d'une ligne de contact en avancée. Mon travail dévoile deux régimes dont la transition est contrôlée par la taille des particules. Les forces de tension de surface empêchent sans doute des réarrangements et la croissance de l'instabilité. J'ai entamé une collaboration avec des numériciens afin d'accéder à la structure du film mince lors de sa déstabilisation. La fin de ma thèse sera consacrée à ce projet avec un travail approfondi sur la théorie et des expériences supplémentaires qui viseront à étudier l'effet de l'épaisseur du film pour quantifier l'effet du confinement sur le ralentissement de l'instabilité et sur le diamètre de transition entre les deux régimes.

En conclusion, les écoulements avec surface libre de suspensions granulaires n'ont été que marginalement explorés en dépit de leur importance. Les approches utilisant les modèles classiques avec la viscosité de volume ne peuvent pas être appliquées, ou du moins nécessitent une correction par une viscosité effective pour de petites particules. Mon projet révèle des comportements radicalement différents quand les particules deviennent trop grandes en comparaison de la longueur pertinente du système. Pour le mouillage dynamique, j'ai proposé une loi d'échelle relative à la taille de la zone dissipative. Avec des particules de taille supérieure, il devient possible d'avoir un fluide très visqueux en volume et peu visqueux du point de vue du mouillage. Pour les films minces, le blocage de l'instabilité pour les grandes tailles de particules pourrait avoir des applications pour la pose de revêtements par exemple. Ce travail offre encore de nombreuses perspectives d'avancées pour la compréhension et la simulation de suspensions denses avec interface libre mais aussi celles des interfaces en général et des écoulements multiphasiques dans leur ensemble (émulsions, mousses, ...).

LIST OF SYMBOLS

If not specified otherwise, the following symbols correspond to

- *A* Factor in front of time in Tanner's law (Chapters 3, 5)
- \mathcal{A} Surface area
- *Bo* Bond number
- \mathcal{C} Surface curvature
- *Ca* Capillary number
- *c* Wavelength of the checkerboard pattern (Chapter 6)
- *d* Particle diameter
- d_1 Small particle diameter in bimodal suspensions
- d_2 Large particle diameter in bimodal suspensions
- g Acceleration of gravity
- *g_r* Radial distribution function
- *H* Distance between the camera and the thin film (Chapter 6)
- *h* Drop height
- h_0 Drop height at the center (Chapters 3, 4, 5)
- h_0 Film thickness undergoing the Rayleigh-Taylor instability (Chapter 6)
- h_g Glass plate thickness (Chapter 6)
- *k* Volume and viscosity independent constant in Tanner's law (Chapters 3, 5)
- *k* Instability wave number (Chapter 6)
- k^* Most unstable wave number (Chapter 6)
- ℓ_c Capillary length
- I_{ν} Modified Bessel function of ν -th order and first kind
- *L* Typical system size
- n_a Air optical index
- $n_{\rm g}$ Glass optical index
- n_f Fluid optical index
- *P* Pressure
- *Q* Flow rate
- *R* Drop radius
- Re Reynolds number
- *S* Spreading coefficient
- St Stokes number
- T Temperature
- U Velocity
- V₀ Drop volume
- V_p Particle volume
- *V_f* Fluid volume

- *γ* Surface tension (between liquid and gas in most cases)
- γ_{LG} Surface tension between liquid and gas
- γ_{LS} Surface tension between liquid and solid
- γ_{SG} Surface tension between solid and gas
- δ Size ratio in bimodal suspensions
- ϵ Shear strain
- $\dot{\epsilon}$ Shear rate
- ζ_{small} Small particle proportion in bimodal suspensions

 η Viscosity

- [η] Intrinsic viscosity
- η_f Fluid viscosity
- η_a Suspension absolute viscosity
- η_s Suspension relative viscosity
- η_T Suspension effective relative viscosity in Tanner's law
- η_w Suspension effective relative viscosity in Cox-Voinov's law
- θ Contact angle
- θ_{app} Apparent contact angle (at a given height)
- θ_e Equilibrium contact angle
- θ_m Microscopic contact angle
- λ Microscopic slip length (Chapters 3, 4, 5)
- λ Instability wavelength (Chapter 6)
- λ^* Selected wavelength from linear analysis (Chapter 6)
- μ_p Microscopic friction coefficient
- ρ Density
- ρ_f Fluid density
- ρ_p Particle density
- $\sigma \qquad \text{Shear stress} \qquad$
- au Instability growth time (Chapter 6)
- τ^* Selected growth time from linear analysis (Chapter 6)
- ϕ Particle volume fraction
- ϕ_c Jamming volume fraction
- φ_6 Local bond orientation parameter

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#### 1.1 General introduction

This thesis lies at the intersection of fluid mechanics, soft matter, and physics of interfaces. The interplay between effects coming from each of these fields naturally raises a number of questions and requires careful and thorough studies to understand the underlying ruling mechanisms. Fortunately, simple and predictable behavior can emerge even out of complex systems. In the present case, granular suspensions have been chosen among the broad class of complex fluids to unveil new aspects of capillary flows.



Figure 1.1: Examples of suspensions (from left to right): fresh concrete poured to make a slab (https://www.concreteconstruction.net/), snow avalanche at Roux-d'Abriès, France, in 2004 (Ancey 2001) and moulding of melted chocolate (https://www.passionpatisserie.fr/).

A suspension is a mixture of particles with a fluid. As illustrated in figure 1.1, human activities extensively use this category of complex fluids for various applications, including cosmetics, paint, food ... For instance, the concrete industry inserts gravel in cement. The physical properties of concrete can be tailored with grain sizes and many other features of the solid and liquid phases. In nature, the physics of suspensions addresses questions related to sediment transports in rivers for instance (Ouriemi et al. 2009). At these large geophysical scales, snow avalanches, landslides and lava flows can be considered as flowing suspensions (Coussot 2005). Finally, objects suspended in a liquid are widely encountered in biological systems such as blood. Understanding the effects of shape and stiffness of the blood cells would lead to major medical improvements in the prevention and treatment of blood diseases (Briole et al. 2021).

In blood capillaries, in pipes, or in any narrow system, **confinement** of suspensions highlights the limits of the continuous description of these fluids. In particular, the effective viscosity, which quantifies energy dissipation in the flow, displays signs of confinement for system sizes smaller than 20 particle diameters (Peyla and Verdier 2011; Ramaswamy et al. 2017).

Addition of a single object in the flow must increase dissipation, simply because of its non-deformability as explained in the review of Guazzelli and Pouliquen (2018). Several objects accentuate this dissipation through hydrodynamic interactions or contacts, especially in crowded systems. For the latter, microstructure is a key factor to understand the overall dissipation and the resulting effective viscosity. Modification of the particle microstructure is thereby expected to be brought into light by confined flows of dense suspensions, as wall effects and steric constraints become more and more significant.

The *wall* confining the suspension can be of different types, be it a rigid or deformable solid or the surface of a liquid. So far, most of the work on confined suspensions has remained in the framework of rigid walls. The established conclusions might be highly affected by another type of confinement, e.g. confinement by an elastic wall or by a completely **deformable boundary such as an interface with another fluid**. In the latter case, the flow of the suspension is then coupled to the dynamics of its boundaries and raises question on how this **multiphase flow** behaves.

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These are precisely the situations I address in this manuscript with different systems. I initiated this work on capillary flows of dense suspensions during one of my internships, dedicated to the study of drop spreading - where particles undergo a strong confinement near the edge of the drop and interplay with the advancing contact line to unveil interesting behavior. This work led to a first publication with many pending questions (Zhao et al. 2020). A deeper investigation of the key elements regarding dissipation in this complex system has been the initial line inquiry of this Ph.D. and led to a second publication (Pelosse et al. 2023). In particular, it explains how drop spreading of granular suspensions offers an interesting point of view on dynamic wetting mechanisms in general.

This manuscript begins with a brief overview and definitions of the main concepts required to study capillary flows of granular suspensions. It sets the framework of this study, namely Stokes and capillary flows of dense granular suspensions made of spherical particles in a Newtonian fluid.

#### 1.2 Granular suspensions

Describing suspensions in the plethora of the cases aforementioned or illustrated in figure 1.1 is way too ambitious. Their physics depends on numerous parameters related to the particle (size, shape, roughness, elasticity ...) or to the fluid phase (rheology, density, ...).

#### 1.2.1 Granular, viscous, non-buoyant suspensions

We focus our attention on suspensions made of **hard spheres** and immersed in a *Newtonian* viscous liquid. The notion of *Newtonian* fluid is detailed in Chapter 2. In a few words, such fluids have a well-defined, constant viscosity, i.e. a linear correlation between the viscous stress and the shear rate under flow. Specifically, their viscosity neither increases (shear-thickening) nor decreases (shear-thinning) under shear. In addition, we only consider suspensions made of large particles, qualified as **granular or non-Brownian**. In a granular suspension, Brownian motion, i.e. thermal agitation of the particles, can be neglected. The typical cut-off size is usually  $d \gtrsim 1 \,\mu\text{m}$ , with *d* the particle diameter. By default, we consider **non-buoyant or density-matched suspensions**, i.e.  $\rho_p = \rho_f$  with  $\rho_f$ ,  $\rho_p$  the fluid and particle density, respectively. Otherwise, a density difference  $\Delta \rho = \rho_p - \rho_f$  between the fluid and the particles would lead to sedimentation ( $\rho_f < \rho_p$ ) or creaming of the particles ( $\rho_f > \rho_d$ ). For a single particle, the drift speed associated with the density mismatch, also called the Stokes settling velocity, reads (Guazzelli and Morris 2011)

$$U_{\rm Stokes} = \frac{d^2 g \Delta \rho}{18\eta},\tag{1.1}$$

with g the acceleration of gravity and  $\eta$  the dynamic viscosity of the surrounding fluid. High fluid viscosity enables us to both study **Stokes flows** and overlook **particle inertia**. The latter can be assessed with the particulate Reynolds number,

$$Re_p = \frac{\rho_p dU}{\eta} \ll 1, \tag{1.2}$$

with U the typical particle velocity. Particle inertia can also be evaluated with the Stokes number, defined as

$$St = \frac{\tau_{\eta}}{T} = \frac{\rho_p d^2}{\eta T},\tag{1.3}$$

with  $\tau_{\eta} = \rho_p d^2/\eta$  the characteristic viscous relaxation time scale of the particle (grain, drop, bubble, ...) and *T* the typical flow timescale (Guazzelli and Morris 2011). For large Stokes numbers,  $St \ge 1$ , inertia of the particles is large enough so that their trajectories differ from the fluid streamlines.

On the contrary, particles follow the flow streamlines similarly to a fluid element if  $St \ll 1$ . It is a necessary condition for a particle to be a good flow tracer for instance.

To quantify the amount of solid immersed in the suspension, we define the **particle volume frac-***tion*,

$$\phi = \frac{V_p}{V_p + V_f},\tag{1.4}$$

with  $V_p$  the total solid volume of the particles and  $V_f$  that of the suspending fluid. This quantity is by definition smaller than one. Actually, its upper bound is smaller than one and corresponds to the situation of a dense particle packing with liquid-filled interstices. This upper bound or **critical packing fraction**  $\phi_c$ , usually lies around 60% for spheres of equal size. This parameter, also named the jamming volume fraction, is closely related to the maximum compacity of the solid phase (random close packing). At this volume fraction, the system becomes fully jammed and stops flowing as the particles cannot make space to reorganize. Either  $\phi$  and  $\phi_c$  play major roles in the understanding of the effective viscosity of suspensions, which quantifies the overall dissipation of the mixture.

#### 1.2.2 Dissipation in granular suspensions: apparent viscosity



Figure 1.2: Relative viscosity of granular suspensions as a function of (a) the solid volume fraction  $\phi$ , and (b) the normalized solid volume fraction  $\phi/\phi_c$ . Graphs from the review on dense suspension rheology by Guazzelli and Pouliquen 2018, with experimental (Boyer et al. 2011; Bonnoit, Darnige, et al. 2010; Dagois-Bohy et al. 2015; Dbouk et al. 2013; Ovarlez et al. 2006; Zarraga et al. 2000) and numerical (Gallier, Lemaire, Peters, et al. 2014; Mari et al. 2014; Sierou and Brady 2002) data for various systems, and viscosity laws of Einstein (1905), Batchelor and Green (1972), Krieger and Dougherty (1959), Maron and Pierce (1956), and Eilers (1941).

At the macroscopic scale, i.e. sizes much larger than a particle diameter, d, the mixture **behaves** as a continuous fluid, thus justifying the use of an **effective viscosity** to quantify the **additional dissipation**. This increase has several origins: the non-deformability of a particle, hydrodynamic interactions of the particles with the liquid or with the other particles and direct contacts between the particles. Depending on the solid volume fraction, some contributions will take over the others. While contacts are insignificant in the dilute limit ( $\phi \leq 20$  %), they progressively prevail over **hydrodynamic interactions** in the dense regime ( $\phi \geq 40$  %) (Gallier, Lemaire, Peters, et al. 2014). The study of suspensions thus belongs mostly to hydrodynamics in dilute cases, while solid mechanics is more relevant to dense systems. Specifically, in the dense case, the suspension rheology can be tackled with the tools of dry granular media governed by particle contacts (Boyer et al. 2011). This

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dense regime displays the major effects of the particle **microstructure** on the macroscopic bulk flow (Jeffrey Morris 2009). In figure 1.2, the **relative viscosity**,  $\eta_s$  i.e. the viscosity of the suspension normalized by the viscosity of the suspending fluid, is plotted as a function of particle volume fraction. Various **monomodal** suspensions are gathered in these graphs, i.e. each one composed of one particle size only. As predicted by theory and confirmed by experiment and numerical simulation, the **viscosity of monomodal granular suspensions does not depend on the particle size** (Guazzelli and Pouliquen 2018). Granular suspensions are *simple* in that way. In addition, the relative viscosity,  $\eta_s$  increases with  $\phi$  and divergence occurs at  $\phi \rightarrow \phi_c$ , as shown by the tight collapse of the points in figure 1.2(b) when  $\phi$  is normalized by the jamming volume fraction,  $\phi_c$ . The value of  $\phi_c$  depends on the system, notably on the particle size distribution, see § 1.2.3. The offsets of divergence in figure 1.2(a) also suggest that  $\phi_c$  depends on the microscopic friction coefficient  $\mu_p$ (Mari et al. 2014; Tapia et al. 2019).

To avoid extreme jamming behavior while keeping a strong effect of the presence of the particles, this work deals with relatively **dense granular suspension** ( $\phi \simeq 40\%$  in most cases). In that case, a rough estimation of  $\phi_c$  is sufficient.

#### 1.2.3 Polydisperse granular suspensions

To address the case of suspensions encountered in nature, one must go beyond the situation of monomodal suspensions and consider these made of particles with multiple sizes. In the laboratory, experiments also benefit from a slight amount of **polydispersity to avoid crystallization** of the particulate phase (Pusey 1987). When dealing with polydisperse suspensions, the main challenge lies in the prediction of their **maximum compacity** which **increases with the spread of the size distribution** (Farr and Groot 2009). Then, using the **relevant maximum packing fraction in common viscosity laws** provides a decent estimate for the viscosity of polydisperse suspensions (Chong et al. 1971; Pednekar et al. 2018).

A first step toward this additional degree of complexity is the **bimodal** solid phase, i.e. a suspension made of a liquid, small particles (diameter  $d_1$ ) and large particles (diameter  $d_2$ ). The composition of such mixtures is described by **4 parameters** ( $\phi$ ,  $d_1$ ,  $d_2$ ,  $\zeta_{\text{small}}$ ) or alternatively ( $\phi$ ,  $d_1$ ,  $\delta$ ,  $\zeta_{\text{small}}$ ) with  $\delta$  the diameter ratio,  $\zeta_{\text{small}}$  the **small particle proportion** in the solid blend, and  $\phi$  the total solid volume fraction,

$$\phi = \frac{V_p}{V_p + V_f} = \frac{V_1 + V_2}{V_1 + V_2 + V_f}, \qquad \delta = \frac{d_2}{d_1} \ge 1, \qquad \zeta_{\text{small}} = \frac{V_1}{V_2 + V_1} = \frac{V_1}{V_p}. \tag{1.5}$$

In comparison with monomodal systems, the maximum compacity of bimodal blends is larger due to the asymmetric steric interactions between the two populations of particles. In particular, the small particles can fill the holes between the large particles. For large size ratio,  $d_1 \ll d_2$ , the maximum packing fraction is reached in the situation of fully-packed large particles, with fully-packed small particles in the holes (Farris 1968; Sengun and Probstein 1989; Probstein et al. 1994). However, for a finite size ratio, the bimodal maximum packing fraction is not obvious. For the small particles, large particles are like walls, thus decreasing locally their concentration (Aim and Le Goff 1968). Moreover, the network of large particles has to expand if the small particles are too large or too numerous in the interstices (Stovall et al. 1986). Experimentally, the **viscosity of bimodal suspensions exhibits a minimum** for  $\zeta_{small} \simeq 25 - 35\%$  (Chang and Powell 1994). In addition, the difference between the bimodal minimum viscosity and the monomodal viscosity increases with the **size ratio** (Chong et al. 1971). A careful characterization of bimodal suspensions is therefore required to fully control their properties and draw meaningful conclusions from these complex systems.

#### 1.2.4 Confined suspensions

All the systems mentioned above were considered infinite, behaving as a continuous fluid with a **bulk viscosity**. This condition is met experimentally if the smallest characteristic size of the system, *L*, is much larger than the particle diameter *d*. Then, particle concentration is almost homogeneous and wall effects are negligible.

However, these results no longer hold when the finite size of particles has to be accounted for. Such situations are encountered in our body, as suspensions of red blood cells flow in thin capillaries. Interestingly, a significant decrease in viscosity can be measured. This phenomenon is called the Fahraeus-Lindqvist effect (Fahraeus and Lindqvist 1931). This decrease is also observed with suspensions of regular hard spheres flowing in a rigid tube. Experiments show non-trivial behavior of the effective viscosity depending on the particle-tube size ratio and on the solid volume fraction (Seshadri and Sutera 1970).

These observations can be rationalized by several factors inducing modifications of the particle spatial distribution under confinement. First, dense and confined suspensions will develop an irreversible inhomogeneity in concentration under shear (Gadala-Maria and Acrivos 1980; Abbott et al. 1991; Han et al. 1999; Snook et al. 2016). This effect is referred to as **shear-induced particle migra-tion** and is understood as a particle flux toward regions of low shear (Leighton and Acrivos 1987). This flux is proportional to the square of the particle diameter and to the shear gradient across the direction of confinement.

Also, steric effects near the walls create a region depleted in particles at short distances, i.e. below a particle radius, and induce a local **layering** at greater distances. Numerical simulation predicts that this layering can span over the whole system in confined situations especially as  $\phi$  increases (Gallier, Lemaire, Lobry, et al. 2016). The stability of the layers would be particularly strong when the gap size is a small integer multiple of the particle diameter (Fornari et al. 2016). The consequences on the effective viscosity are not clear at moderate confinement. Under strong confinement, substantial oscillations of the effective viscosity appear: minima are reached when the gap width is commensurate to the particle diameters, as the system has structured into layers (Gallier, Lemaire, Lobry, et al. 2016).



Figure 1.3: Layering and apparent viscosity under confinement in a shear cell. (a) Viscosity normalized by the value of the bulk as a function of the normalized gap L/d for two solid volume fractions (see legend). (b) Enlargement of (a) in the region  $2 \le L/d \le 5$ . Yellow dots correspond to the values of L/d sketched in subplots (c,d). (c,d) Schematic of the suspension microstructure under extreme confinement, (c) L = 2.5d and (d) L = 3d.

In a shear cell, such layering in dense (38 <  $\phi$  < 52%) suspensions of 2-µm particles has been observed experimentally for channel width *L* below 15 particle diameters (Ramaswamy et al. 2017). Concentration peaks, spaced by one particle diameter, appear across the gap and confirm the development of layering. At a given particle volume fraction, this ordering induces a **decrease in appar-ent viscosity** compared to the bulk suspension, see figure 1.3(a). The decrease is more spectacular at a large particle volume fraction. Under very strong confinement (less than 6 particle diameter), layering spans the whole system and hence corroborates numerical simulation. Also in line with numerical simulation, the apparent viscosity oscillates with gap size and shows local minima when it is a multiple integer of particle diameter, see figure 1.3(b,c,d).

**Polydispersity** is reported to **strongly disrupt the ordering** and therefore hinder the decrease in viscosity at small gaps. It is an efficient and effective way to test the influence of ordering on the overall dissipation in confined environments. We remind the reader that polymodal bulk viscosity is smaller than that of monomodal systems which might conceal the effects of confinement, thus justifying the need to characterize the bulk rheology of these materials in the best way possible.

Similar experiments using a regular rheometer with dilute granular suspensions ( $\phi \le 0.2$ ), seem to contradict the previous results (Peyla and Verdier 2011). A monotonic increase of the viscosity with confinement has been reported without any decrease at moderate confinement. The discrepancy may stem from the difficulty of these experiments but also from the very different particle sizes and solid volume fractions. Indeed, the effects of layering at moderate confinement seem to fade strongly with decreasing volume fraction, see figure 1.3(a). Also, regular rheometers are not meant to work at small gaps (typically below 500 µm) due to issues of tool alignment and gap uncertainty. In addition, confined flow could affect differently the hydrodynamic interactions and the contact network. The consequences of confinement on the bulk viscosity could therefore differ in the dilute and in the dense regime. In particular, it can be expected that layering does not develop even under high confinement in dilute suspensions.

Numerical investigation can overcome experimental limitations and discriminate between the mechanisms leading to viscosity variations. In 2D simulation, dilute and semi-dilute suspensions often exhibit an increase of the hydrodynamic interactions under confinement (and thus of the apparent viscosity), due to the enhanced dissipation of fluid squeezed near the wall (Doyeux et al. 2016). However, when two particles align along the shear direction, a dip in the dissipation of energy would appear in-between, explained by the screening of the imposed shear by the particles. Such dissipation anomaly can lead to a strong decrease in the overall dissipation, but depends on the proportion of aligned disks in the confined shear flow.

In conclusion, **confinement unambiguously alters the suspension microstructure** and affects macroscopic dissipation. Experiments and numerical investigations indicate that its effects appear below 20 particle sizes. However, its global effect on suspension rheology is not clear and highly depends on the particle volume fraction. Confinement can locally decrease particle concentration through shear-induced particle migration and trigger particle layering near the wall. Under extreme confinement, commensurability of the system size with a particle diameter seems critical in the overall dissipation and can be rationalized by the stability of the layers of particles. Polydispersity can be used to intefere with large size microstructure and the resulting decreases in effective viscosity compared to the value of the bulk. Also, while the hydrodynamics contribution to dissipation would increase with confinement, dense systems could be less dissipative because of the shear screening by the particles. Again addressing these questions is a real challenge experimentally and numerically and all the above conclusions must be taken carefully.

#### 1.3 Capillary effects

The present thesis questions the effect of confinement induced by at least one **free surface**. In contrast, for all the results previously presented, confinement is imposed by two rigid walls. From another perspective, this work also addresses the effects of particles on the deformable interface. A quick reminder of useful concepts relative to free surfaces is presented in this section, to prepare the discussions regarding this soft confinement developed in § 1.4.

#### 1.3.1 Free surface energy and surface tension

Let us consider a system made of two immiscible fluids, for instance a liquid and a gas, separated by a free surface. A deformation of the interface is associated with a cost or a gain in energy,  $dE_{surface}$ , that can be expressed as,

$$dE_{\rm surface} = \gamma d\mathcal{A} \tag{1.6}$$

with dA the variation of the surface area and  $\gamma$  the **surface tension** between the two fluids. At a microscopic scale, surface tension is related to the cohesion between the molecules in the liquid (De Gennes et al. 2004). To create a new free surface dA, the energy  $dE_{surface}$  must be provided to the molecules that must go from a liquid-bulk environment to an air/liquid interface. Actually, surface tension is defined for any kind of interface, involving solid, liquid, or gas, with the same definition (1.6).

#### 1.3.2 Capillary force and Laplace pressure

Along a deformable interface, the minimization of surface energy yields a capillary force. The work of this force is directly related to the variations of surface energy upon surface variation. Therefore, surface tension can be seen either as an **energy per unit area** or as a **force per unit length** arising from liquid cohesion (De Gennes et al. 2004).

For instance, in the 2D problem sketched in figure 1.4, the projection  $F_x$  of the sum of the capillary forces of the three interfaces along the *x*-direction reads

$$F_x = \gamma_{SG} - \gamma_{LS} - \gamma_{LG} \cos(\theta). \tag{1.7}$$

Equilibrium of the contact line gives in turn,

$$F_x = 0 \quad \Longleftrightarrow \quad \cos(\theta_e) = \frac{\gamma_{SG} - \gamma_{LS}}{\gamma_{LG}}.$$
 (1.8)



Figure 1.4: Schematic of a 2D problem of a moving contact line on a solid substrate.



1.3



Figure 1.5: Spreading of a droplet on a solid substrate, (a) in partial wetting and (b) in complete wetting.

This relation, known as Young-Dupré law, predicts the **equilibrium contact angle** of a liquid on a solid,  $\theta_e$  (Young 1805; Dupré 1869). The wettability of the substrate by the liquid depends on the spreading coefficient  $S = \gamma_{SG} - \gamma_{LS} - \gamma_{LG} = \gamma_{LG} (\cos(\theta_e) - 1)$ . As illustrated in figure 1.5(a), for S < 0, the liquid partially wets the substrate with a finite equilibrium contact angle. On the contrary, it completely wets the substrate if S > 0, i.e.  $\theta_e = 0$ , see figure 1.5(b).

While the final equilibrium state in drop spreading is quite simple, the dynamical regime is more puzzling. In particular, the contact line motion is not compatible with the usual no-slip condition along the solid wall. This paradox, first raised by Huh and Scriven (1971), notably leads to unphysical diverging dissipation. All these issues are circumvented with more complex models involving different physical ingredients at nano, micro and macro scale (Bonn et al. 2009).

In addition, capillary forces do not only act on contact lines but also on any free surface. They result in a **pressure difference across the interface** between the liquid and the air. The pressure drop, named **Laplace pressure**, can be derived from Young-Laplace equation (Young 1805; Laplace 1805),

$$\Delta P = P_{liquid} - P_{air} = \gamma C \tag{1.9}$$

with *C* the **curvature** of the interface. Curvature can be computed from the curvature radii  $R_1$  and  $R_2$  according to,

$$C = \frac{1}{R_1} + \frac{1}{R_2} \tag{1.10}$$

A small radius of curvature corresponds to a strong bending of the surface and a strong Laplace pressure. For instance, in a droplet of radius  $r = R_1 = R_2$ , the pressure drop is  $\Delta P = 2\gamma/r$  which diverges as droplet radius diminishes.

In conclusion, a system with a free interface is subject to capillary phenomena inducing a force along its contact lines and pressure over its surface. When the system size decreases, the Laplace pressure becomes stronger as the radius of curvature diminishes. In particular, when a particle is trapped in a liquid film, curvature radii can become very small and induce strong capillary effects. Systems harnessing this interesting configuration are presented in the next section.

#### 1.4 Ordering, binding and sieving of objects by a free surface

Microscopic objects near a free surface are ubiquitous in nature and in industrial processes to take advantage of capillary forces at small scales.

In natural systems, for instance, emulsions of crude oils in sea water can become highly stable as fine clay particles are trapped irreversibly by capillary forces at the droplet interfaces (Ramsden 1904; Binks and Horozov 2006). Whether wanted or not, this kind of **solid shell** around fluid droplets greatly **stabilizes emulsions and foams** as illustrated in figure 1.6. Today, many industrial processes (food, cosmetics, ...) add particles in biphasic products to enhance their stability.



Figure 1.6: Stabilization of foam and emulsion by Pickering effect (Pickering 1907). (a) A regular oil/water emulsion is not stable and a phase separation is observed. (b) Addition of colloidal particles to the initial emulsion stabilizes oil droplets by means of a solid shell of particles trapped at the oil/water interfaces by the capillary forces.

When small particles are not trapped at the interface but below, capillary pressure can lead to spectacular effects if liquid evaporates or withdraws. For instance, in **capillary-driven collective** assembly, capillary pressure moves the particles, gathers them, and confines them, see the scheme in figure 1.7(a). Under strong confinement, particles tend to self-organize in high density crystalline packing (Denkov et al. 1992). Such capillary-driven collective assembly is a fast process to realize crystal coating deposition by dragging a volume of dense suspension along a solid substrate, as sketched in figure 1.7(b) (Prevo and Velev 2004). The ordering level, number of layers and packing mode (hexagonal/square) can easily be tuned by varying the speed deposition, particle concentration, or solvent evaporative flux. Such methods can create a 1D, 2D and 3D crystalline matrix, used as macroporous materials for photonics, biomedical and optical applications (Cong et al. 2013). In addition, as liquid disappears, the pressure exerted on sufficiently small particles can become large enough to **bind particles irreversibly**. Indeed, with particles of 5 µm diameter and less, the capillary pressure pushes together the particles and leads to a permanent cohesion of the glass beads (Seiphoori et al. 2020). A bridge of micron-sized glass particles is then sealed with water. In the polydisperse case, particles will hierarchically bind according to their size: this solid bridging by smaller particles leads to a cohesion force up to 20 times greater than the monodisperse phenomenon. This simple system illustrates the incredible strength of capillary forces acting on small objects.

The interplay of larger granular particles with a free interface can also exhibit different kinds of interesting behavior for instance during pinch-off or dip-coating experiments with a granular suspension. In dip-coating, an object is immersed in and withdrawn from a bath to coat its surface. When the bath is made of a regular liquid, the thickness of the entrained liquid film varies with fluid properties and withdrawal speed (Landau and Levich 1988). Using a granular suspension instead of a continuous fluid, dip-coating now exhibits several entrainment behaviors, from a pure fluid film to a heterogeneous monolayer of particles and eventually to multiple layers of particles at large speed (Gans et al. 2019; Palma and Henri Lhuissier 2019). The transition between the regimes is set by the size ratio between the particle diameter and the film thickness. This system is then able to **sieve and sort particles** with a withdrawal speed adapted to entrain only small particles (Sauret et al. 2019; Jeong et al. 2022). Despite the high degree of confinement of the particles and the spatial inhomogeneity in concentration, the continuous model of Landau and Levich (1988) for regular fluid still holds, provided one uses an effective wetting viscosity (Gans et al. 2019; Jeong et al. 2022). During the pinch-off of granular suspensions, a similar transition from a Newtonian-like to a discontinuous regime is reported when the filament neck thins down and confines the particles (Bertrand et al. 2012; Bonnoit, Bertrand, et al. 2012; Château et al. 2018).



Figure 1.7: Capillary-induced self-assembly. (a) Under confinement, particles are gathered by capillary pressure of the free surface. (b) This effect can create highly regular structures behind a receeding contact line.

#### 1.5 Manuscript outline

The present experimental and theoretical work offers a reflection on questions related to the poorly addressed issues of capillary flows of granular suspensions. In particular, we investigate the breakdown of the continuous approach of granular suspensions presented in § 1.2.1 when the particles are confined below a free surface by the capillary forces introduced in § 1.3.2. These systems may exhibit new behavior arising from complex dissipation mechanisms compared to the bulk situation described in § 1.2.2. In light of the literature results presented in § 1.2.4, a different microstructure is expected to develop with increasing effect as the confinement tightens. Polymodal suspensions are studied to extend and confirm the conclusions drawn in the monomodal case, but also to hinder ordering and to study the effects of microstructure in capillary flows of granular suspensions. In addition, these fluids can be used to gain a better understanding of the high complexity of these flows, involving decades of length scales, even in the continuous case. The next chapter introduces the suspensions used in the experiments.

The first two projects are related to the **spreading of droplets of granular suspensions**. Theory and literature review about this phenomenon for continuous fluids are presented in Chapter 3. Several theoretical approaches are compared to understand key elements in the conceptualization of drop spreading. In Chapter 4, one of these approaches is used to study the spreading of granular droplets. It focuses on the region near the moving contact line, referred to as a **local approach**. In contrast, in Chapter 5, drop spreading of granular suspensions is tackled a with a **global approach**. These three chapters and the comparison of theory with experiments according to the local or the global approaches, raise numerous questions related to the wetting of granular suspensions but also related to dynamics of wetting itself.

In Chapter 6, a new configuration is examined. Contrary to the situation of drop spreading with capillary forces promoting the flow, we investigate a **thin film of fluid above air**. The free interface is **destabilized by gravity and stabilized by surface tension**, leading to characteristic patterns. This instability, historically named after Lord **Rayleigh** and Sir **Taylor**, is investigated for a thin film of granular suspension. Again, a comparison between theory, experiments with a continuous fluid and experiments with granular suspensions unveils interesting effects.

# 2

## Suspensions: Methods & characterization

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#### 2.1 Particle characterization

Depending on the project, different particles were used. Particles are made of plastic and are spherical. The first type, mostly used in the projects presented in Chapter 4 and Chapter 5, are polystyrene (PS) particles of various sizes, produced by the Norwegian brand Microbeads. The other type, poly(methyl methacrylate) (PMMA) particles, were used in Chapter 5 and Chapter 6. They come from either Microbeads or the French brand Arkema, depending on the desired size. Details and specifications of these different particles are given in this section.

#### 2.1.1 Dynoseeds® TS particles (Microbeads)

#### 2.1.1.1 Properties and production

The Dynoseeds[®] particles from Microbeads are highly monodisperse spherical particles made of polystyrene by a patented process. The available diameters (10  $\mu$ m, 20  $\mu$ m, 40  $\mu$ m, 80  $\mu$ m, 140  $\mu$ m, 250  $\mu$ m and 550  $\mu$ m), are called TS10, TS20,... in their catalog. A stabilizer is added during production so that these particles can be dispersed in water without flocculation, despite the hydrophobic behavior of polystyrene alone. The production process depends on the size of the particles, according to different patents registered by Microbeads (Nyhus et al. 2005; Jorgedal 2010). The smallest particles are produced according to a first process with a high level of monodispersity. The larger particles are produced by polymeric expansion (expandable polystyrene (EPS) beads): the process starts with small particles onto which monomers are grafted. The latter method produces particles up to millimeter size (Jorgedal 2010). It seems that polyvinylpyrrolidone (PVP) is efficient to stabilize the sub-25-µm particles, while cellulose works best to stabilize diameters larger than 15 µm. (Nyhus et al. 2005). Although we can guess the stabilizier choice for most particles, we don't know how the 20-µm particles are stabilized in water.

#### 2.1.1.2 Surface imaging

Imaging with a scanning electron microscope (SEM) was done at the Institut Pierre-Gilles de Gennes with the help of Lily Blaiset. Before imaging, particles are fixed on a piece of copper tape and metallized with a 20-nm gold layer using a vapor deposition chamber. This preliminary step is necessary for non-conductive samples (such as plastic beads) to avoid charge accumulation on their surface, which interferes with good imaging. The metallic layer also protects the sample from the powerful electron beam and prevents thermal damage. Figure 2.1 shows typical SEM images. They show that polydispersity, shape, and surface texture depend on particle size. In particular, large particles (TS140, TS250) appear less regular, rougher, and more polydisperse. Smaller particles (TS10, TS20, TS40, TS80) appear to be more monodisperse with a smooth surface, except for the TS20 which show a heterogeneous coating. Size distributions are presented in § 2.1.1.3.

Cleaning the particles with water and/or ethanol does not change anything on the rehology of the suspensions made with TS80 particles. With ethanol, the TS10 particles release a substance that forms a beige fibrous crust after drying. Dispersion of the particles in water after this cleaning step is no longer possible. Cleaning the TS20 particles with water and ethanol has also been tried in vain. However, their strange surface does not affect the properties of the suspension. For all these reasons, the particles are used without any cleaning step.



Figure 2.1: SEM images of polystyrene Dynoseeds[®] particles. Scale bars in the lower right corner for each image. An enlargement of the particle surface is shown for each size. Bottom images: batches of TS40 and TS250 particles.
#### 2.1.1.3 Size distribution

Based on the large size polydispersity of the TS250 particles observed in the lower right image in figure 2.1, large particles are sieved to remove small particles, dust and broken particle fragments. TS140 particles are sieved on a 50-µm mesh. TS250 particles are sieved through a 280-µm mesh and fragments are removed with a 224-µm mesh. TS550 particles are sieved through a 500-µm mesh. On the contrary, SEM images of the sub-80-µm particles indicate that sieving the small particle sizes is an unnecessary precaution due to their high monodispersity.

A series of snapshots taken with an optical microscope (Hamamatsu Photonics) and a camera (sC-MOS orca-Flash 4.0 V2, 2048×2048 pixel) are used to characterize the size distributions of small particles and sieved large particles. The lens used depends on the particle size, a ×20 magnification for the largest particles (1.5 pixel. $\mu$ m⁻¹) or a ×63 for the smallest (10 pixel. $\mu$ m⁻¹).

Automatic size analysis has been implemented in Python using the skimage package. The main steps are shown in the figure 2.2. The raw image (a) undergoes Scharr filtering shown in the subplot (c) to obtain the intensity gradient. It is thresholded to determine particle edges shown in subplot (d). Hough analysis can then be performed on the contours. A sufficiently large radius range must be specified to perform the circular Hough analysis, see the vertical dashed line in the subplot (f). The subplot (e) shows the Hough dual space of a given radius r. It locates the most probable positions of circles with radius r. Peak coordinates in the dual space are extracted by thresholding. It can happen that a circle is detected several times, i.e. in dual spaces corresponding to different radii. To avoid redundant circles, circles with close coordinates are grouped and the associated radius is determined by averaging their radii. After this grouping step, the program returns the positions and radii of the detected circles, dispalyed in subplot (b), and their radius distribution is presented in subplot (f). The results have been checked against manual measurements.

Histograms of size distributions are presented in figure 2.3 and statistics are collected in table 2.1. To obtain meaningful results, I try to image with as many particles as possible, usually N > 1000. It turns out to be difficult to achieve these large numbers for the largest particles (250 and 550 µm). For these particles, the magnification is too large to reach this number. As expected from the SEM images, a high monodispersity is observed for the smallest diameters (TS10, TS20, TS40, and TS80) corresponding to the subplots from (a) to (d). In contrast, TS140, TS250, and TS550 particles are less regular.

The aspect ratio of the particles was also measured using ImageJ's particle detection macro with ellipse fitting. The analyzed samples contain fewer particles due to a less efficient particle detection method than the one implemented in Python. A major weakness of the ImageJ particle detection method is the difficulty in detecting a particle when it touches another particle. The aspect ratio reported in the last line of the table 2.1 is the ratio of the major axis of the ellipse divided by the minor axis. In line with SEM images, the small particles are more spherical than the TS250.

Particles	TS10	TS20	TS40	TS80	TS140	TS250	TS550
Sample size N	1980	1383	1289	1734	1297	156	582
<b>Mean diameter</b> (µm)	11.11	21.90	41.4	78.38	144.14	250.36	587.4
<b>Standard deviation</b> (µm)	0.5	3.3	2.6	12.6	14.7	6.4	16.4
Aspect ratio	1.04	1.03		1.03	1.05	1.15	

Table 2.1: Size distribution and aspect ratio of the polystyrene Dynoseeds® particles.

2.1



Figure 2.2: (a) Raw image and (b) circles detected by Hough analysis. The intensity gradient given by the Scharr filter (c) is thresholded to detect particle edges (d). It then undergoes a Hough transform for different radii, from 36 pixel to 60 pixel, blue dashed lines in (f). Subplot (e) shows the dual space for a radius of r = 46 pixel. Peak positions correspond to the positions of the circles of radius 46 pixel detected in subplot (d). Circle detection is achieved by thresholding in dual space. Particles detected in multiple dual spaces, i.e. for multiple radii, are grouped together. Size distribution of the 66 particles detected in subplot (b) is shown in subplot (f).

Chapter 2 : Suspensions: methods & characterization 2.1 Particle characterization



Figure 2.3: Size distribution of polystyrene Dynoseeds[®] particles given by the Hough analysis. (a) TS10, (b) TS20, (c) TS40, (d) TS80, (e) TS140, (f) TS250, and (g) TS550. Balck dashed lines: mean diameters, and black dotted lines: standard deviations of the size distributions. (h) Particle distributions, where bandwidths are twice the distribution standard deviations.

# 2.1.2 Spheromers[®] CA particles (Microbeads)

#### 2.1.2.1 Properties and production

The Spheromers[®] particles by Microbeads are highly monodisperse spherical particles made of acrylic crosslinked polymers (PMMA). They can be used in cosmetics or in paint to obtain a soft touch feel or a smooth surface with nice optical effects. Again, the patented process enables dispersing the particles in water. The available diameters (10  $\mu$ m, 20  $\mu$ m and 60  $\mu$ m), are named CA10, CA20, and CA60 in their catalog. The patents registered by Microbeads concern both Dynoseeds[®] and Spheromers[®] particles, see § 2.1.1.1.

#### 2.1.2.2 Surface imaging

Two sizes, the 10-µm and 60-µm particles, have been imaged using SEM with the same procedure as the one described in § 2.1.1.2. High monodispersity and sphericity are observed as shown in figure 2.4. The last picture of each line is an enlargement of particle surfaces that look very similar to the TS20 coating in figure 2.1.

#### 2.1.2.3 Size distribution

Owing to their high monodispersity, no sieving was performed on the Spheromers[®]. Similarly to the polystyrene Dynoseeds[®] particles, snapshots of PMMA particles were taken with the microscope at a ×63 magnification (10 pixel.µm⁻¹).

The same automatic size analysis implemented on Python has been used. Histograms for the 3 particle sizes are presented in figure 2.5. As expected from the SEM imaging, a high monodispersity is observed for any size. As well, aspect ratio analysis also shows high sphericity of the Spheromers[®], see table 2.2.



Figure 2.4: SEM imaging of the Spheromers[®]. CA10 (first column) and CA60 (second column) particles are shown with different magnifications. Scale bars in the bottom right corner for each picture.

2

Chapter 2 : Suspensions: methods & characterization 2.1 Particle characterization



Figure 2.5: Size distribution of Spheromers[®] particles (a) CA10, (b) CA20, and (c) CA60. Dashed solid lines show the average diameters and the dotted lines the distribution widths (standard deviations).

Particles	CA10	CA20	CA60
Sample size N	2843	3257	413
<b>Mean diameter</b> (μm)	10.12	19.89	59.48
Standard deviation (µm)	0.41	1.08	1.43
Aspect ratio	1.03	1.05	1.03

Table 2.2: Size and aspect ratio of the PMMA Spheromers® particles from Microbeads.

#### 2.1.3 Altuglas® BS beads (Arkema)

#### 2.1.3.1 Properties and production

The acrylic polymer Altuglas[®] is a transparent and rigid thermoplastic registered by the French group Arkema. It can be bought as spherical beads (BS series) with broad size distributions centered around 270  $\mu$ m (BS572) and 170  $\mu$ m (BS440). Specifications from Arkema concerning the different references are gathered in table 2.3. Unlike Microbeads particles, the Altuglas[®] beads are not (or poorly) crosslinked. They dissolve in acetone to make a paste-like material once the solvent is removed.

38574	BS440
PMMA	Copolymer MMA
800	150-200
High	Medium
3 5 5	8574 MMA 00 ligh

Table 2.3: Specifications of the Altuglas® BS-series beads provided by Arkema.

#### 2.1.3.2 Particle imaging

SEM pictures of the BS572 particles provided by Lily Blaiset are shown in figure 2.6. Particles look rather spherical and smooth but highly polydisperse.



Figure 2.6: SEM imaging of the Altuglas[®] BS572 particles. Scale bars are in the bottom right corner for each picture.

#### 2.1.3.3 Size distribution

Size distributions of the BS574 and BS440 has been realized by Lily Blaiset. The results are gathered in figure 2.7. In agreement with the size ranges provided by Arkema in table 2.4, the average diameters of the BS572 and BS440 particles are 270  $\mu$ m and 170  $\mu$ m, respectively. Though, as one can guess from the SEM imaging figure 2.6, the two series show high polydispersity with respective standard deviations of 69  $\mu$ m and 45  $\mu$ m. While this polydispersity could be a pitfall in some situations, we turned it into an asset by sieving to make our own size distributions with particles from the same batch in Chapter 6.



Figure 2.7: Size distribution of the Altuglas[®] particles (a) BS572 and (b) BS440. Dashed solid lines show the average diameters and the dotted lines the distribution widths (standard deviations).

Particles	BS572	BS440	
Sample size N	159	133	
<b>Mean diameter</b> (μm)	270.28	169.74	
Standard deviation (µm)	69.09	47.60	

Table 2.4: Results of the size distribution analysis of the Altuglas® BS572 and BS440 beads.

## 2.2 Suspension preparation and characterization

This section describes the different mixtures, their preparation and their physical properties, summarized in table 2.5. The fluid used as the suspending phase depends on the particles. To prevent sedimentation/creaming of the solid phase, good density matching is required. In the following, all the suspensions are density-matched ( $\rho = \rho_p = \rho_f$ ). The high viscosity of the fluid prevents inertial effects ( $Re = U\rho d/\eta_f \ll 1$ ). In some experiments, index matching between the fluid and the particles can also be required. In that case, the suspension is transparent.

Particles	Polystyrene	РММА
Fluid	PEG	Triton X-100, ZnCl ₂ , Water
<b>Density</b> $\rho$ (kg/m ³ )	1056	1190
Fluid viscosity $\eta_f$ (Pa.s)	2.3±0.2	3.3±0.1
<b>Fluid surface tension</b> γ (mN/m)	35	32±2
Optical index	1.46 (tabulated at 20 $^{\circ}$ C)	1.45

Table 2.5: Summary of the different suspension properties.

#### 2.2.1 Preparation of suspensions

Suspensions are prepared one or two days before the day of the experiment. A mass  $m_f = \rho V_f$  of fluid is first poured into a tube and weighed. The desired mass of particles  $m_p = \rho V_p = m_f \phi/(1 - \phi)$  necessary to reach the target volume fraction,  $\phi$ , is collected in a small dish and poured into the tube with the fluid. Mixing is first hand-made using a spatula and followed by slow mixing, achieved using a rolling device overnight. This method removes air bubbles entrapped during the mixing while keeping a homogeneous suspension.

#### 2.2.2 Surface tension of granular suspensions

The surface tension,  $\gamma$ , of the suspensions is expected to be the one of the pure fluid if the particle surface is well wetted. Prior publications agree on this fact for these suspensions made of the same polystyrene particles dispersed in PEG (Couturier et al. 2011). The good wettability of these particles has been thoroughly checked over several days and pendant-drop experiments have also been done to measure the surface tension of the suspensions. We find that the surface tension of the polystyrene-PEG suspensions is the same as the PEG alone,  $\gamma \approx 35 \text{ mN.m}^{-1}$ .

#### 2.2.3 Suspensions with polystyrene particles

#### 2.2.3.1 Suspending fluid: PEG copolymer



Figure 2.8: Poly(ethylene glycol-ran-propylee glyol) monobutul ether used to have density-matched suspensions with polystyrene particles.

The fluid used to obtain decent density matching with polystyrene particles is a PEG copolymer bought from Sigma-Aldrich (reference 438 189, CAS: 9038-95-3). To be more specific, we are using a Poly(ethylene glycol-r-an-propylee glyol) monobutyl ether with an average molecular weight of 3900 g.mol⁻¹ but we will name it PEG in this manuscript for the sake of readability. Its topological formula is given in figure 2.8.

This fluid is transparent, viscous, and hygroscopic in a moderate way. Its density at 25 °C is tabulated at 1056 kg.m⁻³ and its kinematic viscosity at 20 °C is declared to be 3600 m².s⁻¹. However, the precise knowledge of which is crucial for the discussion of the experiments, and is thoroughly checked over time to account for any temperature effects or water sucking by the fluid. The PEG copolymer is expected to be Newtonian, meaning that its shear viscosity,  $\eta_f$ , does not depend on shear rate  $\dot{\epsilon}$ . These two elements (Newtonian behavior and temperature dependency) are investigated in the following paragraphs.

#### 2.2.3.2 PEG viscosity

#### Dynamic viscosity

The dynamic viscosity of a fluid,  $\eta$ , is defined as,

$$\eta = \frac{\sigma}{\epsilon},\tag{2.1}$$

where  $\sigma$  is the viscous stress and  $\dot{\epsilon}$  the shear rate of the flow, i.e. the time derivative of the local strain  $\epsilon$ . Its unit is the Pa.s (or kg.m⁻¹.s⁻¹).

For a Newtonian fluid, this quantity does not depend on the shear rate as aforementioned. To provide some orders of magnitude, the dynamic viscosity of water at ambiant temperature is roughly 1 mPa.s, and the fluids we use are 1000 times more viscous.

In practice, viscosity can be measured with a rotational rheometer, see § 2.3.2. A small quantity of fluid is inserted between a static and a rotating tool with several possible geometries: plate-plate (PP), cone-plate (CP), Couette ... Depending on the type of rheometer, a given shear rate  $\dot{\epsilon}$ , or shear stress  $\sigma$ , imposes the flow with the rotationnal tool. The torque or the stress applied on the static tool is measured by a transducer to compute the shear viscosity of the medium using (2.1). More details regarding rheometry can be provided by Macosko (1994).

Figure 2.9 presents stress and viscosity measurements in cone-plate ( $\blacklozenge$ ) and plate-plate geometry ( $\blacksquare$ ) for different shear rates. Figure 2.9(a) displays the stress,  $\sigma$ , as a function of the shear rate,  $\dot{e}$  and figure 2.9(b), the viscosity,  $\eta$ , as a function of the shear rate. Each point comes from a time averaging of the stress over 60 s for a given shear rate. The small disagreement between the two tools may come from calibration errors. In figure 2.9(a), one observes that the stress,  $\sigma$ , increases linearly with the shear rate,  $\dot{e}$ . The coefficient, namely the viscosity according to (2.1), is plotted in figure 2.9(b). For any value of  $\dot{e}$  and for any tool, its value lies around 2.35±0.10 Pa.s. The PEG is thus a Newtonian fluid over this range of shear rates. Small deviations at low and high shear rates may come from insufficient time averaging and inertia effects, respectively. A back-and-forth sweep has been used to obtain the two curves of the cone-plate geometry. The upper one corresponds to the  $\dot{e}$ -decreasing procedure. The "high" viscosity measured at a shear rate 10 s⁻¹ in figure 2.9(b) is thus likely explained by residual flow from the previous high-shear stages. When studying complex fluids, this back-and-forth procedure can reveal hysteresis. On the contrary, for regular fluids like the PEG, such precaution is usually considered unnecessary.



Figure 2.9: PEG rheology using ( $\blacklozenge$ ) a 25-mm cone-plate geometry (cone angle 0.1° rad), and ( $\blacksquare$ ) a 25-mm plate-plate geometry at 25 °C. (a) Stress,  $\sigma$ , and (b) shear viscosity,  $\eta$ , as a function of shear rate,  $\dot{\epsilon}$ . Dashed line: viscosity average over the shear rates.

Temperature variations lead to major viscosity variations of PEG. As shown in figure 2.10, the viscosity increases two folds when temperature decreases from 30 °C to 16 °C. This temperature dependency of the PEG viscosity therefore requires to be accounted for any experiment. Yet, performing a measurement with a rheometer for each and every experimental condition that we probe in this manuscript is a tedious task. Instead, a quick, local and reliable method, relying on a capillary viscometer is used simultaneously to all experiments. A sketch of such glassware is presented in figure 2.11. It is made of a fluid reservoir (roughly 1 cm³) above a capillary tube (approximate diameter 1 mm). The liquid is aspirated by means of a bulb pipette up to the top of the reservoir. Once the upper mark (in red) is reached, the bulb is removed and the fluid is left to flow under the influence of gravity. The time delay between the two red marks,  $\Delta t$ , can be converted into a viscosity using the equation of the stationnary volume flow rate, Q, through a thin tube (Poiseuille flow):

$$Q = \frac{V_0}{\Delta t} = \frac{\pi R^4}{8\eta} \frac{\Delta P}{L},$$
(2.2)

whith *R* the inner radius of the lower capillary,  $\Delta P$  the pressure drop in the capillary and *L* its length. Again, the time delay is the one necessary to empty the resevoir mounting the capillary tube. If its volume,  $V_0$  is such that  $V_0^{1/3} \ll L$ , the pressure drop between the capillary ends reads  $\Delta P \simeq \rho g L$ , leading to

$$\eta = \frac{\pi R^4 g}{8V_0} \rho \Delta t = K \rho \Delta t.$$
(2.3)

The constant K = 0.003 75 m².s⁻² of the capillary viscometer has been calibrated for different fluids with a rheometer. For the PEG viscosity, one measurement takes roughly 10 min. Shortly after, or during an experiment, one or two viscosity measurements are done with the capillary viscometer to track any viscosity variation due to temperature or water sucking by the PEG over time.



Figure 2.10: PEG viscosity a function of temperature using a 25-mm plate-plate geometry between 16 °C and 30 °C. Each point come from the averaging over 200 s at the end of temperature steps of 420 s of increasing and decreasing sweeps.



Figure 2.11: Sketch of the capillary viscometer used to monitor viscosity variations of the PEG. Capillary tube diameter is about 1 mm, reservoir volume 1 cm³ and capillary length 15 cm.

2

#### 2.2.4 Suspensions with PMMA particles

With PMMA particles, density and optical index can be matched with a mixture made of liquid Triton X-100 (t-Octylphenoxypolyethoxyethanol, Polyethylene glycol tert-octylphenyl ether, Sigma Aldrich, see figure 2.12), solid zinc chloride (ZnCl₂, Sigma-Aldrich) and water.



Figure 2.12: Triton X-100 molecule used in the mixture matching optical index and density of PMMA particles.

#### 2.2.4.1 Preparation of the Triton mixture

Triton X-100, zinc chloride, and water must constitute 73%, 16%, and 11% of the mass, respectively. Triton X-100 is first poured and weighed in a bottle. The corresponding mass of zinc chloride is collected in a beaker and the tare of the scale is set to zero. The required mass of water is then added in the beaker and stirring is performed until complete dissociation of the salt. Rhodamine 6G can be dispersed in water before salt dissociation, see § 2.2.4.2. Salt dissociation being highly exothermic, it requires precautions and evaporated water compensation after solution cooling. Once the water mass is adjusted, two or three drops of hydrochloric acid HCl are added to increase the pH and prevent salt precipitation. The acid-aqueous zinc-chloride solution can then be poured into the Triton X-100 bottle. Hand mixing is followed by a slower roller-device mixing at least one or two days until getting a clear solution. In the beginning, lumps and strings of gel form and the mixture looks cloudy. The aspect of the solution after one or two days of mixing must however be perfectly homogeneous and clear.

#### 2.2.4.2 Index matching and fluorescing fluid

By matching the fluid refractive index with the one of the particles, light is not deviated at a fluid-particle interface, which results in negligible light diffusion or intensity lessening in the sample. Therefore, the suspension remains transparent whatever the solid volume fraction. Mixture index has been measured with an optical refractometer. The experimental value,  $n_f = 1.47\pm0.01$ , matches well with the index range of PMMA found on the internet  $1.49\pm0.10$ . While polystyrene suspensions are completely opaque, dense PMMA suspensions can then be transparent and particles become invisible once immersed in the Triton mixture as shown for the right sample in figure 2.13.

This matching can be used to visualize bulk flow in suspensions by the means of a fluorescent agent, a laser



Figure 2.13: Pictures of two suspensions with 30 % of 60-µm PMMA particles. Whithout index matching on the left and with index matching on the right.

sheet and a light filter. For instance, it becomes possible for us to see the fluid and the particles in a horizontal slice of a spreading drop of suspension with the apparatus sketched in figure 2.14(a).

To that end, a small quantity of rhodamine 6G, displayed in figure 2.15(a) is dispersed in water before salt dissociation. A green laser sheet ( $\lambda = 532$  nm, 50 mW) is used to illuminate a section of fluid and triggers rhodamine fluorescence, see absorption spectrum in figure 2.15(b). The fluorescence emission of rhodamine 6G can be easily extracted by a camera behind a high-pass filter, see the emission spectrum in figure 2.15(b) and apparatus sketched in figure 2.14(a). While the green laser light goes through without deviation, the rhodamine in the fluid fluoresces in all directions, see figure 2.14(b). The camera behind the filter receives only the red rhodamine light and no green laser light. The particles then appear dark, while the fluid is bright as shown in figure 2.14(c).



Figure 2.14: (a) Apparatus used to visualize an horizontal slice of a spreading drop. A green laser sheet illuminates the drop and a camera is located above a red filter. (b) Green light is not deviated in the indexmatched suspension. Rhodamine in the fluid though fluoresces in all directions and the emitted red light can be collected by the camera located above. (c) Picture of an horizontal slice of suspension made of 300-µm PMMA particles. The fluid appears bright with rhodamine fluorescence while particles are dark.



Figure 2.15: Rhodamine 6G used as a fluorescent agent (a) molecule and (b) absorption (green cruve) and emission (red curve) spectra. The excitation laser wavelength,  $\lambda = 532$  nm, is indicated by the green dashed line and the high-pass filter,  $\lambda \ge 550$  nm used to extract the emission signal, is shown by the red rectangle.

2.2

#### 2.2.4.3 Viscosity of the Triton-mixture



Figure 2.16: Viscosity of ( $\blacksquare$ ) pure Triton, and of ( $\blacklozenge$ ) the mixture matching the density and the optical index of PMMA using a 25-mm parallel-plate geometry at 25 °C. (a) Shear viscosity, as a function of shear rate,  $\dot{\epsilon}$ . Dashed line: viscosity average for  $1 \le \dot{\epsilon} \le 10 \text{ s}^{-1}$ . (b) Shear viscosity, as a function of temperature.

Figure 2.16(a) presents the viscosity of pure Triton X-100 and of the mixture as a function of the shear rate  $\dot{e}$ . Pure Triton ( $\blacksquare$ ) viscosity departs from a plateau of 0.25 Pa.s for a shear rate below 1 s⁻¹. Conversely, the mixture viscosity ( $\blacklozenge$ ) is constant over a large range of shear rates. It is thus Newtonian with a viscosity lying around 3.3 Pa.s. This increase in viscosity compared to that of pure Triton X-100 can be explained by a gelation-like process. This phenomenon can raise issues at low temperatures with a significant increase in viscosity as shown in figure 2.16(b). Water evaporation and aging are other issues with this mixture leading to viscosity variations. For instance, in figures 2.16(a) and (b) the viscosity at 25 °C of the two different samples are 3.3 Pa.s and 4.0 Pa.s, respectively. Again, the viscosity of the fluid must be carefully monitored to account at best for this variability.

# 2.3 Rheology of granular suspensions

Rheology is the study of the mechanical properties of materials, solid or liquid, when they are subjected to strains or stresses. In the case of suspensions, it can be for instance measuring the viscosity of the mixture but other quantities can be of interest (e.g. the normal force, the elastic modulus ...).

#### 2.3.1 Relative viscosity of granular suspensions and jamming volume fraction

#### **Relative viscosity of suspensions**

When dealing with suspensions, we usually report the **relative viscosity**,  $\eta_s$  defined as:

η

$$\eta_s = \frac{\eta_a}{\eta_f},\tag{2.4}$$

with  $\eta_a$  the absolute dynamic viscosity of the suspension, and  $\eta_f$  the dynamic viscosity of the suspending fluid.

The relative viscosity,  $\eta_s$  has no unit. This normalized quantity displays the effects of the particles only? and removes environmental variations (temperature, humidity, ...). Indeed, these variations affect mostly the solvent viscosity  $\eta_f$ .

#### Relative viscosity of granular suspensions

A granular suspension made with a Newtonian solvent and flowing at low Reynolds number,  $Re \ll 1$ , exhibits a relative viscosity that only depends on the particle volume fraction  $\phi$ ,

n

$$s = \eta_s(\phi). \tag{2.5}$$

In particular, particle size, d, and flow shear rate,  $\dot{\epsilon}$ , do not affect  $\eta_s$ . Granular suspensions can hence be considered *pseudo-Newtonian*.

Since particles increase dissipation in the mixture, the suspension viscosity increases with  $\phi$ . The  $\phi$ -dependence of the relative viscosity depends on the particle volume fraction range, commonly split into 3 groups: dilute, semi-dilute and dense suspensions. A non-exhaustive list of empirical and analytical expressions of the relative viscosity in these different regimes are gathered in table 2.6.

Regime	Dilute	Semi-dilute	Dense
$\phi$ range	0 - 10%	10% - 20%	20% - $\phi_c$
			Krieger and Dougherty (1959) $\eta_s = (1 - \phi/\phi_c)^{-[\eta]\phi_c}$
Interpolation	Einstein (1905)	Batchelor and Green (1972)	Eilers (1941)
	$\eta_s = 1 + \tfrac{5}{2}\phi$	and (Batchelor 1977)	$\eta_s = \left(1 + \frac{[\eta]}{2} \frac{\phi}{1 - \phi/\phi_c}\right)^2$
		$\eta_s = 1 + \frac{5}{2}\phi + 6.2\phi^2$	Mooney (1951)
			$\eta_s = \exp\left(\frac{[\eta]\phi}{1-\phi/\phi_c}\right)$

Table 2.6: Relative viscosity of granular suspensions in different  $\phi$ -regimes. We define  $[\eta] = \lim_{\phi \to 0} \frac{\eta_s - 1}{\phi} = 2.5$  the intrinsic viscosity of the suspension.

For the semi-dilute regime, the quadratic term in Batchelor's formula comes from particleparticle interactions while only fluid-particle interactions are used to derive the Einstein formula in the dilute regime. In the dense regime, an additional parameter, the **jamming volume fraction**,  $\phi_c$ , is involved in all correlations. It corresponds to the maximum solid volume fraction one can immerse in the liquid. Depending on the shear stress, particle size distribution, friction, or flow history, one must use the random loose packing,  $\phi_c \approx 0.6$  (Scott 1960) or smaller values of  $\phi_c$  (Krieger and Dougherty 1959; Guazzelli and Pouliquen 2018; Tapia et al. 2019). Higher packing fractions can be reached with particle crystallization. For instance, for 3D-hexagonal close packing and facecentered cubic packing,  $\phi_c \approx 0.74$  (Scott 1960). In the following, attention will be put on dense granular suspensions far from jamming, typically  $\phi = 30 - 40\%$ .

#### 2.3.2 Methods for viscosity measurement

#### 2.3.2.1 Rheometer

Most of the measurements presented in this part have been realized with an ARES-G2 rotationnal rheometer from TA Instruments. The lower tool sets the strain  $\epsilon$  and the shear rate  $\dot{\epsilon}$  while the upper tool is connected to a transducer that measures the torque  $\Gamma$  and the normal force  $F_N$  transmitted

by the sheared sample. For this model of rheometer, the motor and the transducer are separated, leading to better rheological measurements. The viscosity is computed according to the relation (2.1) and measurements are performed in the steady regime. The specifications of the operating ranges of the ARES-G2 rheometer are gathered in table 2.7. Beneath the lower tool, a Peltier device regulates the sample temperature.

	Minimum	Maximum	Resolution
<b>Torque</b> Γ	0.05 μN.m (oscillations) 0.1 μN.m (steady)	200 mN.m	1 nN.m
Normal force $F_N$	1 mN	200 N	-
Strain $\epsilon$	1 μrad	Unlimited	0.04 µrad
Angular velocity Ω Angular frequency	1 μrad.s ⁻¹ 0.1 μrad.s ⁻¹	300 rad.s ⁻¹ 628 rad.s ⁻¹	-

Table 2.7: Specifications of the ARES-G2 rheometer provided by TA.

#### 2.3.2.2 Parallel plates (PP) geometry



Figure 2.17: Sketch of proper filling and parameters in parallel-plate geometry.

Bulk viscosity of granular suspensions is measured using a parallel-plate geometry, see figure 2.17. The upper tool has a radius R = 12.5 mm. The lower tool is a stainless steel plate. Rough surfaces must be used if one suspects particle slip, see § 2.3.2.4. Parallel plate geometry is prefered to cone-plate geometry when studying granular suspensions to avoid the confinement of the particles near the cone tip. In this section, only **bulk suspension viscosity** is discussed, which is the suspension effective viscosity when the mixture can be approximated by a **continuous medium**. In that case, typical geometry sizes (R, h) are much greater than the particles and wall effects become negligible. The minimum gap depends on particle size but also on the solid volume fraction  $\phi$  (Barnes 2000). In practice,  $R \gg d$  and one must check that  $h \ge 20d$  to remove gap effects (Peyla and Verdier 2011; Ramaswamy et al. 2017). Once the gap is properly adjusted, it is also necessary to verify that the loaded volume of fluid correctly fills the gap (see figure 2.17) as significant errors arise from gap overfilling (Cardinaels et al. 2019) or underfilling (Hellström et al. 2014).

In PP geometry, the relation between the shear rate and the shear stress leading to the viscosity reads:

$$\eta = \frac{\sigma}{\dot{\epsilon}} = \frac{2\Gamma h}{\pi R^4 \Omega}.$$
(2.6)

2.3

To derive relation (2.6), one must establish the expression of the shear rate and shear stress in PP geometry. The flow is along the azimuthal  $\mathbf{e}_{\theta}$  direction due to the rotation of the lower tool, see figure 2.17. Since the upper tool is kept fixed, the shear is along the vertical direction,  $\mathbf{e}_z$ . The azimuthal velocity obeys  $v_{\theta} = r\Omega(z - h)/h$  where *h* is the gap size and  $\Omega$  the rotational speed of the lower tool. The strain and the shear rate exerted over a volume of fluid depend on its radial position  $0 \le r \le R$  and read  $\epsilon = r\Delta\theta/h$  and  $\dot{\epsilon} = r\Omega/h \Rightarrow \dot{\epsilon}(r = R) = R\Omega/h$ , respectively. Again, the shear rate is not homogeneous along the radial coordinate contrary to the cone-plate geometry. For a Newtonian fluid, the integration over the surface of the upper tool shows that the shear stress at r = R and the global torque are related according to  $\sigma_{\theta z}(r = R) = 2\Gamma/(\pi R^3)$  (Macosko 1994). The stress and shear rate expressions lead to relation (2.6). In our case, *R* is specified by the user and the rotational velocity,  $\Omega$ , is imposed by the motor. The gap size, *h* and the torque  $\Gamma$  are measured by the rheometer.

One can easily understand from (2.6) that gap errors are significantly larger for small gaps. In addition, large gaps prevent parallelism errors and secondary flow effects (Macosko 1994) and importantly, avoid particle confinement. The gap size is then set around 1.5 mm for the particles of diameter from 10 µm to 80 µm. However, for the 140-µm and larger particles, the non-confinement condition,  $h \ge 20d \ge 3$  mm is challenging. Indeed, while increasing the gap size, fluid loading becomes an issue if a meniscus appears (Cardinaels et al. 2019). This phenomenon can cause an apparent viscosity increase of 30% and must be avoided. The next section explains how to circumvent this problem with an adapted geometry.

#### 2.3.2.3 Parallel plates with a reservoir

Reaching large gaps ( $h \gtrsim 2$  mm) while limiting the formation of a meniscus is not feasible in practice in regular PP geometry. For this reason, a custom *reservoir geometry*, i.e a  $2\beta R$ -wide reservoir made of transparent plastic is mounted on the rheometer lower tool and filled with a layer of suspension of thickness  $h = \alpha R$ , see figure 2.18. This modified PP geometry has been previously used by Chateau and Lhuissier (2019) and Palma and Henri Lhuissier (2019) for instance. The upper tool is lowered until it touches the surface of the liquid.



Figure 2.18: Plate-plate geometry with a reservoir.

The analytical solution of such flow is given by Vrentas et al. (1991) and returns the additional torque exerted by the liquid ring at  $R < r \le \beta R$ . The total apparent torque measured by the rheometer then reads as:

$$\Gamma_{\text{reservoir}} = \Gamma_0(f+1), \tag{2.7}$$

with  $\Gamma_0$  the torque in regular PP geometry without the reservoir.

The relative additional contribution depends on the geometry parameter, namely the liquid thickness  $\alpha R$  and the reservoir radius  $\beta R$ . The value returned by the rheometer,  $\eta_{\text{reservoir}}$ , must then be corrected to remove the additional contribution of the outer liquid ring.

#### Reservoir for the viscosity of large-particle suspensions

It follows from (2.6) that the viscosity  $\eta_{\text{reservoir}}$  returned by the rheometer in a reservoir geometry (sketched in figure 2.18) is

$$\eta_{\text{reservoir}} = \Gamma_{\text{reservoir}} \frac{2h}{\Omega \pi R^4} = \Gamma_{\text{reservoir}} \frac{\eta_0}{\Gamma_0} = \eta_0 \left( f(\alpha, \beta) + 1 \right), \tag{2.8}$$

where  $\alpha R$  is the fluid depth,  $\beta R$  the reservoir radius, and  $\eta_0$  the true viscosity of the fluid in the reservoir. Working at larger gaps than the regular plate-plate geometry becomes possible with such a geometry.

The correction f can thus be either computed with the analytical expression from Vrentas et al. (1991), see figure 2.19(a), or derived experimentally from the ratio  $\eta_{reservoir}/\eta_0 = f + 1$  (see table 2.8) for a given set of parameters ( $\alpha$ ,  $\beta$ ). Computation of  $f(\alpha, \beta)$  according to Vrentas et al. (1991) has been implemented and the results presented in figure 2.19(b) reproduce the published ones, enabling us to extrapolate to our reservoir parameters. Eexperimental calibration of the reservoir with ( $\alpha$ ,  $\beta$ ) = (0.4, 2) has been done with regular viscous fluids and a granular suspension of 80-µm particles, see table 2.8. The experimental value,  $f_{exp} = 1.05 \pm 0.15$ , is in relatively good agreement with the prediction  $f_{th} = 0.88$ . In the following, we take f = 0.9 to correct the value of viscosity when the reservoir is used.



Figure 2.19: Realtive correction to apply on values returned by the rheometer according to (2.8). (a) Values from literature (Vrentas et al. 1991), (b) validation of the implementation prior to extrapolation with our reservoir parameters.

#### 2.3.2.4 Rough surfaces

Near moving walls, particles can slip due to a lubricating film of liquid, see figure 2.20(a). Such a phenomenon can lead to major errors in viscosity measurements, especially for dense suspensions of large particles (Medhi et al. 2011). As slip depends on gap size, its presence and the resulting underestimation of the viscosity can be detected by comparing the viscosity measurements at two

Fluide	Viscosity in regular PP geometry	Apparent viscosity with the reservoir	<b>Ratio</b> <i>f</i> + 1
Glycerol	0.9	1.8	2.0
PEG	2.1	4.9	2.3
Pure Ucon	46.2	86.4	1.9
Ucon 90 wt% = water	25.4	49.5	2.0
Ucon 80 wt% + water	13.5	25.6	1.9
<b>80 μm,</b> φ = 0.2	4.7	10.3	2.2
Theory	-	-	1.88

Table 2.8: Experimental calibration of the PP geometry with a reservoir,  $\beta = 2$  and  $\alpha = 0.4$  and analytical prediction according to Vrentas et al. (1991).

gap sizes in PP geometry (Yoshimura and Prud'homme 1988). This method has been used to ensure that slip is negligible for the smallest particles,  $d \le 80 \,\mu\text{m}$ . On the contrary, rough walls have to be used for the largest particles of diameter larger than of 140  $\mu\text{m}$ . In that case, we use rough crosshatched tools bought at TA Instruments whose surfaces are square-based pyramids of height 1 mm. As sketched in figure 2.20(b), the effective wall roughness is the particle diameter *d* since the holes are filled with particles that create roughness to entrain the above grains (Coussot 2005).



Figure 2.20: (a) Particle slippage due to a liquid lubrication film near a moving wall. The strain of the particulate phase (orange), is smaller than that of the moving wall (dark blue), and that of the liquid in the lubrication film (turquoise). (b) Effect of wall roughness of a moving wall. A small number of particles gets caught in the wall bumps and creates a rough pattern with typical size *d*. The upper particulate phase is then dragged by this rough surface at the same velocity that the one imposed by the moving wall.

#### 2.3.3 Experimental viscosity of dense granular suspensions

#### 2.3.3.1 Viscosity of monomodal suspensions

2.3

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Figure 2.21: Experimental viscosity of monomodal granular suspensions made with TS particles and PEG. (a) Absolute viscosity of pure fluid ( $\star$  symbols) and monomodal granular suspensions as a function of the shear rate. (b) Relative viscosity of monomodal granular suspensions as a function of particle volume fraction. Dotted and plain lines are plots of Krieger's and Eiler's interpolations, respectively (see table 2.6). Comparison with measurements found in literature ( $\blacklozenge$  symbols) of 10-µm and 140-µm particles reported by Chateau and Lhuissier (2019) and Palma and Henri Lhuissier (2019).

1 mm. Since drop thickness falls in this range, we expect the suspensions to behave like a Newtonian fluid despite the presence of the particle solid phase. Moreover, one can see in figure 2.21(b) that for a given particle volume fraction,  $\phi$ , the bulk viscosity does not depend on the particle size. In the end, as aforementioned, the relative viscosity of monomodal granular suspensions is solely a function of the particle volume fraction,

$$\eta_s(\phi, \dot{\epsilon}, d) = \eta_s(\phi). \tag{2.9}$$

This result can be found theoretically by dimensional analysis in the inertialess regime ( $Re \ll$ 1) starting from the flow equations around spherical, monosized, and non-interacting particles (Guazzelli and Pouliquen 2018). This prediction holds experimentally over a large size range (5  $\leq$  $d \le 105 \,\mu\text{m}$ ) and for solid volume fractions up to 50% (T. Lewis and Nielsen 1968). At higher volume fractions and higher shear rates, non-Brownian suspensions exhibit complex shear-thinning behavior (Ferrini et al. 1979; Chatté et al. 2018). As shown in figure 2.21(b) and widely reported in the literature, the suspension viscosity is an increasing function of  $\phi$  and diverges at a maximum value,  $\phi_c$ , the jamming volume fraction. The increase with  $\phi$  comes from several effects. First, the addition of a single particle creates dissipation because of its non-deformability (Guazzelli and Pouliquen 2018). Then, interactions between several particles enhance dissipation due to particle hydrodynamic interactions or solid contacts at high concentration. Jamming divergence happens when the solid phase can not distort while remaining immersed in the available liquid. Our data agree with the Kriegger and the Eilers interpolations using  $\phi_c \simeq 0.53$ . However, this value is just an estimation and not a real measurement of the jamming volume fraction. Measuring  $\phi_c$  would require a more detailed investigation at higher volume fractions ( $\phi \rightarrow \phi_c$ ) or a more adapted method, such as pressure-imposed rheometry (Boyer et al. 2011; Guazzelli and Pouliquen 2018). By means of this device, a continuous increase in solid volume fraction is made possible by removing fluid through permeable walls. Jamming transition can then be approached very closely unlike volume-imposed rheology that fails at such concentrations.

#### 2.3.3.2 Viscosity of bimodal suspensions

In the monomodal case, the maximum packing fraction  $\phi_c$  does not depend on the particle size. Conversely,  $\phi_c$  increases with polydispersity (Macosko 1994). When two sizes of particles are involved, one can figure out that a smart choice of proportion can optimize solid loading by filling large particle holes with small ones. The jamming volume fraction thus depends on two additional parameters in the bimodal case. The first one is the particle sizes or more precisely the diameter ratio with  $d_1 < d_2$ . The second parameter is  $\zeta_{small}$ , the volume fraction of small particles in the solid phase:

$$\zeta_{small} = \frac{V_{small}}{V_{small} + V_{large}}$$
(2.10)

Experimental studies of bimodal systems found in the literature indicate that the viscosity of dense granular bimodal suspensions is similar to that of monomodal suspensions using the bimodal maximum packing fraction,  $\phi_c(d_1, d_2, \zeta_{small})$  (Chong et al. 1971; Chang and Powell 1994; Dörr et al. 2013; Spangenberg et al. 2014). For a given volume fraction  $\phi$ , the viscosity exhibits a minimum at  $\zeta_{small} \sim 1/3$ , i.e. for a third of small particles. This observation can be rationalized by the fact that whatever the size ratio, the largest  $\phi_c$  is reached for  $\zeta_{small}$  ranging between 25 % and 50 %. The experimental viscosity measurements made with a PP geometry at constant  $\phi$  confirm this minimum of the viscosity when varying  $\zeta_{small}$ , see figure 2.22. For a given size ratio  $d_2/d_1$ , the relative bulk viscosity,  $\eta_s$ , decreases with increasing  $\zeta_{small}$  from its monomodal value at  $\zeta_{small} = 0$  %, reaches this minimum, and then increases back to the monomodal value at  $\zeta_{small} = 100$  %. This lessening effect is enhanced with increasing  $d_2/d_1$ .



Figure 2.22: Experimental realtive viscosity of bimodal granular suspensions made with polystyrene particles and PEG at a total solid volume fraction of 40%. For a given size duet, the proportion of small particles in the solid blend  $\zeta_{small}$  varies from 0% (large particles only) to 100% (small particles only).

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# 3

# Theory of drop spreading: local and global approaches

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This chapter presents the theory of drop spreading. In the first section, the drop profile equations are derived for regular (continuous) fluids. The different regions of the drop will be treated separately to obtain local equations. Theoretical developments regarding a dissipation length scale near a moving contact line are presented in this section. The second section presents spreading dynamics at a global scale. Specifically, it returns the radius dynamics that is not provided directly by the previous local approach. Connections and comparisons between the two points of view are discussed at the end of this section.

# 3.1 Spreading of regular liquids: local profile equations

We study a droplet of a simple Newtonian fluid, of radius R(t) and central height  $h_0(t)$  on the surface of a rigid substrate, as illustrated in figure 3.1. In the following, cylindrical coordinates (r, z) will be used under the assumption of **axisymmetry** of the problem. The *z*-axis is thus the axis of symmetry and the radial coordinate is *r*.



Figure 3.1: Sketch of a fluid droplet spreading on a rigid substrate.

We define  $\gamma$ ,  $\rho$ ,  $\eta$ , the fluid surface tension, density, dynamic viscosity, respectively, and  $g = 9.81 \text{ m.s}^{-2}$  the acceleration of gravity. The expression of the equivalent spherical radius of the drop is

$$R_0 = \left(\frac{V_0}{\frac{4}{3}\pi}\right)^{1/3},\tag{3.1}$$

with  $V_0$  the constant drop volume (evaporation is overlooked). It provides the macroscopic length scale of the system. Unless otherwise specified, the drop volume is held constant,  $V_0 = 300 \,\mu\text{L}$  leading to  $R_0 = 4.2 \,\text{mm}$ . Physical properties of fluids of interest are gathered in table 3.1. They are all highly viscous, leading to significant simplifications in the flow equations to be introduced.

Fluid	PEG	Glycerol	Silicone oil V1000
<b>Surface tension</b> $\gamma$ (N.m ⁻¹ )	0.035	0.063	0.021
<b>Density</b> $\rho$ (kg.m ⁻³ )	1050	1260	997
<b>Dynamical viscosity</b> $\eta$ (Pa.s)	2.3	1.2	1.0
Capillary length $\ell_c$ (mm)	1.8	2.3	1.5

Table 3.1: Physical properties of the fluids used in this chapter.

#### 3.1.1 Equation of the drop profile

#### 3.1.1.1 General equation

The drop profile h(r, t) is governed by the dynamic spreading flow at any time. The velocity field  $\mathbf{v} = (v_r(t), v_{\theta}(t), v_z(t))$  follows the Navier-Stokes equations (Foias et al. 2001),

$$\rho \left[\partial_t \mathbf{v} + (\mathbf{v} \cdot \nabla) \mathbf{v}\right] = -\nabla P + \eta \Delta \mathbf{v} + \Sigma \mathbf{f}, \qquad (3.2)$$

with  $\nabla$  the gradient operator,  $\Delta = \nabla^2$  the Laplacian operator, *P* the fluid pressure and  $\Sigma \mathbf{f}$  the external volume forces. The left-hand side in (3.2) accounts for the flow inertia, while the right-hand side gathers flow pressure, viscous dissipation, and external forces. Inertia-related terms become negligible in the **Stokes regime**.

Stokes flow and Reynolds number

The flow in the experiments is considered to be in the **Stokes regime**. It is evidenced by the Reynolds number, computed across drop thickness,

$$Re = \frac{U\rho h_0}{\eta} \ll 1, \tag{3.3}$$

with U a typical velocity of the flow and  $h_0$  the typical drop thickness. This dimensionless number compares inertia with viscous dissipation in the flow.

For instance, in drop spreading experiments of  $300-\mu$ L viscous drops, the maximum speed is of  $U \approx 1 \text{ mm.s}^{-1}$  and the typical thickness,  $h_0$ , is of a few millimeters. In that case,  $Re \sim 10^{-3}$  corresponds to a Stokes flow regime using the values of  $\rho$  and  $\eta$  in table 3.1. Under this assumption, the Navier-Stokes equations along each coordinate now read,

$$0 = -\frac{\partial P}{\partial r} + \eta \left( \frac{\partial}{\partial r} \frac{1}{r} \frac{\partial r v_r}{\partial r} + \frac{1}{r^2} \frac{\partial^2 v_r}{\partial \theta^2} + \frac{\partial^2 v_r}{\partial z^2} - \frac{2}{r^2} \frac{\partial v_\theta}{\partial \theta} \right) + \Sigma f_r,$$
  

$$0 = -\frac{1}{r} \frac{\partial P}{\partial \theta} + \eta \left( \frac{\partial}{\partial r} \frac{1}{r} \frac{\partial r v_\theta}{\partial r} + \frac{1}{r^2} \frac{\partial^2 v_\theta}{\partial \theta^2} + \frac{\partial^2 v_\theta}{\partial z^2} + \frac{2}{r^2} \frac{\partial v_r}{\partial \theta} \right) + \Sigma f_\theta,$$
  

$$0 = -\frac{\partial P}{\partial z} + \eta \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_z}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 v_z}{\partial \theta^2} + \frac{\partial^2 v_z}{\partial z^2} \right) + \Sigma f_z.$$
  
(3.4)

Also, the velocity field must obey the continuity equation of an incompressible flow,

$$\nabla \cdot \mathbf{v} = \frac{1}{r} \frac{\partial r v_r}{\partial r} + \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{\partial v_z}{\partial z} = 0.$$
(3.5)

Rotational symmetry of the flow ensures  $\partial_{\theta}Q = 0$  for any physical quantity Q. Besides, as the drop spreads, we also rapidly meet a thin-film situation, i.e.  $h_0 \ll R$ . In that case, equations must obey the **lubrication approximation**, i.e.  $\partial_z Q \gg \partial_r Q$ . Since  $r \gg z$ , the continuity equation (3.5) yields  $v_z \ll v_r$  meaning that the flow is mainly radial. Also, its variations in the *r*-direction can be neglected compared to the vertical ones.

Owing to the previous simplifications and assuming that gravity is the only external force,  $\mathbf{f} = -\rho g \mathbf{e}_z$ , the set of equations required to describe the flow becomes (Hocking 1983):

$$\frac{\partial P}{\partial r} = \eta \frac{\partial^2 v_r}{\partial z^2},$$

$$\frac{\partial P}{\partial z} = -\rho g,$$

$$\frac{1}{r} \frac{\partial r v_r}{\partial r} + \frac{\partial v_z}{\partial z} = 0.$$
(3.6)

#### 3.1.1.2 Boundary conditions

At the free interface i.e. for z = h(r, t), the stress balance in the normal and tangential directions are respectively given by,

$$P(r, z = h, t) = P^{\text{ext}} - \gamma \left( \frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} \right) \bigg|_{z=h} \quad \text{and} \quad \left. \frac{\partial v_r}{\partial z} \right|_{z=h} = 0.$$
(3.7)

The first equality comes from the Laplace pressure drop, due to the liquid surface tension with  $P^{\text{ext}}$  the constant ambient pressure. The second condition comes from the very small air viscosity in

comparison with that of the liquid, leading to a vanishing tangential stress over the free surface. In addition, the kinematic condition relating the change of height with the flow field reads:

$$\frac{\partial h}{\partial t} + v_r|_{z=h} \frac{\partial h}{\partial r} = v_z|_{z=h}.$$
(3.8)

Eventually, the bottom solid surface imposes purely radial flow, and a tangential Navier slip (Navier 1823; Huh and Scriven 1971) is imposed at z = 0. These boundary conditions read respectively

$$v_z|_{z=0} = 0$$
 and  $v_r|_{z=0} = \lambda \frac{\partial v_r}{\partial z}\Big|_{z=0}$ , (3.9)

where  $\lambda$  is the slip length. Slip is further discussed in the following paragraphs.

#### 3.1.1.3 Drop profile equation

The first two equations of (3.6) lead to

$$P(r, z, t) = -\rho g z + \eta q(r, t) \quad \text{and} \quad \frac{\partial q}{\partial r} = \frac{\partial^2 v_r}{\partial z^2}, \tag{3.10}$$

with q a strain rate independent of the *z*-coordinate, which accounts for the effects of drop shape in the pressure field. The second equation can be integrated twice relatively to *z* using the vanishing tangential stress (3.7) and the slip condition (3.9) such that,

$$v_r(r, z, t) = \left(\frac{z^2}{2} - hz - h\lambda\right) \frac{\partial q}{\partial r}.$$
(3.11)

The third equation in (3.6) and the bottom boundary condition (3.9) lead to:

$$\upsilon_{z}(r, z, t) = \int_{0}^{z} -\frac{1}{r} \frac{\partial}{\partial r} \left[ r \left( \frac{z^{2}}{2} - hz - h\lambda \right) \frac{\partial q}{\partial r} \right] dz$$

$$= \left( \frac{-z^{3}}{6} + \frac{hz^{2}}{2} + \lambda hz \right) \left( \frac{\partial^{2} q}{\partial r^{2}} + \frac{1}{r} \frac{\partial q}{\partial r} \right) + \left( \frac{z^{2}}{2} + \lambda z \right) \frac{\partial h}{\partial r} \frac{\partial q}{\partial r}.$$
(3.12)

If one evaluates (3.11) at z = h,

$$\upsilon_r|_{z=h} = \left(\frac{-h^2}{2} - h\lambda\right) \frac{\partial q}{\partial r},\tag{3.13}$$

and doing the same with (3.12),

$$v_{z}|_{z=h} = \left(\frac{h^{3}}{3} + \lambda h^{2}\right) \left(\frac{\partial^{2}q}{\partial r^{2}} + \frac{1}{r}\frac{\partial q}{\partial r}\right) + \left(\frac{h^{2}}{2} + \lambda h\right)\frac{\partial h}{\partial r}\frac{\partial q}{\partial r},$$
(3.14)

these two relations can be injected in the free surface kinematic condition (3.8),

$$\frac{\partial h}{\partial t} = \left(\frac{h^3}{3} + \lambda h^2\right) \left(\frac{\partial^2 q}{\partial r^2} + \frac{1}{r}\frac{\partial q}{\partial r}\right) = \frac{1}{3r}\frac{\partial}{\partial r}\left(r\left(h^3 + 3\lambda h^2\right)\frac{\partial q}{\partial r}\right),\tag{3.15}$$

and the missing function q(r, t) can be determined using

$$P(r,h(r),t) = -\rho g h(r) + \eta q(r,t) = P^{ext} - \gamma \left( \frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} \right) \bigg|_{z=h}.$$
(3.16)

Spreading is also assumed to be **quasistatic**, meaning that the temporal variations of the flow are much smaller than the diffusion time of momentum. In other words, whenever a parameter is changed, the system immediately adjusts to the equilibrium state defined by the boundary conditions at that moment. In that case, the temporal derivative can be written  $\partial_t Q = U \partial_r Q$ , meaning that the variations of Q come purely from advection with fluid motion. As a result, when spreading a viscous liquid, the drop profile immediately adjusts to any change in velocity with no transient. The combination of (3.15), the differentiation of (3.16) with respect to r, and the quasistatic approximation lead to the differential equation for the drop profile (Hocking 1981; Hocking 1983).

Drop profile: general equations

$$3\eta U\frac{\partial h}{\partial r} + \frac{1}{r}\frac{\partial}{\partial r}\left[h^2\left(h+3\lambda\right)r\frac{\partial}{\partial r}\left(\gamma\left(\frac{\partial^2 h}{\partial r^2} + \frac{1}{r}\frac{\partial h}{\partial r}\right) - \rho gh\right)\right] = 0.$$
(3.17)

This differential equation is solved using volume conservation, vanishing height and microscopic contact angle,  $\theta_m$ , at the contact line, reading respectively

$$\int_{r=0}^{R} 2\pi r h(r,t) dr = V_0 \quad , \quad h|_{r \to R} = 0 \quad \text{and} \quad \left. \frac{\partial h}{\partial r} \right|_{r \to R} = \theta_m. \tag{3.18}$$

In 2D, the spreading in the *x*-direction obeys (Savva and Kalliadasis 2009; Savva and Kalliadasis 2012).

$$3\eta U \frac{\partial h}{\partial x} + \frac{\partial}{\partial x} \left[ h^2 \left( h + 3\lambda \right) \left( \gamma \frac{\partial^3 h}{\partial x^3} - \rho g \frac{\partial h}{\partial x} \right) \right] = 0$$
(3.19)

#### 3.1.2 Analysis of the equation

#### 3.1.2.1 Regions & length scales



Figure 3.2: Sketch of the regions near the moving contact line.

The equation (3.17) has **three intrinsic length scales**, which are displayed in figure 3.2. The smallest length scale,  $\lambda$ , is the microscopic slip length in (3.9) which circumvents viscous divergence at vanishing heights (Navier 1823). Note that for complex fluids (suspensions, emulsions, polymer melts,...) an additional particle slip coming from the microstructure can exist (Malkin and Patlazhan 2018). In the following,  $\lambda$  will only refer to the slip length of the pure fluid without the particles. The second typical length is the capillary length  $\ell_c \gg \lambda$ , which compares the effects of capillarity and gravity,

$$\ell_c = \left(\frac{\gamma}{\rho g}\right)^{1/2}.$$
(3.20)

This quantity appears in the last term of the equation when dividing (3.17) by  $\gamma$ . Above this length scale, gravity can not be overlooked in the shape of the interface. Finally, the third length scale  $R_0$  is the typical macroscopic size of the drop.

As aforementioned, only **large drops** are considered in this work. This criterion is relative to the capillary length  $\ell_c$  and can be expressed with the Bond number of the problem.

#### Large drops: Bond number

The condition  $R_0 > \ell_c$  can be written using the drop Bond number,

$$Bo = \frac{R_0^2}{\ell_c^2} = \frac{R_0^2 \gamma}{\rho g} > 1.$$
(3.21)

This dimensionless number compares the effects of capillarity and gravity.

Gravity does not play any role in a system of typical size  $R_0 < \ell_c$ . Such small drops have the shape of a spherical cap as sketched in figure 3.3(a). In the opposite case, when  $R_0 > \ell_c$ , drop forms a puddle with a wide flat region in the center due to gravity as shown in figure 3.3(b). For each of the fluids presented in the table 3.1,  $Bo \approx 5$  and the condition (3.21) is thus satisfied so that the effects of gravity are not negligible.



Figure 3.3: Sketch of (a) a spherical cap (small drops,  $Bo \ll 1$ ) and of (b) a puddle (large drops,  $Bo \gg 1$ ).

While the capillary length is inherent to the fluid, the microscopic and the macroscopic size depends on the problem studied. Interestingly, these three lengths are here very distinct  $R_0 \gg \ell_c \gg \lambda$  and characterize different regions of the drop. With this separation of scales sketched in figure 3.2, these regions governed by different contributions can be treated separately as explained in the following paragraphs. While capillarity and viscosity dominate near the contact line, at very small drop thickness (see § 3.1.2.2), viscous effects become negligible at larger drop heights and is replaced by gravity (see § 3.1.2.3). In between, the three contributions, namely viscous, capillary, and gravity forces must be accounted for, as explained in § 3.1.2.4.

Such scale separation justifies the strategies commonly used to tackle the resolution of the drop profile. Analytical solution of the dynamical profile (3.17) then often treat separately the vicinity of the contact line, referred to as the *inner region* in literature, and the rest of the drop. This region is asymptotically matched to the *outer solution* via an *intermediate matching region* (Trevino et al. 1998; Bonn et al. 2009; Savva and Kalliadasis 2009; Savva and Kalliadasis 2012). The drop profile in the inner region can be solved with first or second-order expansions in the capillary number  $Ca = U\eta/\gamma$  (Hocking 1983; Cox 1986). With this method, the dynamical behavior is treated as a perturbation of the static shape of the drop and mainly modifies the inner and the intermediate matching region. These analytical solutions can be compared with the full numerical solution and show high robustness at any scale (Savva and Kalliadasis 2009; Savva and Kalliadasis 2012). In addition, the comparison of the different Ca-expansions with the full numerical solution suggests that the need for an intermediate matching region disappears when increasing the expansion order (Sibley et al. 2015). Another method uses quasi-self-similar solutions i.e. ensembles of self-similar solutions parametrized by time-dependent quantities (Gratton et al. 1996).

In the following, we analyze the drop profile equation (3.17) in the three regions defined in figure 3.2. Here, our goal is not to redo the full resolution of the profile but rather to gain a better understanding of the underlying physics.

#### 3.1.2.2 Viscous-capillary region, $x \gtrsim \lambda$

In the viscous-capillary region, gravity can be neglected. This microscopic region corresponds to the neighborhood of the contact line, at a typical distance of  $\lambda \ll$ lc. see figure 3.4. Near the contact line, the fluid undergoes significant shear due to the small drop thickness. The viscous dissipation does not diverge because of a microscopic cutoff,  $\lambda$  which encompasses all the phenomena at smaller lengths. It is sometimes interpreted as an effective slip length (Navier 1823) and is crucial to recover realistic flows (Huh and Scriven 1971; Dussan and Davis 1974).



Figure 3.4: Sketch of the profile shape in the viscouscapillary region near the contact line,  $x \sim \lambda$ .

Other models describe the contact line dynamics, for instance with a precursor film (De Gennes 1985), that have been observed experimentally (Ausserré et al. 1986; Kavehpour et al. 2003). Also the Molecular Kinetic Theory based on hopping diffusion of the molecules near the edge (Blake and Haynes 1969; Blake and De Coninck 2002; Blake 2006) or height-dependent interfacial tension (Pahlavan et al. 2015) help circumventing the viscous stress divergence at the contact line. The reality of liquid slip near a solid wall is beyond the scope of this work but it is worth mentioning that liquid slip lengths have been measured experimentally and range from 1 to a few hundred nanometers for continuous fluids (Neto et al. 2005; Lauga et al. 2007). In this work, the Navier liquid-slip model is conveniently used to encompass all the microscopic details in the very close vicinity of the contact line. With suspensions, one can reasonably assume that the contact-line slip length  $\lambda$  remains constant. Adding micron-sized particles indeed unlikely affects  $\lambda$  considering the very different length scales,  $\lambda \ll d$ .

#### Viscous-capillary region: Governing equations

Near the contact line, capillary and viscous forces rule the quasistatic drop profile according to

$$3Ca\frac{\partial h}{\partial r} + \frac{1}{r}\frac{\partial}{\partial r}\left[h^2\left(h+3\lambda\right)r\frac{\partial}{\partial r}\left(\frac{\partial^2 h}{\partial r^2} + \frac{1}{r}\frac{\partial h}{\partial r}\right)\right] = 0.$$
(3.22)

In the previous equation,

$$Ca = \frac{\eta U}{\gamma} \ll 1, \tag{3.23}$$

is the **capillary number** associated with the contact-line motion. This dimensionless number can be interpreted as a normalized velocity, with  $\gamma/\eta$  a viscous-capillary speed characteristic of the interface. In this region, the solution of (3.22) must satisfy the boundary conditions,

$$\theta(x = \lambda) = \theta_m \quad \text{and} \quad h(x = \lambda) = h_m,$$
 (3.24)

with  $\theta_m$  the microscopic contact angle near the contact line and  $h_m$  a microscopic cutoff length scale of similar magnitude than  $\lambda$ .

The microscopic contact angle  $\theta_m$  is set by forces acting at molecular scales. It should be the same for an advancing or a receding contact line and it is often assumed to lie near the static contact angle

value,  $\theta_e$  (Cox 1986). Some models predict a spreading-velocity correction for  $\theta_m$  (Voinov 1976; Cox 1986; Bonn et al. 2009). In the following,  $\theta_m$  is assumed to be constant or at least small enough such that  $|\theta_m^3| \ll |Ca|$ . This assumption is valid for (nearly) perfectly wetting liquids with small static contact angles.

For a drop of viscous liquid spreading in the air, a good approximation of the solution of (3.22) is given by the Cox-Voinov law for small capillary numbers.

#### **Cox-Voinov law**

In the viscous-capillary region, near the moving contact line, the shape of the interface obeys the Cox-Voinov relation (Voinov 1976; Cox 1986),

$$\theta_{app}^{3}(x) = \theta_{m}^{3} + 9Ca\log\left(\frac{x}{\lambda}\right), \qquad (3.25)$$

This relation gives the local slope at a distance x = R - r from the moving rim of the droplet. This law results from the balance of capillary and viscous forces, and thus involves the capillary number *Ca*. The relation holds for both advancing (*Ca* > 0) and receding (*Ca* < 0) contact lines and is valid for large slopes  $\theta \leq 3\pi/4$  (Voinov 1976; Snoeijer 2006).

One can immediately check the microscopic matching condition  $\theta(x = \lambda) = \theta_m$ . Also, the logarithm factor weakly depends on x for  $x \gg \lambda$ . The typical values reported in the literature lie around 10 and 15. Again, for (nearly) perfectly wetting liquids,  $|\theta_m|^3 \sim |\theta_e|^3 \ll |Ca \ln(x/\lambda)|$  and the apparent contact angle thus evolves as  $\theta_{app}(x) \simeq [9Ca \ln(x/\lambda)]^{1/3}$ .

The derivation of (3.25) in the general case of two viscous fluids is given by Cox (1986). When the surrounding fluid has a negligible viscosity (air for instance), the apparent contact angle near the contact line obeys

$$g\left(\theta_{app}\right) = g\left(\theta_{m}\right) + Ca\ln\left(\frac{x}{\lambda}\right) \quad \text{with} \quad g(\theta) = \int_{0}^{\theta} \frac{\alpha - \sin\alpha\cos\alpha}{2\sin\alpha} d\alpha.$$
 (3.26)

The approximation  $g(\theta) \approx \theta^3/9$  works well for  $\theta \leq 3\pi/4$  and establishes the Cox-Voinov law as written in (3.25). Using *h* as a variable instead of *x* leads to a similar relation, which is precisely the derivation made by Voinov (1976),

$$\theta_{app}^{3}(h) = \theta_{m}^{3} + 9Ca\log\left(\frac{h}{h_{m}}\right).$$
(3.27)

The logarithm factor is roughly the same in (3.25) or (3.27) for any point of the interface with coordinates (x, h(x)) since  $\lambda \sim h_m \ll x \sim h(x)$ . One can also check that at the microscopic cutoff length,  $\theta_{app}(h = h_m) = \theta_m$ .

Note at this point that the profile near an advancing contact line (Ca > 0) is convex. According to the equations (3.25) or (3.27), the slope increases with x (or h), as sketched in figure 3.4.

#### **3.1.2.3** Capillary-gravity region $x \sim R_0$

This region corresponds to the opposite limit, as r 0, or equiva- $\rightarrow$ lently as x $\rightarrow$   $R(t) \gtrsim R_0.$ In this region, the drop height,  $h(r, t) \sim$  $h_0 \sim 1 \text{ mm}$  is greater by orders of magnitude than the slip length  $\lambda \sim 1$  nm, which is thus neglected in (3.17). In addition, viscous forces become negligible as fluid thickness increases, and the time-derivative term in (3.17) can be dropped. In the end, the macroscopic shape of a spreading drop is similar to the static shape of a drop of equal volume  $V_0$  and contact radius R(t).



Figure 3.5: Sketch of the drop profile in the gravity-capillary region far from the contact line,  $x \gg \ell_c$ .

#### Capillary-gravity region: Governing equations

At the macroscopic scale, the shape of the drop is thus governed by a capillary-gravity balance,

$$\frac{\partial}{\partial r} \left[ h^3 r \frac{\partial}{\partial r} \left( \frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} - \frac{\rho g}{\gamma} h \right) \right] = 0, \qquad (3.28)$$

with vanishing height at the contact line and volume conservation, reading respectively,

$$h(r = R(t)) = 0$$
 and  $V_0 = \int_{\mathcal{V}} dV = \int_{r=0}^{R(t)} 2\pi r h(r, t) dr.$  (3.29)

The constant coming from a first integration of (3.28) is found to be zero using h(r = R) = 0. Therefore, after a second integration with respect to *r*,

$$\forall r, \quad h^3 r \frac{\partial}{\partial r} \left( \frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} - \frac{\rho g}{\gamma} h \right) = 0 \quad \Longrightarrow \quad \frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} - \frac{h}{\ell_c^2} = C, \tag{3.30}$$

where *C* is a constant left to determined and  $\ell_c$  is the capillary length introduced in (3.20). To obtain a non-dimensional form of this equation, we use  $R_0$  as the typical length, i.e.  $\tilde{r} := r/R_0$  and  $\tilde{h} := h/R_0$ , with the tilde used for dimensionless variables. The Bond number appears upon normalization, so that

$$\frac{\partial^2 \tilde{h}}{\partial \tilde{r}^2} + \frac{1}{\tilde{r}} \frac{\partial \tilde{h}}{\partial \tilde{r}} - \tilde{h}Bo = CR_0.$$
(3.31)

With  $X := \tilde{r}Bo^{1/2}$ , equation (3.31) gives in turn,

$$\frac{\partial^2 \hat{h}}{\partial X^2} + \frac{1}{X} \frac{\partial \hat{h}}{\partial X} - \tilde{h} = C \frac{R_0}{Bo}.$$
(3.32)

A solution of the homogeneous equation is the modified Bessel function of the first kind and 0 order with  $I_{\nu}$  the modified Bessel function of the first kind and  $\nu$ -th order ( $\nu \in \mathbb{R}$ ) defined as (Bowman 2012),

$$I_{\nu}(X) = \left(\frac{X^2}{2}\right)^{\nu} \sum_{k=0}^{\infty} \frac{X^{2k}}{4^k (k!)^2 \Gamma(\nu + k + 1)},$$
(3.33)

where  $\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt$  is the gamma function. With respect to the boundary conditions (3.29), the solution is then  $h(r) = K [I_0(R/\ell_c) - I_0(r/\ell_c)]$ . The factor *K* and consequently the constant  $C = -KI_0(R/\ell_c)Bo/R_0$  are set according to volume conservation,

$$V_{0} = \int_{r=0}^{R(t)} 2\pi r h(r) dr$$
  
=  $\int_{r=0}^{R(t)} 2\pi r K \left[ I_{0} \left( \frac{R(t)}{\ell_{c}} \right) - I_{0} \left( \frac{r}{\ell_{c}} \right) \right] dr$  (3.34)  
=  $2\pi K \left[ I_{0} \left( \frac{R(t)}{\ell_{c}} \right) \frac{R(t)^{2}}{2} - \int_{r=0}^{R(t)} r I_{0} \left( \frac{r}{\ell_{c}} \right) dr \right].$ 

The modified Bessel functions obey the recurrence relations,

$$\frac{2\nu}{x}I_{\nu}(x) = I_{\nu-1}(x) - I_{\nu+1}(x), \qquad (3.35)$$

$$2I_{\nu}(x)' = I_{\nu-1}(x) + I_{\nu+1}(x), \qquad (3.36)$$

so that  $(xI_1(x))' = xI_0(x)$ . If we define  $x := r/\ell_c$ , then

$$\int_{r=0}^{R(t)} r I_0\left(\frac{r}{\ell_c}\right) dr = \ell_c^2 \int_0^{R(t)/\ell_c} x I_0(x) dx$$
  
=  $\ell_c^2 [x I_1(x)]_0^{R(t)/\ell_c}$   
=  $R(t) \ell_c I_1\left(\frac{R(t)}{\ell_c}\right).$  (3.37)

With the previous result and the recurrence relation (3.35) for v = 1, we can simplify the equation (3.34) and use the result to compute the value of *K* (or *C*).

$$\begin{split} V_{0} &= 2\pi K \left[ I_{0} \left( \frac{R(t)}{\ell_{c}} \right) \frac{R(t)^{2}}{2} - R(t)\ell_{c}I_{1} \left( \frac{R(t)}{\ell_{c}} \right) \right] \\ &= \pi R(t)^{2} K \left[ I_{0} \left( \frac{R(t)}{\ell_{c}} \right) - 2 \frac{\ell_{c}}{R(t)}I_{1} \left( \frac{R(t)}{\ell_{c}} \right) \right] \\ &= \pi R(t)^{2} K I_{2} \left( \frac{R(t)}{\ell_{c}} \right). \end{split}$$
(3.38)

Capillary-gravity region: Shape of the drop

For a moderate to large Bond numbers,  $Bo \gtrsim 1$ , the macroscopic shape of a drop of volume  $V_0 = 4\pi R_0^3/3$  and of contact radius R(t) is given by

$$h(r) = \frac{V_0}{\pi R(t)^2 I_2\left(\frac{R(t)}{\ell_c}\right)} \left[ I_0\left(\frac{R(t)}{\ell_c}\right) - I_0\left(\frac{r}{\ell_c}\right) \right].$$
(3.39)

The thickness at the center,  $h_0$ , is thus related to the contact radius, R(t), according to

$$h_0 = \frac{V_0}{\pi R(t)^2 I_2\left(\frac{R(t)}{\ell_c}\right)} \left[ I_0\left(\frac{R(t)}{\ell_c}\right) - 1 \right]$$
(3.40)

Note that in this macroscopic region, the profile is concave, i.e. has a negative curvature (see figure 3.6). Also shown in figure 3.6, the solution (3.39) is very similar to that derived by Tanner (1979),

$$h(r,t) = h_0(t) \frac{\cosh\left(\frac{R(t)}{r_1}\right) - \cosh\left(\frac{r}{r_1}\right)}{\cosh\left(\frac{R(t)}{r_1}\right) - 1}, \quad \text{with} \quad r_1 = \sqrt{\frac{4}{3}}\ell_c, \tag{3.41}$$

with  $h_0$  such that  $V_0 = \int_0^R 2\pi r h(r) dr$ .



Figure 3.6: Solid lines: drop height in the capillary-gravity region according to (3.39) for different contact radius R(t). Drop volume  $V_0 = 300 \,\mu$ L, capillary length  $\ell_c = 1.8 \,\text{mm}$ . Dash-dotted lines: solution (3.41) coming from Tanner (1979). Dashed lines: exponential approximation coming from the 2D model (see below). Inset: local curvature along the profile.

In the 2D situation, i.e. during the spreading of a rivulet in the  $\pm x$ -direction, the differential equation ruling the large-scale drop profile simplifies in

$$\frac{\mathrm{d}h}{\mathrm{d}x} = -\frac{(h-h_0)}{\ell_c}.\tag{3.42}$$

This differential equation can be derived from the balance of the hydrostatic and capillary pressures,

$$\int_{0}^{h} \rho g(h_{0} - z) dz = \gamma_{SL} + \gamma \cos(\theta) - \gamma_{SG} \iff \rho g \left[ h_{0} h(x) - \frac{h(x)^{2}}{2} \right] = \gamma \left[ \cos(\theta) - \cos(\theta_{e}) \right]$$
(3.43)

where  $\theta_e$  is the equilibrium contact angle in the Young-Dupré law (Young 1805; Dupré 1869),  $\gamma_{SG} - \gamma_{SL} = \gamma \cos(\theta_e)$ . At the center of the drop,  $\theta(x = 0) = 0$  and  $h(x = 0) = h_0$  leading to

$$\cos\left(\theta_{e}\right) = 1 - \frac{1}{\ell_{c}^{2}} \frac{h_{0}^{2}}{2}.$$
(3.44)

Using the cosinus linearization,

$$\cos(\theta) \simeq \frac{\mathrm{d}x}{\sqrt{\mathrm{d}x^2 + \mathrm{d}h^2}} \simeq \frac{1}{\sqrt{1 + \left(\frac{\mathrm{d}h}{\mathrm{d}x}\right)^2}},\tag{3.45}$$

with the expression of  $\cos(\theta_e)$ , the pressure balance now reads

$$\frac{1}{\sqrt{1 + \left(\frac{dh}{dx}\right)^2}} = \left(1 - \frac{h_0^2}{2\ell_c^2}\right) + \frac{1}{\ell_c^2}\left(h_0h - \frac{h^2}{2}\right) = 1 - \frac{(h - h_0)^2}{2\ell_c^2},\tag{3.46}$$

leading to the differential equation

$$\frac{dh}{dx} = \sqrt{\left(1 - \frac{\left[h(x) - h_0\right]^2}{2\ell_c^2}\right)^{-2} - 1}.$$
(3.47)

For  $|h - h_0| \ll \ell_c$ , we recover the equation (3.42). The solution of this first order differential equation is an exponential function with a decreasing rate  $\ell_c^{-1}$ :  $h^{2D}(r) = K\left(1 - \exp\left(\frac{r-R}{\ell_c}\right)\right)$ . Again, the factor K can be computed with the volume conservation,

$$V_0 = \int_{r=0}^{R} 2\pi Kr \left( 1 - \exp\left(\frac{r-R}{\ell_c}\right) \right) dr \Longrightarrow K = \frac{V_0}{2\pi \left[\frac{R^2}{2} - R\ell_c + \ell_c^2 - \ell_c^2 \exp\left(\frac{-R}{\ell_c}\right)\right]},$$
(3.48)

leading to the profile equation,

$$h(r) = \frac{V_0}{2\pi \left[\frac{R^2}{2} - R\ell_c + \ell_c^2 - \ell_c^2 \exp\left(\frac{-R}{\ell_c}\right)\right]} \left[1 - \exp\left(\frac{r - R}{\ell_c}\right)\right].$$
 (3.49)

As shown in figure 3.6, the exponential solution coming from the 2D model is very similar to the 3D solution, especially when  $R \gg \ell_c$ .

#### 3.1.2.4 Viscous-capillary-gravity region

To obtain the shape of the interface in between the two previous regions, all the contributions must remain in (3.17). This intermediate region, sketched in figure 3.7, corresponds to the mesoscopic vicinity of the contact line where the static shape is affected by the flow. The typical horizontal length scale is much larger than  $\lambda$  but much smaller than  $R_0$ . The sole remaining length scale is thus the capillary length defined in (3.20). Using again the quasistatic approximation such that  $\partial_t h = U \partial_r h$  and the fact that  $r, h \gg \lambda$ , equation (3.17) becomes





We define the dimensionless variables as

$$\hat{r} := \frac{r}{\ell_c}, \quad \text{and} \quad \hat{h} := \frac{h}{h^\star},$$
(3.51)

where  $h^*$  is the (still unknown) relevant scale for the drop height in the vertical direction. The renormalizations in (3.50) finally yields

$$3Ca\frac{\partial\hat{h}}{\partial\hat{r}} + \left(\frac{h^{\star}}{\ell_{c}}\right)^{3}\frac{1}{\hat{r}}\frac{\partial}{\partial\hat{r}}\left[\hat{h}^{3}\hat{r}\frac{\partial}{\partial\hat{r}}\left(\frac{\partial^{2}\hat{h}}{\partial\hat{r}^{2}} + \frac{1}{\hat{r}}\frac{\partial\hat{h}}{\partial\hat{r}} - \hat{h}\right)\right] = 0.$$
(3.52)

To obtain a **self-similar solution**, the two terms in (3.52) need to be of the same order of magnitude, leading to a scaling law for  $h^*$ .

#### Scaling law for *h*^{*}

The characteristic vertical length scale in the viscous-capillary-gravity region is given by self-similar arguments and reads

$$h^{\star} = \ell_c C a^{1/3}. \tag{3.53}$$

This length scale displays the contributions of the three competing forces through  $\ell_c$  and Ca. It sets the transition height from the region where the drop shape is governed by the Cox-Voinov law to the region where gravity comes into play in the force balance. Equivalently,  $h^*$  is the typical range of viscous effects, the latter becoming negligible above. It can thus be seen as a **viscous cutoff length**. Interestingly,  $h^*$  also delineates the change in surface curvature from convex (viscous-capillary region) to concave (capillary-gravity region). It should then lie near the **inflection point** of the drop interface.

This idea of cross-over between different regions has been investigated experimentally for sliding drops by balancing viscosity and gravity contributions with PIV measurements (Snoeijer et al. 2005). The equation of the frontier, corresponding to  $h = h^*$  in our experiments, is not derived. In previous publications on spreading drops, e.g. (Redon et al. 1992), this length scale  $h^*$  appears but the interpretation in terms of viscous cutoff has never been mentioned nor investigated before the work presented in the Chapter 4. At best, it is introduced as the typical height of the quasistatic region (Brochard-Wyart et al. 1991).

#### 3.1.3 Motivations

The scaling (3.53) predicts a value of a few hundred microns with capillary numbers typically ranging from  $10^{-3}$  to  $3.10^{-2}$  during drop spreading and  $\ell_c \approx 2$  mm for any of the fluids in table 3.1. It thus seems to be a measurable quantity with an appropriate experiment. However, as mentionned earlier, the value and the prediction of the viscous cutoff near an advancing contact line has not been reported elsewhere and barely studied. It is yet an interesting quantity to gain a better understanding of dynamical wetting.

Measuring  $h^*$  or equivalently probing dissipation is not trivial but it could be made possible with a **tunable viscosity**. For instance, some fluids have an intrinsic length scale where dissipation mechanisms change abruptly. In the next chapter, we argue that granular suspensions can be used to that end. Interestingly, adding density-matched particles should not modify the drop behavior in the gravity driven-region but it definitively enhances dissipation in the regions the particle can reach. The interplay of  $h^*$  with this intrinsic particle length scale may result in non-trivial behaviors during the spreading of drops made of granular suspensions.

3.1

## 3.2 Global approach: Tanner's law

Equation 3.17 in the previous section rules the shape of the interface of a spreading drop. Focusing separately on different regions, we obtain local information regarding the shape of the drop but not really about the spreading itself, e.g. the outer radius as a function of time. Yet, this dynamic has to be hidden in this equation to access what we will refer to as the "macroscopic" or "global" spreading behavior. A simple analysis, based on volume conservation and scaling arguments is first presented. This result, referred to as Tanner's law in the literature, has been adapted to different situations and predicts how the drop radius depends on time. In particular, as explained in § 3.2.1, the dynamical behavior depends on the drop volume. Section § 3.2.2 presents experimental works found in the literature and compares their results with the theory. The connection between Tanner's law and previously established equations is addressed in § 3.2.3, § 3.2.4 and § 3.2.5.

#### 3.2.1 Tanner's law: Capillary & gravity driven spreading of drops

In his paper, Tanner (1979) derives the behavior of the apparent contact angle as a function of radius growth, and ends with a Cox-Voinov like relation, i.e.  $\theta_{app}^3 \propto \frac{\eta}{\gamma} \frac{dR}{dt} = Ca$ . In the present case, the measurement was specifically done at the interface inflection point. The experiments strongly suggest a power-law behavior of the apparent contact angle with a power  $\alpha$ . Based on self-similarity and volume conservation arguments, this behavior can be extended to other drop features presented in table 3.2. For instance, such considerations suggest a radius growth according to

$$R(t) \propto t^n, \tag{3.54}$$

with  $n = \alpha/3$ . These results are established assuming that the apparent contact angle and the drop volume can be written as  $\theta_{app} \propto h_0/R$  and  $V_0 \propto h_0 R^2 \propto \theta_{app} R^3$ , respectively. In the latter expressions,  $h_0$  is the drop thickness at its center. The values of  $\alpha$  (or n) in table 3.2 are explained in the following paragraph.

		Temporal evolution	$\alpha = 3/10$ ( <i>n</i> = 1/10)	$\alpha = 3/8$ $(n = 1/8)$
Drop volume	$V_0$	Constant	Constant	Constant
Apparent contact angle	$\theta_{app}$	$t^{-\alpha} = t^{-3n}$	$t^{-3/10}$	$t^{-3/8}$
Drop radius	R	$t^{\alpha/3} = t^n$	$t^{1/10}$	$t^{1/8}$
Drop height	$h_0$	$t^{-2\alpha/3} = t^{-2n}$	$t^{-1/5}$	$t^{-1/4}$
Radius growth rate	$U = \mathrm{d}R/\mathrm{d}t$	$t^{\alpha/3-1} = t^{n-1}$	$t^{-9/10}$	$t^{-7/8}$

Table 3.2: Temporal variations of the apparent contact angle and other variables inferred from volume conservation (Tanner 1979).

Dimensional analysis can predict the value of  $\alpha$  by balancing viscous dissipation with the force driving the spreading (Cazabat and Stuart 1986). In a spreading drop, vertical velocity gradients generate a tangential viscous stress  $\eta \partial_z v_x \sim \eta U/h_0$  in the *xy* plane, *x* being the spreading direction and *z* the vertical direction. By integrating over the *x*-direction, the viscous force per unit length in the *y*-direction scales as

$$F_{\eta} \sim R\left(\eta \frac{U}{h_0}\right),\tag{3.55}$$

since the typical length in the *x*-direction is *R* (Cazabat and Stuart 1986; Levinson et al. 1988). In the case of small drops (i.e.  $R < \ell_c$  or Bo < 1), gravity is negligible and the motion of the contact line is

driven by capillary forces. At small contact angles ( $\theta_{app} \ll 1$ ) and for a perfectly wetting liquid, the capillary force per unit length in the *y*-direction can be written as (De Gennes et al. 2004),

$$F_c = \gamma_{SG} - \gamma_{SL} - \gamma \cos \theta_{app} \simeq \frac{1}{2} \gamma \theta_{app}^2.$$
(3.56)

The balance of these two terms with the approximation  $\theta_{app} \simeq h_0/R$ , and  $U = \frac{dR}{dt}$  leads to

$$\underbrace{\eta \frac{R}{h_0} \frac{dR}{dt}}_{\text{Viscous stress}} \sim \underbrace{\gamma \left(\frac{h_0}{R}\right)^2}_{\text{Capillary pressure}} .$$
(3.57)

Using again the volume conservation  $h_0 \sim V_0/R^2$ , we end up with

$$R^9 \frac{\mathrm{d}R}{\mathrm{d}t} \sim \frac{\gamma}{\eta} V_0^3 \qquad \text{or} \qquad \frac{\eta}{\gamma} \frac{\mathrm{d}R}{\mathrm{d}t} \sim \theta_{app}^3,$$
 (3.58)

which are two equivalent forms of Tanner's law. This relation can be supplemented with a missing factor in the Cox-Voinov law (3.25).

Similar reasoning can be carried out with large drops, i.e. when the drop radius is greater than the capillary length  $\ell_c$ . In this case, the interface is mostly flat and the driving force is gravity. The pressure on a vertical column, per unit length in the *y*-direction, yields

$$F_g = \int_0^{h_0} \rho g(h_0 - z) dz = \frac{1}{2} \rho g h_0^2, \qquad (3.59)$$

that once balanced with viscous force (3.55) simplifies to

$$\underbrace{\eta \frac{R}{h_0} \frac{\mathrm{d}R}{\mathrm{d}t}}_{\text{Viscous stress}} \simeq \underbrace{\rho g h_0^2}_{\text{Gravity}} \implies R^7 \frac{\mathrm{d}R}{\mathrm{d}t} \sim \frac{\rho g}{\eta} V_0^3.$$
(3.60)

#### Scaling-laws of drop spreading: Tanner's laws

For small droplets ( $Bo \ll 1$ ), dimensional analysis (3.58) of the force balance predicts a radius growth according to

$$R(t) = k_c \left(\frac{\gamma V_0^3}{\eta} t\right)^{1/10}.$$
 (3.61)

In the other limit ( $Bo \gg 1$ ), (3.60) suggests

$$R(t) = k_g \left(\frac{\rho g V_0^3}{\eta} t\right)^{1/8}.$$
 (3.62)

Capillary effects still exist for large drops, especially at the beginning when the drop interface is curved. Laplace pressure gradients may then transiently prevail over gravity. In this case, radius growth can exhibit two stages, with a gravity regime following a capillary one (Cazabat and Stuart 1986). However, once the interface has flattened, gravity becomes the driving force of the drop spreading. The factors  $k_{c/g}$  in (3.61) and (3.62), respectively, are a priori different. In the literature, only a very few authors comment on these quantities. Also, for large drops, a final stage driven by intermolecular forces would exhibit a radius growth  $R \propto t^{1/7}$  (Lopez et al. 1976; Ehrhard and Davis 1991).
Article	Fluid	Viscosity	Volume	Bond number
Tanner (1979)	Silicone oil	1.08-13 Pa.s	0.8-3.5 μL	0.2-0.4
Cazabat and Stuart (1986)	Silicone oil	0.2-1 Pa.s	0.35-37.9 μL	0.1-2.0
Levinson et al. (1988)	Silicone oil	0.2-100 Pa.s	0.4-40 μL	0.1-2.1
Redon et al. (1992)	Silicone oil	11.78 Pa.s	58-276.4 μL	2.6-7.4

Table 3.3: Summary of experimental works on drop spreading.

#### 3.2.2 Experimental validations

Some experimental works dealing with drop spreading on smooth substrates are gathered in table 3.3. Silicone oils are used extensively to avoid evaporation and hygroscopic effects but also to vary the fluid viscosity at relatively constant density and surface tension. Experimental work in the capillary regime is much more abundant than in the gravity regime. Data from these publications have been extracted and gathered in a log-log plot in figure 3.8(a). From this graph, it appears that radius growth follows a power law. Fitting the various data sets with the equation  $R(t) = A(t - t_0)^n$ determines the parameters  $t_0$ , A, and n. The parameter  $t_0$  is not of much interest, unlike the factor A, which will be discussed in the next section. As for the exponent *n*, two groups emerge, divided into two subplots in figure 3.8(b,c) and shown in the inset in figure 3.9(a). Additional results from experiments with PEG and glycerol are used in figure 3.9. In figure 3.8(b) and in the inset in figure 3.9(a), for large Bond numbers, the best fit of n lies around 1/8. On the contrary, for the smallest Bond numbers, the fit yields a smallest exponent,  $n \approx 1/10$ , see figure 3.8(c) and the inset in figure 3.9(a). For increasing drop volume (from 1  $\mu$ L to 40  $\mu$ L) and with a highly viscous oil ( $\eta$  = 100 Pa.s), the slope of the log-log plot changes continuously from n = 1/10 to n = 1/8 (Levinson et al. 1988). Experiments with silicone oils thus confirm the theoretical predictions regarding drop spreading, and more specifically the transition from a capillary to a gravity-driven dynamics around Bo = 1.

The factor *A* also agrees well with the predictions of (3.61) and (3.62). In the main plot in figure 3.9(a), its value obtained by the same fitting process, is plotted as a function of the drop volume. For a given fluid, *A* increases with the drop volume and follows either a  $V_0^{3/10}$  or a  $V_0^{3/8}$  power law for small and large Bond numbers, respectively. In figure 3.9(b), volume, density, surface tension and viscosity effects are removed according to the spreading regime. Such normalization leads to the determination of  $k_c = A \left( \eta/(\gamma V_0^3) \right)^{1/10}$  for Bo < 1 and  $k_g = A \left( \eta/(\rho g V_0^3) \right)^{1/8}$  for Bo > 1. The inferred values collapse properly for the two regimes at  $k_c \approx 0.90$  and  $k_g \approx 0.62$  as shown in figure 3.9(b). In particular, the value of  $k_g$  obtained with different silicone oil agrees with that of the PEG measured experimentally,  $k_g = 0.61 \pm 0.02$  and that of glycerol  $k_g = 0.62 \pm 0.03$  for  $100 \ \mu L \le V_0 \le 3000 \ \mu L$ .

#### 3.2.3 From profile equations to Tanner's law

Tanner's law can be derived from the general equations of a spreading drop presented at the beginning of this chapter. In the following, we derive analytical expressions for h(r, t) and R(t) from these equations in the limit  $Bo \gg 1$  (Lopez et al. 1976).

#### 3.2.3.1 Flow fields

In § 3.1.1.1, flow equations for  $v_r$  and  $v_z$  were introduced to derive the drop profile h(r, t). The intermediate forms of  $v_r$  and  $v_z$ , (3.11) and (3.12), respectively, both depend on q(r, t), a function to be determined such that  $P(r, z, t) = -\rho g z + \eta q(r, t)$ . Using the conservation of the volume flux Q in



Figure 3.8: (a) Experimental radius growth for silicone oil drops of different volumes extracted from the publications gathered in table 3.3. (b) Normalized radius  $R/(\rho g V_0^3/\eta)^{1/8}$  of drops with large Bond numbers according to (3.62). (c) Normalized radius  $R/(\gamma V_0^3/\eta)^{1/8}$  of drops with small Bond numbers according to (3.61). For the publication of Tanner (1979), the volume is computed from the drop radius and contact angle of a spherical cap:  $V_0 = \frac{\pi}{2} R^2 h_0 \left(1 + \frac{3h_0^2}{2R^2}\right) = \frac{\pi R^3}{2} \frac{1-\cos(\theta)}{\sin(\theta)} \left(1 + \frac{3(1-\cos(\theta))^2}{2\sin(\theta)^2}\right)$  with  $\tan(\theta) = 2h_0 R/(R^2 - h_0^2)$ . The constants  $k_{c/g}$  gathered in the legend are computed using (3.61)/(3.62) from the value of A returned by the fitting  $R(t) = A(t - t_0)^n$ .

3.2

3

Chapter 3 : Theory of drop spreading 3.2 Global approach: Tanner's law



Figure 3.9: (a) Parameters returned by the fit of experimental results,  $R(t) = A(t-t_0)^n$  for drops of viscous fluids and different volumes. Main graph: factor A, inset: exponent n. Silicone oil: see legend in figure 3.8(a), PEG ( $\odot$ ) and glycerol ( $\Diamond$ ). (b) Factor  $k_{c/g}$  of Tanner's law as a function of the drop Bond number,  $Bo = (3V_0/4\pi)^{2/3}/\ell_c^2$ , computed according to the spreading regime, i.e.  $k_c = A \left( \eta/(\gamma V_0^3) \right)^{1/10}$  for Bo < 1 and  $k_g = A \left( \eta/(\rho g V_0^3) \right)^{1/8}$  for Bo > 1. Capillary regime:  $k_c \approx 0.90$  (pink dashed line), gravity regime:  $k_g \approx 0.62$  (turquoise dashed line).

the radial direction, for any r, we can determine the radial derivative of q,

$$Q = \left[U\frac{r}{R}\right]h(r,t) = \int_{0}^{h} v_{r}(r,z,t)dz = \int_{0}^{h} \left(\frac{z^{2}}{2} - h(r)z - h(r)\lambda\right)\frac{\partial q}{\partial r}dz,$$
  

$$\implies \frac{\partial q}{\partial r} = \frac{-U\frac{r}{R}}{\frac{h^{2}}{3} - \lambda h} \approx \frac{-3Ur}{Rh^{2}}.$$
(3.63)

This expression of  $\partial_r q$  leads to the flow field equations in the spreading drop,

$$v_r(r, z, t) \simeq \frac{3Ur}{2Rh^2} \left[ -z^2 + 2zh(r, t) \right]$$
  
$$v_z(r, z, t) \simeq \frac{Uz^2}{Rh^3} \left[ z \left( h - r \frac{\partial h}{\partial r} \right) + \frac{3}{2} \left( -2h^2 + rh \frac{\partial h}{\partial r} \right) \right]$$
(3.64)

Spreading of a rivulet (2D problem) - For a rivulet spreading in the x-direction,

$$Q = Uh(x, t) = \int_0^h v_x(x, z, t) dz \implies \frac{\partial q}{\partial x} \simeq \frac{-3U}{h^2}, \qquad (3.65)$$

and

$$\upsilon_{x}(x, z, t) \simeq \frac{3U}{2h^{2}} \left[ 2zh(x, t) - z^{2} \right]$$

$$\upsilon_{z}(x, z, t) \simeq \frac{z^{2}U}{h^{3}} \frac{\partial h}{\partial x} \left[ \frac{3}{2}h(x, t) - z \right].$$
(3.66)

The 3D flow fields are plotted in figure 3.10(a, b) at two different times. In the subplots (c,d) and (e,f), the mapping of the radial and vertical velocity fields, respectively, show that  $v_r > 0$  and  $v_z < 0$ . These mappings also confirm the apparent vanishing velocity along the solid substrate due to the negligible slip at the macroscopic scale ( $\lambda \ll R, h_0$ ). Figure 3.10 also illustrates the lubrication approximation, i.e.  $|v_r| \gg |v_z|$ .



Figure 3.10: Flow fields at two different times for a drop such that  $V_0 = 300 \ \mu$ L,  $\eta = 2.3$  Pa.s,  $\lambda = 1$  nm,  $\ell_c = 1.8$  mm. The relation between the radius *R* and the contact line speed *U* comes from Tanner's law. (a,b) Flow fields, arrow color corresponds to the norm of the velocity. (c,d) Mapping of the radial velocity  $v_r$ . (e,f) Mapping of the vertical velocity  $v_z$ .

3.2

#### 3.2.3.2 Derivation of Tanner's law

The momentum balance in the *r*-direction using the expression of  $v_r$  in (3.64) leads to,

$$\frac{\partial P}{\partial r} = \eta \frac{\partial^2 v_r}{\partial_z^2} = -\eta \frac{3Ur}{Rh^2}.$$
(3.67)

For very large drops,  $Bo \gg 1$ , capillary forces are neglected and fluid pressure is set by hydrostatics such that  $P(r, z, t) = P^{ext} + \rho g(h - z)$ . The momentum balance becomes (Brochard-Wyart et al. 1991)

$$-3\eta \frac{Ur}{Rh^2} = \rho g \frac{\partial h}{\partial r}.$$
(3.68)

To go further and obtain a relation between U(t), R(t) and h(r, t), Lopez et al. (1976) have sought a self-similar solution of the form,

$$h(r,t) = h_0(t)f(\tilde{r}) \quad \text{with} \quad \tilde{r} = \frac{r}{R}.$$
(3.69)

From variable separation in the momentum balance equation, we find that

$$-3\eta \frac{U(t)\tilde{r}}{\left(h_0(t)f(\tilde{r})\right)^2} = \frac{\rho g}{R} \frac{\partial h_0(t)f(\tilde{r})}{\partial \tilde{r}} \quad \Longleftrightarrow \quad -C = \frac{f^2}{\tilde{r}} \frac{\partial f}{\partial \tilde{r}} = -3\eta \frac{U(t)R}{\rho g h_0(t)^3}, \tag{3.70}$$

with *C* a positive constant (since  $\partial_{\tilde{r}} f < 0$ ). Using f(1) = 0 for r = R, the function f can therefore be written

$$f(\tilde{r}) = f\left(\frac{r}{R}\right) = \tilde{C}\left(1 - \left(\frac{r}{R}\right)^2\right)^{1/3},\tag{3.71}$$

with  $\tilde{C} = \left(\frac{3C}{2}\right)^{1/3}$ . If we take f such that  $h(r = 0, t) = h_0(t) \iff f(0) = 1$ , then  $C = \frac{2}{3}$  and  $f(u) = (1 - u^2)^{1/3}$ . The volume conservation imposes

$$V_{0} = \int_{r=0}^{R} 2\pi h r dr = \pi h_{0}(t) R^{2}(t) \int_{u=0}^{1} 2u f(u) du = \pi h_{0}(t) R^{2}(t) \left[ -\frac{3}{4} \left( 1 - u^{2} \right)^{4/3} \right]_{0}^{1} = \frac{3}{4} \pi h_{0}(t) R^{2}(t).$$
(3.72)

Finally, using  $C = \frac{2}{3}$  and the previous result in (3.70),

$$-\frac{2}{3} = -3\eta \frac{U(t)R}{\rho g \left(\frac{4}{3} \frac{V_0}{\pi R^2}\right)^3} \quad \iff \quad 8R^7 \frac{\mathrm{d}R}{\mathrm{d}t} = 8\frac{2 \cdot 4^3 \rho g V_0^3}{9 \cdot 3^3 \pi^3 \eta}.$$
 (3.73)

#### Self-similar solution of spreading in the gravity regime

With the initial condition R(t = 0) = 0, we recover Tanner's law, first derived thanks to a power balance (3.60). The full derivation gives a prediction of the value of the factor  $k_g$ ,

$$R(t) = k_g^{\text{theo}} \left(\frac{\rho g V_0^3 t}{\eta}\right)^{1/8} \quad \text{with} \quad k_g^{\text{theo}} = \left(\frac{2^{10}}{3^5 \pi^3}\right)^{1/8} \simeq 0.77, \tag{3.74}$$

and the corresponding height profile,

$$h(r,t) = \frac{4V_0}{3\pi R^2} \left(1 - \left(\frac{r}{R}\right)^2\right)^{1/3}.$$
(3.75)

3.2





Figure 3.11: Experiments with the PEG copolymer,  $V_0$ = 300 µL. (a) Thickness at the center of the drop  $h_0$  (from side-view movies), as a function of the drop radius *R* (from top-view movies). (b) Normalized volume  $V_0/(\pi R^2 h_0)$  as a function of normalized radius  $R/\ell_c$ . Theoretical predictions from Lopez et al. (1976) (grey dashed line), Hocking (1983) (grey dash-dotted line) and spherical cap (pink solid line).

The solution for a 2D situation, i.e. a rivulet spreading in the *x*-direction, is given in the publication of Lopez et al. (1976). The prediction for the value of the factor  $k_g$  is close to the experimental measurements displayed in figure 3.9(b). Also, the normalized volume  $V_0/\pi R^2 h_0$  plotted in figure 3.11(b), is much closer to the prediction of (3.75),  $V_0/\pi R^2 h_0 = 3/4$ , than to the spherical cap assumption,  $V_0/\pi R^2 h_0 = 1/2$  (Redon et al. 1992). However, the variations of the normalized volume as a function of *R* would indicate that the viscosity-gravity regime is not yet reached, as emphasized by Redon et al. (1992). Indeed, capillary forces would become negligible in comparison with viscosity and gravity for  $R \gtrsim 7$  cm (Brochard-Wyart et al. 1991). Such a radius is not reached in the present experiments, see figure 3.11(a). The quasistatic gravity-capillary model of (Hocking 1983) best fits the experimental data, see figure 3.11.

#### 3.2.4 Drop profile: Hocking, Tanner, and Lopez

In § 3.1.2.3, we have derived a quasistatic drop profile, far from the meniscus where the viscosity can be neglected for moderate Bond numbers, i.e. Bo = O(1) (Hocking 1983). In this region, the differential equation of drop height (3.17) simplifies into (3.28) to give the solution  $h^{(0)}(R, V_0)$  (3.39). The profile  $h^{(0)}$  can be interpreted as a *static* solution, since it results purely from the balance of gravity and capillary forces for a given radius and a given volume. It provides the drop profile for a vanishing contact line velocity and implicitly depends on time through R(t). Tanner (1979) found a similar solution (3.41) based on the same arguments.

In spreading, to account for the viscous term in (3.17), perturbations can be added to these static solutions via a *Ca* expansion  $h = h^{(0)} + Cah^{(1)} + ...$  with *Ca*  $\ll$  1 (Bonn et al. 2009). These perturbations are concentrated near the contact line (Hocking 1983) and obey the Cox-Voinov law (3.25). Slip is also added by these additional terms. By pushing the *Ca* expansion to further orders, one recovers the solution of (3.17) obtained by numerical integration (Sibley et al. 2015).

On the other hand, in § 3.2.3.2, the solution presented by Lopez et al. (1976) is built by seeking a self-similar solution from the gravity and viscosity balance and returns Tanner's law. The drop profile is a priori only valid for large Bond numbers (Lopez et al. 1976; Hocking 1983) but the pre-



Figure 3.12: Experiments with the PEG copolymer,  $V_0 = 300 \,\mu$ L. (a) Thickness at the center of the drop,  $h_0$ , from side-view movies, as a function of time (main) and drop radius, *R*, from top-view movies, as a function of time (inset). The red dashed line in the inset is the result of the fit by Tanner's law (3.62) and the blue dashed line in the main graph is the thickness predicted by (3.40). The large dots correspond to the experimental profiles plotted in the subplots (b, c) with solid lines. (b) Comparison with the drop shape established by Lopez et al. (1976) (dashed lines). (c) Comparison with the drop shape established by Hocking (1983) (dotted lines) and Tanner (1979) (dash-dotted lines).

diction of the radius growth interestingly works down to Bo = O(1), see figure 3.8. In the present experiments, for a drop volume  $V_0 = 300 \,\mu\text{L}$ , the best agreement regarding the drop shape is met with the solution (3.39) from Hocking (1983), see figure 3.12. The profile of Lopez et al. (1976) is particularly poor at predicting the shape near the edge.

#### 3.2.5 Connection with Cox-Voinov

In each of the aforementioned macroscopic profiles, either the viscosity or the capillary contributions have been neglected. However, these two ingredients are crucial near the edge, where the drop thickness vanishes and where the interface bends. Therefore, the macroscopic profile must be connected to a local solution that takes into account the relevant force balance, and consequently obeys the Cox-Voinov law (3.25) or (3.27). More specifically, for a given fluid at a given measurement height, the equation (3.27) imposes  $U \propto \theta_{app}^3$ .

Such a prediction is obtained by Tanner (1979) for small drops from dimensional analysis (see table 3.2 for  $\alpha = 3/10$ ). The agreement is expected since both Cox-Voinov's and Tanner's laws come from a viscous-capillary balance, at the local and macroscopic level, respectively, when  $Bo \ll 1$ .

Conversely, for large drops,  $Bo \gtrsim 1$ , gravity must be considered to establish the macroscopic profile. One can therefore question to what extent the drop shape does not conform to the Cox-Voinov law. The first obvious case is the self-similar shape derived from a pure viscosity-gravity balance (Lopez et al. 1976) and shown in figure 3.12(b). The slope of the profile (3.75) near the edge diverges for  $r \rightarrow R$ , and the contact angle is thus always  $\theta_{app} = \pi/2$ ,

$$\left|\frac{\mathrm{d}h}{\mathrm{d}r}\right| = \frac{4V_0}{3\pi R^2} \frac{2r}{3R^2} \frac{1}{\left(1 - \left(\frac{r}{R}\right)^2\right)^{2/3}} \xrightarrow[r \to R]{} +\infty.$$
(3.76)

It is therefore incompatible with the Cox-Voinov law. For the moderate Bond number solution (3.39)



Figure 3.13: Contact angle according to the different models. Drop volume  $V_0 = 300 \,\mu$ L, radii  $R = 8.8 \,\text{mm}$ , 11.7 mm, 15.6 mm, 20.8 mm and 27.7 mm (from navy blue to tangerine). (a,b) Local profile angle as a function of the normalized radial coordinate r/R for different drop radii according to the profile of (a) Lopez in (3.75) and (b) Hocking in (3.39). (c) Contact angle as a function of drop radius according to the profile of Hocking (dash-dotted line) and prediction of Cox-Voinov (3.78) (solid line). The large dots correspond to the profiles plotted in (b).

plotted in figure 3.12(c), the macroscopic contact angle behaves according to

$$\tan\left(\theta_{app}\right) = \left|\frac{\mathrm{d}h}{\mathrm{d}r}\right|_{r=R} = \frac{V_0}{\ell_c \pi R^2 I_2\left(\frac{R}{\ell_c}\right)} I_1\left(\frac{R}{\ell_c}\right). \tag{3.77}$$

with  $I'_0 = I_1$  from the relations (3.35) and (3.36) for v = 0. The local angle for a series of drop radii is plotted in figure 3.13(b). It confirms that the slope is finite near the edge of the drop and varies as it spreads. To compare the local prediction of Cox-Voinov  $\theta_{app}(U)$  with the prediction from the global shape  $\theta_{app}(R)$ , one needs a relation between  $U = \frac{dR}{dt}$  and R. Using Tanner's law (3.62) for large Bond numbers, i.e.  $R(t) = At^{1/8}$ , we obtain

$$U(t) = \frac{A}{8}t^{-7/8} = \frac{A^8}{8}R^{-7} \implies \theta_{app} = \left[9\frac{\eta A^8}{8\gamma}R^{-7}\ln\left(\frac{L_{macro}}{L_{micro}}\right)\right]^{1/3}.$$
 (3.78)

Experimentally,  $\ln\left(\frac{L_{macro}}{L_{micro}}\right) \approx 12$ . The comparison of the contact angle predicted by the quasistatic profile and Cox-Voinov law is displayed in figure 3.13(c). While not perfect, the agreement is satisfactory, considering the numerous hypotheses drawn to obtain this result. In any case, bulk flow is expected to alter the profile near the meniscus, which is governed by the Cox-Voinov law. This effect is seen for  $Bo \geq 1$  and increases with the capillary number (Reznik and Yarin 2002).

# 3.3 Summary and concluding remarks

In summary, for large drops,  $Bo \gg 1$ , drop spreading is driven by a competition between gravity and viscosity and radius growth should follow a power-law growth with an exponent n = 1/8. This exponent can be predicted by a force balance presented in § 3.2.1 or derived from the equations of hydrodynamics. By omitting the capillary contribution in the equations, this derivation presented in § 3.2.3, yields the exponent and a theoretical drop profile.

This exponent is very robust experimentally, down to relatively small drops, i.e.  $Bo \approx 1$ , as shown in § 3.2.2. However, the associated profile fails to capture the shape of the drop for these moderate values of Bond number, as demonstrated in § 3.2.4. Other profile solutions in this range of Bond numbers yield good results but do not predict the radius dynamics. These analytical profiles, together with the radius dynamics from Tanner's law, recover experimental measurements of the radius dynamics and the dynamic drop profile.

In particular, there is a qualitatively good agreement between the dynamic contact angle at the macroscopic scale and the Cox-Voinov law introduced in § 3.1.2.2. This law is not specific to drop spreading and describes the contact angle dynamics of any dynamic contact line (Marsh, Garoff, et al. 1993). The study of contact angle dynamics is therefore a more *universal* problem and will be the subject of Chapter 4. In this chapter, we will examine the effect of the addition of solid particles on dynamic wetting at a local scale, near the contact line. Then, in Chapter 5, we will zoom out to see if the conclusions drawn on the local scale extend to the overall dynamics of drop spreading.

# 4

# Drop spreading of granular suspensions: dynamic contact line

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In this chapter, we investigate the results presented in the previous chapter at a mesoscopic scale, in the vicinity of the contact line. The first section describes in detail the experimental methods and the numerical image analysis developed to extract the drop profile. The second section presents experimental results with regular fluids to investigate the dissipation length  $h^*$  predicted in § 3.1.2.4. These reflections are further enriched in the third section with the addition of particles in the fluid. The text in this chapter is an adaptation of a paper in the Journal of Fluid Mechanics (Pelosse et al. 2023), with additional results and analysis.

# 4.1 Methods: tracking the drop profile

The spreading of granular suspensions is studied following a simple reproducible protocol with the suspensions prepared according to the methods presented in § 2.2.3. The experimental apparatus and the automatic picture analysis are detailed in this section.

### 4.1.1 Experimental apparatus



Figure 4.1: Sketch of the experimental apparatus.

In this chapter, we keep the **drop volume constant**,  $V_0 = 300 \,\mu\text{L}$  (spherical radius  $R_0 = 4.15 \,\text{mm}$ ). As sketched in figure 4.1, a syringe pump pushes the fluid at a flow rate of 10 mL.min⁻¹. The drops are made out of a steel needle with an inner diameter of 4 mm. The lower end of the needle is 5 mm above the solid substrate, which is a silicon wafer (Si-Mat, total thickness variation < 1  $\mu$ m). The drops then gently touch the solid substrate, detach from the needle and spread over the wafer. Prior to an experiment, the wafer surface is cleaned with ethanol and ultrapure water and dried with clean-room wipes. Plasma cleaning does not alter the results or the quality of the data and was therefore considered an unnecessary precaution.

Side and top view series of pictures are captured with two synchronized monochrome cameras (Basler acA2440-35um, 2000×2448 pixels) on which 1:1 macro lenses are mounted (I2S visions, MC series). These optics have **no distortion and a high spatial resolution** (3.45  $\mu$ m/pixel). The camera frame rates are either 5 or 10 fps for the side view. Such time resolution is necessary at the beginning when the drop spreads quickly. Frame rates of 0.5 fps are enough for top views. Indeed, very little information can be extracted at the beginning of the spreading due to the steepness of the interface. On the contrary, interesting phenomena are observed with these top views at long times when the spreading slows down.

For a given suspension composition, the corresponding set of experiments is usually made of 10 runs, corresponding to 10 different spreading drops. To avoid any concentration gradient out of the tube/needle, the first 10 drops are released before the first acquisition (i.e. a total amount of ~ 3 ml). After performing these blank runs, the experiments are reproducible, indicating that the outgoing fluid is a homogeneous suspension at the desired volume fraction  $\phi$ . Temperature and humidity variations are monitored thanks to systematic viscosity measurements performed during the experiments using a capillary viscometer, see § 2.2.3.2.

#### 4.1.2 Side view analysis

With appropriate lighting and with a background covered with black papers, the drops captured by the side camera appear bright on a dark background, as seen in figure 4.2(a). The drop outlines shown in figure 4.2(b) are obtained with the sobel function of the skimage.filters package in Python. It is further thresholded to extract the contact line coordinates and the drop profile, h(x) (x = 0being the position of the contact line). As seen in figure 4.2(c), the drop profile is smoothed with a spline of degree 3, i. e. a piece-wise polynomial function. With these functions regular at zero, first, and second order of derivation, the profile slope and its curvature are continuous. The distance between knots (points where the spline is tied) is initially small for large slopes to ensure good spline adjustment. It is then increased to prevent meaningless oscillations at small slopes, when the drop flattens. The smoothed drop profile in plotted in figure 4.2(d). The dynamic contact angle,  $\theta_{app}$ , plotted in figure 4.2(d), is inferred from the derivative of the spline. The contact line velocity, U, is obtained by locating the triple contact line. Improper fits are discarded if necessary. The results are found to be similar to those obtained by adjusting manually a straight line to the air/liquid interface near the contact line in the range of  $30^{\circ} \leq \theta_{app} \leq 85^{\circ}$ . Once performed, the fitted profile can be differentiated once or twice at any point of the interface.

With this automatic surface detection and fitting process, only the position of the contact line and the spline coefficients have to be stored. Contrary to our first paper with hand-made measurements of contact angles (Zhao et al. 2020), it is easier to choose and set the measurement height, h, with this algorithm. This precaution regarding the measurement height of the contact angle is often overlooked in the literature. However, the contact angle depends on the measurement height/distance to the contact line, see figure 4.2(d).



Figure 4.2: Data extraction from a picture of a spreading drop. Reflection on the wafer helps to detect the advancing contact line. (a) Raw picture, the red rectangle corresponds to the region enlarged in panel (c). (b) Sobel filtering of the raw picture. (c) Enlargement of the vicinity of the contact line showing the fitted spline of the drop profile (orange curve) and the contact line (orange dot). (d) Results extracted from the spline fitting. Right axis: drop height, h(x) (orange line), as a function of the distance to the contact line, x. Left axis: contact angle (gray line) computed from the spline derivation according to  $\theta_{app}(x) = \tan^{-1}(\frac{dh}{dx})$ .

## 4.2 Dynamical wetting of continuous, Newtonian fluids

#### 4.2.1 Cox-Voinov law for regular fluids

Drop-spreading experiments with 3 regular viscous liquids (PEG, glycerol and silicone oil) have been performed. Thier properties are gathered in table 3.1. For a given fluid, the experiment is reproducible. Again, please note that viscosity variations are accounted for in the capillary number,  $Ca = \eta U/\gamma$ . The apparent contact angle  $\theta_{app}$  is measured at a drop height,  $h = 50 \mu m$ , and plotted as a function of the contact line speed U in figure 4.3(a). The choice of the measurement height is justified in the following.

In figure 4.3(b),  $\theta_{app}^3$  is plotted in log-log representation, as a function of the capillary number for the three fluids. They all obey the Cox-Voinov law (3.27) since  $\theta_{app}^3 \propto Ca$ . Yet, the collapse is not perfect and the relative offset of the 3 curves in the log-log plot may come from a variation of the factor  $\ln(h/h_m)$ . This factor depends on  $h_m$ , the vertical microscopic cut-off length that is related to the slip length  $\lambda$  which varies with the fluid (Neto et al. 2005; Lauga et al. 2007). In particular, for polar liquids, a higher dipole moment seems to be related to a lower slip length and therefore leads to a larger factor (Cho et al. 2004).

#### 4.2.2 Inflection point

In § 3.1.2.4, we have identified the length scale,  $h^*$ , that characterizes the height of the interface at the transition between the viscous-capillary regime governed by the Cox-Voinov relation (3.27) and the viscous-capillary-gravity regime where gravity starts to prevail and where an inflection point should exist. We start our experimental characterization of  $h^*$  by investigating the shape of the interface in the case of simple fluids. Inspired by the form of the Cox-Voinov law (3.27), we measure, for capillary numbers in the range  $0.0025 \le Ca \le 0.0125$ , how the cube of the angle between the interface and the horizontal,  $\theta^3_{app}$ , depends on the interface height, h, see figure 4.4(a).

The data come from the average over 7 experimental runs. We identify two regions. Starting from the contact line, for any capillary number,  $\theta_{app}^3$  is first independent of the height at which it is measured, see figure 4.4(a). A **plateau** can thus be defined for *h* ranging from 10 to almost 100 µm. Discussion of these results in the light of the Cox-Voinov law would lead us to expect that  $\theta_{app}^3$  is an increasing function of *h*. However, two experimental facts may prevent us from seeing this increase. First, an inflection point can be seen in some experiments, see for instance figure 4.2(d), but the process of averaging over several runs likely smears out the change of curvature. Second, the length scales that we can probe are at least three orders of magnitude larger than the nanometric cut-off scale,  $\lambda$ . We thus expect the logarithmic term to increase slowly with distance, leading to difficulties in distinguishing the shape of the interface from a straight line. Similar conclusions regarding the local slope near the contact line have been reached by (Rio 2005). It is worth mentioning that the plateau value increases with the capillary number as expected from the Cox-Voinov law (3.27). Away from the contact line, the angle decreases, suggesting a growing contribution of gravity to the force balance.

Comparison of the datasets is made easier if we normalize  $\theta_{app}^3(h)$  by its asymptotic value  $\theta_{app}^3(h \rightarrow 0)$  and h by the capillary length  $\ell_c$ , see figure 4.4(b). From these plots, we define the experimental transition height  $h^*$  as the height at which  $\theta_{app}^3(h)$  departs from  $\theta_{app}^3(h \rightarrow 0)$  by 10 %. Figure 4.4(c) shows the inferred  $h^*$  as a function of *Ca* for different simple fluids. Normalized transition heights,  $h^*/\ell_c$  plotted in figure 4.4(d), collapse for the different fluids and increase as  $Ca^{1/3}$ , in agreement with the prediction (3.53) of dimensional analysis in § 3.1.2.4. We also report in this graph the measurements of the inflection point of the interface obtained by Tanner (1986), although the present interpretation as an upper limit of dissipation was not mentioned in this work. These data agree well with the present estimates of  $h^*$  as well as with the  $Ca^{1/3}$  scaling in (3.53). Note that this scaling still



Figure 4.3: Spreading of 300-µL drops made of regular Newtonian fluids: PEG ( $\blacklozenge$  7 runs), silicone oil V1000 ( $\blacksquare$  7 runs), and glycerol ( $\blacktriangle$  6 runs). (a) Contact angle,  $\theta_{app}$ , as a function of the contact line speed, measurement height: 50 µm. (b)  $\theta_{app}^3/9$  as a function of the capillary number, *Ca*. The value of the factor  $\ln(h/h_m)$  is inferred from the equations of the straight lines.

holds when varying the threshold between 5 % and 15 % as shown in figure 4.5. The threshold of 10 % provides the best match with the measurements of Tanner (1986). If we grant  $h^*$  the interpretation of a viscous-capillary cut-off length and refer to figure 4.4(d), we can thus conclude that measuring contact angles at heights well below 100 µm warrants probing the region of the droplet where the apparent dynamic contact angle is not set by a balance between viscous dissipation and capillarity.

In the following, we define the apparent contact angle  $\theta_{app}$  as the **unequivocal inflection angle that we measure at**  $h = 50 \,\mu\text{m}$ . Most of the time, little care is given to the definition of where the contact angle is measured. The few cautious publications also measure it at the inflection point i.e. on the plateaus observed in figure 4.4(a,b) (Tanner 1986; Pahlavan et al. 2015).



Figure 4.4: (a) Cube of the contact angle,  $\theta_{app}^3$ , versus the measurement height, h, averaged over 7 experimental runs for 5 capillary numbers, Ca = 0.0025 ( $\diamond$ ), 0.005 ( $\circ$ ), 0.0075 ( $\diamond$ ), 0.01 ( $\Box$ ), 0.0125 ( $\nabla$ ), using a Newtonian fluid (PEG copolymer). (b) Normalized cube of the contact angle,  $\theta_{app}^3/\theta_{app}^3(h \to 0)$ , versus normalized height,  $h/\ell_c$ , with  $\ell_c = 1.82$  mm. Black dotted line: threshold for the plateau length at  $\theta^3(h^*) = 0.9\theta^3(h \to 0)$ . (c,d) Transition height,  $h^*$ , and normalized transition height,  $h^*/\ell_c$ , versus the capillary number, Ca, for 3 Newtonian fluids: PEG ( $\blacklozenge$ ), silicone oil V1000 ( $\blacksquare$ ,  $\rho = 970$  kg/m³,  $\gamma = 21$  mN/m,  $\eta = 1.0$  Pa.s,  $\ell_c = 1.46$  mm), and glycerol ( $\blacktriangle$ ,  $\rho = 1260$  kg/m³,  $\gamma = 63$  mN/m,  $\eta = 1.3$  Pa.s,  $\ell_c = 2.23$  mm). Inflection-point measurements ( $\bigstar$ ) of Tanner (1986) with highly viscous silicone oil. Black solid line:  $h^*/\ell_c = 0.3 Ca^{1/3}$ .

Chapter 4 : Dynamic contact line & suspensions 4.3 Granular suspensions: probing dissipation with particles



Figure 4.5: Effect of the threshold (from 5 % to 15 %) to measure  $h^*$  as shown in figure 4.4(b) for PEG experiments. A value of 10 % appears to be the best match to recover the inflection heights reported by Tanner (1986) with silicone oil.

## 4.3 Granular suspensions: probing dissipation with particles

#### 4.3.1 Cox-Voinov law

We now test the relevance of  $h^{\star}$  to the spreading of drops of granular suspensions. Because they are density-matched to the suspending fluid and do not modify surface tension, the particles are expected to modify only viscous dissipation and to leave gravitational and capillary effects unchanged. Figure 4.6(a) presents the variation of  $\theta_{app}^3$  with the measurement height, *h*, for monomodal granular suspensions of 10-µm particles and bimodal suspensions of 10-80 µm particles with  $\zeta_{10}$  = 50 %, at a constant capillary number  $Ca_0 = \eta_f U/\gamma_f$ , where subscript 0 in the capillary number emphasizes that it is computed using properties of the suspending fluid. The inset presents the corresponding normalized quantities,  $\theta_{app}^3/\theta_{app}^3(h \to 0)$  and  $h/\ell_c$ , respectively. Reference data for the pure suspending fluid at  $Ca_0$  are also provided for comparison in figure 4.6(a). The behavior of  $\theta_{app}^3(h)$  for the suspensions is similar to that seen for the reference fluid, see also figure 4.4(a,b). A plateau region is again observed close to the contact line, for 10  $\lesssim h \lesssim$  100 µm, while there is a decay at larger distances. Addition of particles leads to an increase in the plateau value of  $\theta_{app}^3$ , which depends on the particle mixture components. Provided measurements are undertaken within the plateau region at constant height across all experiments, we can obtain an unequivocal apparent contact angle, at a given capillary number. The dependence between these two quantities is then *a priori* interpretable in terms of the Cox-Voinov relation. Again, the measurement height is set at  $h = 50 \ \mu\text{m}$ . This chosen height seems a good compromise between smaller heights having large measurement noise and larger heights that might fall outside of the region where viscosity matters. Note that taking h in the range of 20 µm to 100 µm yields similar results for the apparent wetting viscosity that will be introduced below.

Figure 4.6(b) displays typical variations of  $\theta_{app}^3/9$  as a function of the capillary number of the suspending fluid,  $Ca_0$ . Data from different experimental runs are plotted for the same fluids (suspensions or reference fluid) as those used in figure 4.6(a). For a given fluid, the tight collapse of the



Figure 4.6: (a) Cube of the contact angle,  $\theta_{app}^3$ , versus the measurement height, h, for different fluids: pure suspending fluid ( $\blacktriangle$ ), 10-µm monomodal suspension ( $\blacksquare$ ), and 10-80 µm bimodal suspension at  $\zeta_{10} = 50 \%$  ( $\diamondsuit$ ), resulting from the analysis of 7, 8, and 10 drop-spreading runs, respectively, and at the same fluid capillary number  $Ca_0 = \eta_f U/\gamma_f = 0.0025$ . Inset: normalized cube of the contact angle,  $\theta_{app}^3/\theta_{app}^3(h \rightarrow 0)$ , versus normalized height,  $h/t_c$ . Blue dashed-dotted line: selected measurement height h = 50 µm. (b) Variation of  $\theta_{app}^3/9$  as a function of  $Ca_0$  performed at a height h = 50 µm for the different runs for spreading drops made of pure suspending fluid ( $\blacktriangle$ ), 10-µm monomodal suspension ( $\blacksquare$ ), and 10-80 µm bimodal suspensions at  $\zeta_{10} = 50 \%$  ( $\diamondsuit$ ). The different color shades represent different experiments. The dashed lines correspond to the average of the linear fits of data coming from each run and are used to infer the relative apparent viscosity,  $\eta_w$ .

different  $\theta_{app}^3(Ca_0)$  curves coming from the different runs bears witness to the good reproducibility of the experiments. All the datasets collapse on straight lines with unity slopes in log-log representation, i.e.  $\theta_{app}^3/9 \propto Ca_0$ . For each run, a linear fit is performed and the average (dashed) line for a given fluid is the average of the corresponding linear fits. Angles typically lie between 30° and 90°, the upper limit being set by the algorithm. Tracking is interrupted below 30° due to the failure of the Cox-Voinov law. Protrusions of the particles are observed at small contact angles and might be responsible for this discrepancy. At contact angles larger than 30°, the drop profile remains very smooth and does not exhibit any protrusion as shown for 80-µm particles in figure 4.7.

Data from the suspending fluid are in excellent agreement with the Cox-Voinov law (3.27) as mentioned in § 4.2.1. The logarithm factor for the PEG is found to be 11.9, in good agreement with values in the literature (Voinov 1976). It is important to note that measurements are undertaken at a constant height, h, within the plateau region and not at a constant x. However, since x and hare of the same order of magnitude and sufficiently large compared to  $\lambda$ , the logarithm factor is not varying significantly and can be considered constant.

For suspensions, data for  $\theta_{app}^3(Ca_0)$  in figure 4.6(b) equally collapse on a straight line with a slope of unity in the log-log representation (orange and blue dashed lines): the spreading of these materials still seemingly **follows a Cox-Voinov relation** (3.27). However, since the values of  $\theta_{app}^3$  in the plateau are changed by the addition of particles as shown in figure 4.6(a), the different  $\theta_{app}^3(Ca_0)$  lines are shifted with respect to each other in figure 4.6(b), in agreement with previous experiments (Zhao et al. 2020). Assuming that the logarithmic factor has the same order of magnitude for the pure suspending fluid and for suspensions (as we do not expect the particles to modify the mechanics at the nanometric scale), we can superimpose all curves and recover the Cox-Voinov law (3.27) for all liquids if we adjust the viscosity used in the capillary number,  $Ca = \eta U/\gamma$ , such that  $\eta = \eta_f \eta_w$  and where  $\eta_w$  is the relative apparent wetting viscosity of the suspensions. Again, the shift and



Figure 4.7: Enlargement of the contact line region for a dense-suspension drop made of 80-µm particles (drawn in white). The apparent contact angle indicated by the thin white lines is  $\theta_{app} = 30^{\circ}$ .

consequently the apparent wetting viscosity strongly depends on the particle mixture components. Here, we see that a suspension of 10- $\mu$ m particles has a larger apparent wetting viscosity than a 10-80- $\mu$ m bimodal suspension.

The behavior of the apparent viscosity,  $\eta_w$ , is examined in detail in the following, for suspensions consisting of different particle combinations.

#### 4.3.2 Monomodal suspensions

#### 4.3.2.1 Wetting viscosity of monomodal suspensions

The apparent wetting viscosity of monomodal suspensions,  $\eta_w$  is documented in our first publication (Zhao et al. 2020) for particle sizes ranging from 10 µm to 250 µm and particle volume fractions of 20 %, 30 %, and 40 %. I have performed again the experiments and the analysis for most of the sizes at  $\phi = 40$  % and additional data at  $\phi = 30$  % have been realized by Siham Alaoui during her 2-month internship. The value may differ slightly when comparing manual and automatic measurements but the conclusions are unchanged. Wetting viscosity for different measurement heights and particle sizes are plotted in figure 4.8. As mentioned in the previous paragraph, the choice of the measurement height does not affect too much the apparent contact angle  $\theta_{app}$ , provided it remains in the plateau region, for instance between 20 µm and 100 µm. The apparent wetting viscosity extracted from the  $\theta_{app}(Ca)$ -curves is therefore weakly affected by the choice of *h*, regardless of the particle size, as shown in figure 4.8.

For a given particle size d, the apparent wetting viscosity,  $\eta_w$ , increases with the solid loading of the suspension,  $\phi$ , as would the bulk viscosity. However, unlike the bulk viscosity, figure 4.8 highlights a strong particle size effect on this apparent wetting viscosity. As the particle size increases, the apparent wetting viscosity decreases sharply. For the largest particles, the apparent viscosity derived for the apparent contact angle is close to that of the pure fluid while the bulk one is ten time larger. Interestingly, the effect of particles appears for sizes smaller than 100 µm. It is interesting to notice that even with the smallest particles,  $\eta_w$  is smaller (by a factor of order 2) than the corresponding value of its bulk viscosity. Indeed, at  $\phi = 40\%$ , the suspension relative bulk viscosity



Figure 4.8: Effective relative wetting viscosity,  $\eta_w$ , inferred from the Cox-Voinov law for monomodal suspensions at two solid volume factions  $\phi = 30\%$  (open symbols) and  $\phi = 40\%$  (solid symbols) for three measurements heights of the contact angle, (a)  $h = 50 \mu m$ , (b)  $h = 20 \mu m$ , and (c)  $h = 100 \mu m$ .

lies around  $\eta_s \approx 10$ . This significant decrease is correlated with a region devoid of particles near the contact line, where particles are excluded due to their size as explained in the next paragraphs.

#### 4.3.2.2 Distance to the contact line

In figure 4.9(a,b,d,e), top-view pictures of the edge of monomodal drops are displayed. They reveal a region devoid of any particles in the immediate vicinity of the contact line, between the wafer (black region) and a particulate phase. All these pictures are taken for the same contact angle,  $\theta_{app} = 35^\circ$ , with suspensions made of different particle sizes from 10 µm to 80 µm at a constant solid volume fraction,  $\phi = 40\%$ . The extent of the pure-fluid region increases with the particle size and decreases with the contact angle according to the graph in subplot (c). Basic geometric considerations sketched in figure 4.10, predict a minimum approach distance of a particle in a wedge,

$$\frac{L}{d} = \frac{1}{2} \left( \frac{1}{\tan\left(\theta\right)} + \frac{1}{\sin\left(\theta\right)} - 1 \right),\tag{4.1}$$

where *L* is defined as the size of the pure fluid region, see figure 4.10. This prediction is plotted as a function of the apparent contact angle in the black solid line in figure 4.9(f). It sets the lower bound of the distance of approach for any particle size and appears to predict the distance of approach of the largest particles. Measurements at smaller  $\theta_{app}$  are available in Zhao et al. (2020) (dotted lines). In the following, every consideration is made for  $\theta_{app} \ge 35^{\circ}$  (gray dashed line). Top views reveal that a particle approaches the contact line the closer it can. The inability of the particles to approach the contact line implies that no additional dissipation takes place when the surface height is less than a particle diameter and that the extent of this region is roughly proportional to a particle diameter according to (4.1).



Figure 4.9: Distance of approach of particles for monomodal suspensions at  $\phi = 40$  %. Top view pictures for  $\theta_{app} = 35^{\circ}$ , for (a) 10-µm, (b) 20-µm, (d) 40-µm and (e) 80-µm particles. Picture widths: 250 µm. (c) Size of the pure fluid region *L*, for different particle sizes as a function of the apparent contact angle  $\theta_{app}$ . (f) Normalized size of the pure fluid region, *L*/*d*, for different particle sizes as a function of the apparent contact angle  $\theta_{app}$ . Black solid line: geometrical prediction (4.1), gray dashed line:  $\theta_{app} = 35^{\circ}$ . Dotted lines: data extracted from (Zhao et al. 2020).



Figure 4.10: Schematic of a particle with diameter *d* in a wedge. The minimum distance of approach, *L*, of the particle depends on the particle size and on the contact angle. The angle between the horizontal and the free surface is assumed to be the apparent contact angle  $\theta_{app}$ .

#### 4.3.3 Bimodal suspensions

In nature and in industry, monodisperse suspensions only represent a few exceptions. Bimodal suspensions can be seen as a first step towards polydisperse solid blends. Interestingly, a smart choice of particle sizes and relative fractions in a bidisperse system can partially mimic an equivalent polydisperse suspension (Pednekar et al. 2018).

Using the same method and analysis, the effective wetting viscosity of bimodal suspensions is measured. It is worth emphasizing again that the number of parameters goes from two parameters in the monomodal case ( $\phi$  and d), to four in the bimodal suspensions ( $\phi$ ,  $\zeta_{small}$ ,  $d_1$  and  $d_2$ ). To limit the number of experiments, we fix the total solid volume fraction to  $\phi = 40$  %, leaving nonetheless three parameters to explore. The different size blends used are 10-20 µm, 10-40 µm, 10-80 µm, 20-80 µm, 40-80 µm, 80-140 µm and 80-250 µm with different proportions of small particles, namely different  $\zeta_{small}$ . Therefore,  $\zeta = 0$  % and  $\zeta = 100$  % represent monomodal suspensions made of large and small particles, respectively.

In figure 4.11, top views of the vicinity of the contact line for the different bimodal suspensions are displayed when  $\theta_{app} = 35^{\circ}$ . We observe **strong size segregation, especially at large size ratios**, e.g.  $d_1 = 10 \ \mu\text{m}$  and  $d_2 = 80 \ \mu\text{m}$ . For a given set  $(d_1, d_2)$ , the distance to the contact line of a given particle size seems to depend poorly on  $\zeta_{small}$  contrary to its linear density. See for instance the 40- $\mu\text{m}$  particles with the 10- $\mu\text{m}$  particles at  $\zeta_{10} = 25$ , 75%. While the large particles look tightly packed at  $\zeta_{10} = 25\%$ , the packing looks very loose at  $\zeta_{10} = 75\%$ . However, this statement does not seem to hold for **small size ratios** when the large particles makes up most of the solid phase. In this case, both the large and the small particle **packings look quite loose and disordered**, e.g. 40-80  $\mu\text{m}$  particles at  $\zeta_{small} = 25\%$ . The solid phase organization for bimodal suspension is therefore complex and raises questions regarding dissipation in the vicinity of the contact line.

To this end, the effective wetting viscosity of bimodal suspensions has been been measured and is plotted in figure 4.12. The symbol colors are related to the particle size(s) and the *x*-axis corresponds to the small particle proportion in the bimodal suspension. Special cases are more thoroughly examined in the next paragraphs to gain a better understanding of this complex graph.

#### 4.3.4 Suspensions with particles having a large difference in size

We focus first on suspensions consisting of particles having a large difference in diameter,  $d_1 = 10 \,\mu\text{m}$ and  $d_2 = 80 \,\mu\text{m} (d_2/d_1 = 8)$ . Figure 4.13(a) shows that the relative wetting viscosity of these suspensions,  $\eta_w$ , increases with increasing fraction of the small particles,  $\zeta_{10}$ , with a steeper growth beyond  $\zeta_{10} \approx 50 \,\%$ . This behavior is in stark contrast with the  $\zeta_{10}$ -dependence of the relative bulk viscosity of the same mixtures shown in figure 2.22 and plotted again in the inset in figure 4.13(a). The relative bulk viscosity of the blends presents a minimum at  $\zeta_{10} = 35 \,\%$ , i.e. a mixture containing roughly a third of small particles. This minimum viscosity is 40 % smaller than the values obtained in the monomodal cases at  $\zeta_{10} = 0 \,\%$  and 100 % (consisting of monomodal suspensions of 80 and 10  $\mu$ m, respectively) but still larger than the wetting effective viscosity,  $\eta_w$ .

In figure 4.13(b), top-view pictures of the 10-80 µm bimodal suspensions near the moving contact line support the previous explanation about the origin of the discrepancy between the apparent viscosity from bulk rheology, and its counterpart extracted from the dynamics of spreading. The images are obtained for the same dynamic contact angle,  $\theta_{app} = 35$ °. As shown previously in the monomodal case in figure 4.9, the particles segregate according to their size and the distance to the contact line depends on their diameter. Again, this distance appears to be larger in the case of the 80-µm particles,  $\zeta_{10} = 0\%$  (leftmost picture), than in the 10-µm case,  $\zeta_{10} = 100\%$  (rightmost picture). For intermediate values of  $\zeta_{10}$ , the 10-µm particles are able to move in between the 80-µm particles. The particles closest to the contact line arrange in an orderly, crystalline structure. This ordering



Figure 4.11: Top-view pictures of the vicinity of the contact line for different bimodal suspensions,  $\theta_{app} = 35^{\circ}$ . A line corresponds to a given set of  $(d_1, d_2)$  and a column to a given proportion of small particles  $\zeta_{small}$ .



Figure 4.12: Effective wetting viscosity of bimodal suspensions at  $\phi = 40\%$  as a function of  $\zeta_{small}$ . One-color symbols correspond to the wetting viscosity of monomodal suspensions, plotted in figure 4.8 for  $h = 50 \mu m$ . Two-color symbols correspond to the wetting viscosity of bimodal suspensions, with corresponding colors compared to the monomodal case (see legend). Gray dashed line: pure-fluid case,  $\eta_w = 1$ .

is particularly marked for the 80-µm particles, seen on the left pictures of figure 4.13(b). The large 80-µm particles seem to be maintained at the same distance from the contact line as small 10-µm particles are added, i.e. as  $\zeta_{10}$  is increased, but their linear density decreases.

The real capillary number of all these experiments (using the effective viscosity of the suspension,  $Ca = \eta_w Ca_0$ ) lies around  $2 \cdot 10^{-3}$ , leading to  $h^* \sim 100 \,\mu\text{m}$  according to (3.53) and using the prefactor inferred from the figure 4.4(d), i.e.  $h^* \approx 0.3 \ell_c Ca^{1/3}$ . The discrepancy between the viscosity measured in the bulk and that estimated from spreading experiments recovers the results with monomodal suspensions. The **80-µm particles experience strong confinement in the viscous-capillary region** since  $h^* \sim d_2$ , and only a few of them can penetrate this region and poorly contribute to dissipation. In contrast,  $h^*$  is 10 times larger than the diameter of the 10-µm particles. Even if these small particles experience confinement close to the contact line, a significant part of the viscous-capillary region is filled with a dense phase of small particles akin to a suspension bulk. Thus, the contribution of the 10-µm particles, as reported in experiments with monomodal suspensions. In the case of the 80-µm particles, as reported in experiments with monomodal suspensions. In the case of the suspensions studied in this section, increasing the small particle fraction,  $\zeta_{10}$ , is expected to lead to a continuous increase in  $\eta_w$ , as observed in figure 4.13(a).

#### 4.3.5 Varying the size of the large particles

We now turn to bimodal suspensions consisting of 10-µm particles but with large particles of variable diameter (i.e.  $d_2 = 20, 40, 80 \,\mu$ m). Bimodal suspensions formulated this way should have a minimum bulk viscosity at  $\zeta_{small} = 25\%$  according to figure 2.22. Figure 4.14(a) shows that the apparent wetting viscosity of these suspensions is maximum in the monomodal case and decreases for bimodal suspensions as the large particle size increases, i.e. with increasing  $d_2/d_1$ . This result confirms that particles with a diameter much smaller than  $h^*$  increase the dissipation in the Cox-Voinov region. This trend is similar to that of the bulk viscosity,  $\eta_s$ , with increasing  $d_2/d_1$  for

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Figure 4.13: Experimental results for suspension blends with fixed  $d_1 = 10 \ \mu\text{m}$  and  $d_2 = 80 \ \mu\text{m}$  and varying  $\zeta_{10}$  at  $\phi = 0.4$ . (a) Relative wetting viscosity,  $\eta_w$ , as a function of the fraction of the small particles in the solid phase,  $\zeta_{10}$ . Inset: bulk viscosity,  $\eta_s$ , of the corresponding suspensions versus  $\zeta_{10}$ . The dotted lines are guides for the eyes. (b) Top-view pictures taken when  $\theta_{app} = 35^{\circ}$  at  $h = 50 \ \mu\text{m}$  for  $\zeta_{10} = 0$ , 25, 50, 75, and 100 % from left to right, respectively. Scale bar: 200  $\mu\text{m}$ .

 $\zeta_{small} = 25\%$ , see the inset figure 4.14(a). However, the magnitude of the size-ratio effect comes from two distinct physical origins. For example, the value of the apparent wetting viscosity,  $\eta_w$ , for  $d_2/d_1 = 8$  is close to that of the suspending fluid at small values of  $\zeta_{small}$  whereas the value of the bulk viscosity,  $\eta_s$ , is much larger. The decrease in the bulk viscosity comes from the size ratio affecting the maximum packing fraction  $\phi_c$  (larger for large  $d_2/d_1$ ), while the wetting viscosity reduction comes from confinement effects near the contact line as the dissipation is greater for particles that can efficiently reach the dissipation region near the contact line ( $d \ll h^*$ ). In the case of figure 4.14, the small particles are participating less in the dissipation as  $\zeta_{10}$  is small and the overall dissipation is mostly set by the large particles.

Figure 4.14(b) shows that the distance to the contact line of the large particles, *L*, increases with their diameter  $d_2$  for bimodal suspensions at  $\zeta_{small} = 25 \%$  (two-color symbols) as skected in figure 4.14(d). In addition, the distance to the contact line is not sensibly affected by the small particles and is therefore very close to the one of the large particles alone in monomodal suspensions at  $\phi = 40\%$  (one-color symbols). Again, this length follows the prediction of a geometrical model describing the minimal distance of approach of a particle in a wedge (4.1) (black dashed line). The relation (4.1) thus holds both in monomodal and bimodal using the diameter of the corresponding particles. In the monomodal case, it determines the size of the depleted region (Zhao et al. 2020).

Top-view pictures in figure 4.14(c) confirm the existence of size segregation at the contact line as already mentioned in § 4.3.4 and sketched in figure 4.14(d). The large particles form ordered rows behind the small particle region as already noted in § 4.3.4. However, it seems that the 10-µm particles do not go through the network formed by the 20-µm particles, see the second image in figure 4.14(c). We move to this aspect of suspension spreading in the following section with clearer visualizations with larger particles.

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Figure 4.14: Experimental results for 10-µm monomodal suspension and bimodal blends with  $d_1 = 10$  µm and varying  $d_2$  (= 20, 40, 80 µm) and  $\zeta_{10}$  at fixed  $\phi = 0.4$  (a) Relative wetting viscosity,  $\eta_w$ , as a function of  $\zeta_{10}$ . Inset: bulk viscosity,  $\eta_s$ , of the corresponding suspensions versus  $\zeta_{10}$ . The dashed lines are guides for the eyes. (b) Distance to the contact line of the large particles as a function of  $d_2$  in monomodal (one-color symbols) and bimodal (two-color symbols) suspensions with  $d_1 = 10$  µm and  $\zeta_{10} = 25\%$  at  $\theta_{app} = 35^\circ$ . The dashed line corresponds to the geometrical prediction (4.1). (c) Top-view pictures taken when  $\theta_{app} = 35^\circ$  at h = 50 µm for monomodal suspension of size 10 µm and bimodal suspensions with  $(d_1, \zeta_{10}) = (10 \text{ µm}, 25\%)$  and  $d_2 = 20$ , 40, 80 µm (from top to bottom, respectively). Scale bar: 200 µm. (d) Sketch of a horizontal slice near the contact line, increasing  $d_2$  from top to bottom.

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#### 4.3.6 Varying the size of the small particles

Figure 4.15(a,b) gathers the wetting viscosity,  $\eta_w$ , of the monomodal 80 µm suspension and bimodal blends having a fixed  $d_2 = 80$  µm and varying  $d_1$  and  $\zeta_{small}$ . When the solid phase mainly consists of small particles, i.e.  $\zeta_{small} = 75$  %, corresponding to subplot (a),  $\eta_w$  decreases with increasing  $d_1$ . This observation confirms again that the wetting viscosity is set by the possibility for particles having a diameter much smaller than  $h^*$  to approach close to the contact line. However, a continuous decrease of  $\eta_w$  with  $d_1$  is absent when  $\zeta_{small} = 25$  %, see subplot (b), i.e. when large particles constitute a significant portion of the solid blend. The same trend is observed for  $\zeta_{small} = 50$  %. The relative wetting viscosity,  $\eta_w$ , reaches a maximum around  $d_1/d_2 = 0.25$  but it otherwise shows low values, even lower than those obtained for the monomodal suspensions of 80-µm particles for  $d_1/d_2 = 0.5$  or  $d_1/d_2 = 0.125$ . In other words, for  $\zeta_{small} = 25 - 50$  %, the apparent wetting viscosity of the 10-80 µm and 40-80 µm blends are particularly low compared to that of the 20-80 µm and even to that of the monomodal 80-µm suspension.

Top views shown in figure 4.15(c,d) provide some clues about the behavior of the apparent wetting viscosity. At  $\zeta_{small} = 25\%$ , see subplot (d), for small values of  $d_1/d_2$  (two topmost pictures), small particles flow through the large particle network and get close to the contact line. In contrast, for  $d_1/d_2 = 0.5$  (pictures on the third row from the top), the presence of 40-µm particles disrupts the ordering of the 80-µm particles, compared to the other cases. A similar trend is observed for  $\zeta_{small}$  = 50 %. In contrast, for  $\zeta_{small}$  = 75 % and for any value of  $d_1$ , there is a large amount of ordered small particles, whatever their size, near the contact line in front of the large spheres, see subplot (c). Geometrical considerations can explain the effect observed for  $d_1/d_2 = 0.5$ . Two large particles with a radius  $R_2 = d_2/2$  sitting on the surface of a solid come to contact if the distance, l, between them goes to zero, see figure 4.16. A small particle of radius  $R_1$  can pass through the hole between the two particles and the solid surface if its radius is at most  $R_1 = R_2/4$ . Consequently, while the 10-µm and 20-µm particles can flow through the interstices created by the large 80 µm particles, the 40μm particles cannot. Instead, these particles induce defects in the 80-μm particle network, leading to the distortion of the large-particle matrix when the portion of small particles is not too large  $(\zeta_{small} \lesssim 50\%)$ . This loss of organization seems detrimental to the local dissipation according to the effective viscosity drop in figure 4.15(b). These geometrical considerations coupled with the wetting viscosity measurements suggest that the structure and therefore the local solid volume fraction near the contact line is a key element to explain the value of the wetting viscosity of granular suspensions.

However, the above geometrical arguments cannot explain the lower values of  $\eta_w$  for the 10-80 µm blends compared to those of the 20-80 µm blends for  $\zeta_{small} = 25\%$  in figure 4.15(b). Instead, this lessening effect may be attributed to bulk effects affecting the wetting viscosity. The inset of figure 4.15(b) indicates that the bulk viscosity is significantly smaller for the 10-80 µm blends than for the 20-80 µm blends for a given value of  $\zeta_{small}$ . Moreover, the bulk viscosity for  $\zeta_{small} = 25\%$  is lower than for  $\zeta_{small} = 75\%$  as it corresponds to the minimum bulk viscosity for bimodal blends, as seen in figure 2.22. Bulk effects are therefore evidenced in this specific example to affect the value of  $\eta_w$  and they actually happen to overcome size effects. It is worth noting that, in the monomodal case, the variation in wetting viscosity does not vary with particle size, as shown in figure 2.21. The case of fixed  $d_2$  and increasing  $d_1$  evidences **two competing effects: confinement effect** governing the particle ability to approach the contact line and the **variation of the bulk viscosity** with  $\zeta_{small}$  and  $d_1/d_2$ . In conclusion, for bimodal suspensions, a high wetting viscosity results from a complex compromise between a high fraction of small particles,  $\zeta_{small}$ , a large size ratio,  $d_2/d_1$ , and a high bulk viscosity,  $\eta_s$ , in addition to size effects already demonstrated.



Figure 4.15: Experimental results for suspension blends with  $d_2 = 80 \ \mu\text{m}$  and varying  $d_1$  (= 10, 20, 40 \ \mum) (a,b) Relative wetting viscosity,  $\eta_w$ , as a function of  $d_1$  for  $\zeta_{small} = 75\%$  (a) and  $\zeta_{small} = 25\%$  (b). The blue dashed lines indicate the viscosity value for the monomodal suspension consisting of the sole large particles of size 80 \mum. Inset: bulk viscosity of the corresponding suspensions. (c,d) Top-view pictures taken when  $\theta_{app} = 35^{\circ}$ at  $h = 50 \ \mu\text{m}$  for bimodal suspensions with  $d_2 = 80 \ \mu\text{m}$ ,  $\zeta_{small} = 75\%$  (c) and  $\zeta_{small} = 25\%$  (d). Small particle size is increasing from top to bottom ( $d_1 = 10, 20, 40 \ \mu\text{m}$  and monomodal suspension of size 80 \mum). Scale bars: 200 \mum.

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Figure 4.16: Sketch of two large particles separated by a small one on a solid plane.

## 4.4 Summary & discussion

The spreading of large drops onto a solid substrate is a rich and complex phenomenon by itself that has been mostly studied for regular Newtonian fluids, theoretically, experimentally or numerically. A limited number of works have focused on non-Newtonian fluids (shear-thinning, shear-thickening or viscoelastic fluids) and exhibit non-trivial spreading dynamics that require further attention (Liang et al. 2009). To the best of our knowledge, the spreading of granular suspensions has received little to no attention. Yet, adding particles affects the spreading dynamics in a non-trivial way as there exists a high degree of inhomogeneity in the particulate drop going from a random solid bulk phase far from the contact line ( $h \gg d$ ), to ordered dense monolayers when particles undergo confinement ( $h \gtrsim d$ ), and finally to a particle-depleted region in the very close vicinity of the contact line (h < d). Using granular suspensions nonetheless offers an interesting way to investigate dynamical wetting as one can take advantage of this complex particulate organization to **modify locally the dissipation near the contact line**.

Dimensional analysis of the equation governing the spreading of large drops ( $Bo \gtrsim 1$ ) shows that the profile of the liquid/gas interface between the droplet and the atmosphere is set by a **viscouscapillary balance** as long as its height is smaller than a length scale  $h^* \sim \ell_c C a^{1/3}$  beyond which the drop profile becomes also sensitive to gravity. This **scaling** has been **validated for both simple fluids and suspensions** and care was taken to perform measurements below this length scale (typically 50 µm) to ensure that gravity is negligible across the range of capillary numbers that we can probe. Drops of granular suspensions were then seen to follow the Cox-Voinov law relating the contact angle to the capillary number, in a similar way as that found for regular Newtonian fluids. However, the relative apparent viscosity,  $\eta_w$ , involved in the capillary number, differs from that of the bulk suspension,  $\eta_s$ .

In the present experiments, the typical magnitude of  $h^* \sim 100 \,\mu\text{m}$  lies in the size range of the non-Brownian particles used. Therefore, dissipation is affected by particles during the spreading when  $d \lesssim h^*$ , while the spreading dynamics is close to that of the pure fluid when  $d \gtrsim h^*$ , i.e. when particles cannot reach the viscous-capillary region as sketched in figure 4.17(a,b), respectively. These geometrical considerations help rationalize that the **relative wetting viscosity**,  $\eta_w$ , **depends on the particle size**, *d*, **unlike the relative bulk viscosity**,  $\eta_s$ , which only depends on particle volume fraction,  $\phi$ . The relative wetting viscosity,  $\eta_w$ , is found to be **maximum for the smallest particles** and decreases to values close to the suspending fluid viscosity for  $d \gtrsim 100 \,\mu\text{m}$  even though  $\eta_s$  is much larger than  $\eta_w \approx \eta_f$  for these dense suspensions ( $\phi = 0.4$ ), see figure 4 of Zhao et al. (2020). This size cut-off of the wetting viscosity is thus roughly of the order of  $h^*$ . This confirms that particles affect the wetting dynamics only if their size is small enough for them to reach the region dominated by viscosity.

It may seem surprising that the Cox-Voinov law applies to such a complex system. Indeed, the possibility for the particles to occupy the viscous-capillary region in the case of a spreading droplet evolves with time as  $h^* \propto Ca^{1/3} \propto U^{1/3}$  decreases with increasing time. However, in the present experiments, the variation of *Ca* over only one decade prevents a strong change in  $h^*$ . Performing measurements in a much lower *Ca*-range, while rather challenging, may reveal intriguing effects.

Predicting the value of the apparent wetting viscosity when  $d \leq h^*$  remains a difficult task. The value of the bulk viscosity,  $\eta_s$ , certainly affects the wetting viscosity,  $\eta_w$ . However, knowing whether this observation comes from long-range effects of the bulk phase far from the contact line is not easy. One must also keep in mind that  $\eta_s$  varies with  $\phi_c - \phi$  and strongly diverges as  $\phi \rightarrow \phi_c$ . For bimodal suspensions, a lower  $\eta_s$  is the signature of a higher  $\phi_c$  for the corresponding solid phase and therefore produces a lower  $\eta_w$ , as seen in the present experiments.

Another fundamental ingredient to consider in predicting  $\eta_w$  is the possibility for the particles to crystallize in the viscous region. For monomodal suspensions, a monolayer of several rows of or-

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Figure 4.17: Sketch of two situations during the spreading of a granular suspension. (a) Small particles,  $d < h^*$ , (b) large particles  $d \gtrsim h^*$ .

dered particles is always observed in the vicinity of the contact line. In the bimodal case, crystallization of the two population sizes can be hindered when the small particles cannot flow through largeparticle holes, leading to a significant diminution of the apparent wetting viscosity. The **structure of the particulate network near the contact line** therefore directly affects the drop spreading dynamics captured in  $\eta_w$ . It also explains that even for the smallest particles for which  $d < h^*$ , the wetting viscosity,  $\eta_w$ , cannot reach the bulk value,  $\eta_s$ , because of this ordered region which possesses a lower viscosity.

This **ordering** very likely comes from the **confinement of the particles near the contact line** combined with the pressure of the dense particulate phase farther out. Rheological measurements combined with direct visualization of dense colloidal suspensions ( $\phi = 0.52$ ) have clearly established the relation between a significant viscosity drop and moderate confinement, owing to the ordering of the particulate phase in sliding layers (Ramaswamy et al. 2017). Conversely, for much dilute granular suspensions ( $\phi \le 0.2$ ), rheological measurements have exhibited a monotonous increase in dissipation for gap sizes of ten diameters and less (Peyla and Verdier 2011). This apparent disagreement could be explained by the nature of the solid phase (colloidal/granular) or the dissipation mechanisms (friction/hydrodynamics) which depend on the solid volume fraction (Gallier, Lemaire, Peters, et al. 2014). Indeed, at low volume fraction, dissipation is mainly due to hydrodynamic interactions while frictional contacts dominate for dense suspensions and may crucially depend on the local solid structure (Guazzelli and Pouliquen 2018).

With confinement strengthening, complex behavior becomes even more apparent, e.g. viscosity minima when the gap thickness is commensurate with the particle diameters (Ramaswamy et al. 2017). Such oscillatory values of the viscosity as a function of the gap have been reported under high confinement and high shear in numerical simulation of dense granular suspensions (Fornari et al. 2016). In the present experiments, confinement effects may however be less easy to quantify for the following reasons. Confinement is changing over time as the drop spreads and the local fluid thickness varies with the radial position. Moreover, confinement is set by a solid surface and a free interface that can deform to relax high stress, contrary to solid boundaries in a rheometer and most of the simulations.

Finally, the present work may help to understand the spreading of suspensions that are closer to those used in industrial processes and have a wide range of particle sizes (e.g. from sub-micron to hundreds of microns in cement paste, see Bentz et al. 1999; Celik 2009).

# 5

# Macroscopic spreading of granular drops: Tanner's law and beyond

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In the previous chapter, we examined the drop shape in the region of the contact line at typical measurement heights of less than a hundred microns. The timescales considered were rather "short", typically 300 s.

As discussed in Chapter 3, spreading can also be studied on a global scale by tracking the radius growth over time , see § 3.2. I showed in § 3.2.5 that local and global approaches are connected for a simple continuous fluid. However, extending this property to granular suspensions is not straightforward. In this chapter, global dynamics i.e. the dynamics of the droplet radius, is investigated on much larger timescales, up to 100 000 s, to test the validity of theoretical predictions established for continuous fluids. In particular, we will study how radius evolution is affected by the addition of particles and compare the macroscopic dynamics with that of a regular fluid. We remind the reader that for Bond numbers greater than unity, drop spreading obeys Tanner's gravity-driven law,

$$R(t) = k_g \left(\frac{\rho g V_0^3}{\eta}\right) t^{1/8} \quad \text{for } Bo > 1.$$
(5.1)

# 5.1 Apparatus and methods

Preliminary experiments and testing of the apparatus were carried out with Maël Lebon, a 2-month trainee during the summer of 2022. Drop spreading on a smooth solid substrate is investigated with the apparatus sketched in figure 5.1. Radius growth is recorded with an Imaging Source monochrome camera DMK33UX174 (captor size 2.3 MP) mounted with a distortionless macro lens (reference VS-LLD30). The camera is typically 50 cm above the solid substrate. The spatial resolution is 45  $\mu$ m/pixel. A framerate of 1 s⁻¹ appears as a good compromise to capture the early dynamics of high-viscosity fluids and their long-time spreading dynamics. For some experiments, a synchronized side-view acquisition has been added to capture the drop profile, for instance in § 5.5. Drops are made either using a syringe pump connected to a large needle (inner diameter 3 mm) or manually with a spatula. The latter ensures better control of the solid concentration,  $\phi$ , of the drops of suspensions with the largest particles of 550  $\mu$ m. Drop volume variability is larger with this method. To tackle this issue, **every droplet is carefully weighted** at the end of the experiment with a scale readability of 10 mg i.e. a volume uncertainty smaller than 10  $\mu$ L.

Two kinds of solid substrate have been used: rectangular Microscope slides (Scientific Glass Laboratories Ltd) and circular fused silica substrates made by the French company neyco. In any case, the spreading liquid is in (quasi) total/complete wetting with an equilibrium contact angle close to zero. Anyway, the substrate wettability should not affect the spreading dynamics (Cazabat and Stuart 1986). On the contrary, its roughness is more critical and can lead to a significant slowing of the radius growth (Cazabat and Stuart 1986). Before an experiment, the substrate is cleaned thoroughly with deionized water and ethanol. It is additionally treated with a plasma cleaner (HARRICK PLASMA, PDC-002-CE) during at least 1 min. This last step does not change the early time dynamics studied in the previous chapter, but appears to be an efficient way to avoid pinning the contact line dynamics during longer experiments.



Figure 5.1: Sketch of the experimental apparatus to study radius evolution of a spreading drop.

# 5.2 Data analysis

#### 5.2.1 Drop radius detection

The droplet contact radius, i.e. the distance of the contact line to the center of the droplet, is measured with an automatic routine using the hough_circle function from the transform module of the skimage python package. The raw picture shown in figure 5.2(a) is first blurred over 3-5 pixels using a gaussian kernel (function gaussian from the filters module of skimage), see figure 5.2(b). This preliminary operation leads to better results. The canny function of the feature module then detects the edges, see figure 5.2(c). A circular Hough transform applied to the previous picture detects circles with a specified radius range. In figure 5.2(d), the best circle is plotted.

#### 5.2.2 Time offset, volume and viscosity variations

Tanner's law does not account for the radius evolution through the whole process of spreading, and up to two regimes may precede this Tanner's regime. Before Tanner's regime, drop radius grows as  $R \sim t^{1/2}$  whatever the wetting power of the liquid during an inertial stage (Winkels et al. 2012). Experiments indicate that the duration of this regime increases with the drop size and shortens with the drop viscosity (Biance et al. 2004). This inertial regime is anyhow extremely short, from 10 to 100 ms for millimetric glycerol or water drops, respectively. This regime would be preceded by a primary viscous stage with  $R \sim t$ , of increasing duration with the ambient fluid viscosity (Mitra and Mitra 2016). In any case, the final viscous Tanner's regime (5.1) is reached within a second.

However, the beginning of an experiment is ill-defined with the methods described in § 5.1. Indeed, when the fluid touches the substrate and starts spreading, it is still attached to the needle. Tanner's law is only expected once the drop has detached from the needle. The radius is thus not equal to zero at the beginning of free spreading. Depending on the fluid properties and on the volume, the drop is attached to the needle for a few seconds to one minute. For this reason, radius data are fitted with a parameterized function including a **time offset**  $t_0$  (Redon et al. 1992),

$$R(t, t_0, A) = A(t + t_0)^{1/8}$$
(5.2)

where *t* is the *real* experimental time and the factor should obey  $A = k_g \left(\rho g V_0^3 / \eta\right)^{1/8}$  according to (5.1), with  $k_g$  a constant independent of drop volume, density and viscosity. The fitted parameters  $t_0$  and *A* are estimated by the function curvefit of the scipy.optimize python module. This correction is necessary and efficient to remove the initial bending on raw data curves, see figure 5.3(a, b). Other publications have circumvented this ill-defined initial time with an initial radius, i.e.  $R(t, R_0, A) = R_0 + At^{1/8}$  (Saiseau et al. 2022). This method is not satisfying with our data, see figure 5.3(c). In addition to the bending coming from the initial spreading stage, one needs to account for **volume and viscosity variations**. To remove volume and viscosity effects, a normalized radius,

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$$R^* = R \left( \eta_f / V_0^3 \right)^{1/8}, \tag{5.3}$$

returns very good results and collapses all the experimental curves, see figure 5.3(d). The true drop volume,  $V_0$ , is computed from the mass of the drop and PEG viscosity,  $\eta_f$ , is measured by the means of a capillary viscometer during an experiment, see § 2.2.3.2. This **normalization nicely collapses all the drop volumes along a straight line with slope 1/8 in log-log representation** as evidenced in figure 5.3(d). Experiments with pure, continuous fluid thus confirm the validity of Tanner's law (5.1), regarding the time exponent and the expression of the factor  $A = k_g \left(\frac{\rho g V_0^3}{\eta}\right)^{1/8}$ .

**NB**: With small drops (*Bo* < 1), a transition from a viscous-capillary to a viscous-gravity regime is reported in the literature (Cazabat and Stuart 1986; Levinson et al. 1988). Such a change in power



Figure 5.2: Automatic drop detection of the position of the contact line. The raw picture (a) is blurred locally over 5 pxl (b). Edges (c) are detected using a Canny edge detector with a Gaussian width of 1 pxl. The Hough transform (d) then returns the best circle fitting the outer radius.



Figure 5.3: Experimental measurements of drop radii as a function of time with pure PEG. Target drop volumes: 100 µL ( $\odot$ ), 300 µL ( $\Box$ ), 1000 µL ( $\diamond$ ). (a) Raw data, solid and dashed lines show the slopes expected by Tanner's law in the gravity and capillary regime, respectively. Data corrected with (b) a time offset,  $t_0$ , or (c) a radius offset,  $R_0$ . (d) Data with the time offset correction and radius normalization to remove volume and viscosity variability,  $R^* = R(\eta_f/V_0^3 t)^{1/8}$ .
law is not seen in experiments with large drops (Levinson et al. 1988). In any case, this time offset only affects short time behavior and does not modify the long time dynamics which is undoubtly the result of a balance between gravity and viscosity with a power-law exponent of 1/8, as seen with raw data in figure 5.3(a).

# 5.3 Spreading of pure fluid

We investigate radius dynamics for droplet volumes  $V_0$ , ranging from 100 µL to 3000 µL (corresponding to 2.6 ≤  $Bo \le 24.8$ ) with the pure PEG copolymer. Raw measurements of R(t) are displayed in figure 5.4(a). We observe a gravity-driven spreading, with a final slope 1/8 for all volumes, in agreement with the condition  $R_0 \gg \ell_c$ , i.e. Bo >> 1. As explained in § 5.2.2, data scattering for a given target volume can come from volume and viscosity variations. To correct these effects, normalized radius curves are plotted in figure 5.4(b). Also, the initial bending is removed with a time offset (~ 10 s), see § 5.2.2. The prefactor A in (5.2) is determined from a fit of this law to the data. The resulting values are plotted in the inset of subplot (b) as a function of drop volume. Data collapse on a straight line with slope 3/8, in agreement with the expected volume dependency in (5.1). In the main graph, the collapse of 30 experiments is excellent and leads to a good precision of the experimental determination of the constant  $k_g = 0.61 \pm 0.02$ .

The correct exponent and the factor behavior of the experiments in comparison with (5.1), confirm the **robustness of Tanner's law** in the gravity-driven regime with our suspending fluid. We now present the results of the same experiments, carried out with drops of granular suspensions. Adding particles to the fluid raises numerous questions. In particular, does Tanner's law still hold for these highly discontinuous fluids? If so, looking back at the results obtained when studying the shape of the interface in the vicinity of the contact line, what is the effective viscosity at the global scale? As shown in the previous chapter, this quantity is nontrivial in a wedge. It depends on particle size and is much smaller than the bulk viscosity measured in a regular rheometer. In the next section, we examine at a global scale the drop spreading of granular suspensions.



Figure 5.4: Radius evolution of 30 drops made of pure fluid for volumes ranging from 100  $\mu$ L to 3000  $\mu$ L (see legend). (a) Raw measurements of radius over time. Black solid line has a slope 1/8. (b) Normalized radius,  $R^*$ , with a time offset  $t_0$ . Solid line: best fit of the whole data set,  $R^* = 1.94 (t + t_0)^{1/8}$ . Inset: factor A in (5.2) computed from curve fitting.

# 5.4 Tanner's law & granular suspensions

In all this section, we remain in the **dense regime**, i.e. bulk volume fraction  $\phi = 40\%$ , and restrict the study to three drop volumes,  $V_0 = 100 \mu$ L, 300  $\mu$ L and 1000  $\mu$ L corresponding to Bond numbers Bo = 2.6, 5.3 and 11.9, respectively.

#### 5.4.1 Radius evolution

Figure 5.5 shows normalized radii for suspensions made of PEG copolymer and polystyrene particles of diameters 20 µm, 40 µm, 80 µm, 140 µm, 250 µm and 550 µm in subplots (a, b, c, d, e, f), respectively. Experiments carried out with 10-µm particles exhibit odd behavior discussed in § 5.4.5.1. The three volumes correspond to different symbols, 100 µL ( $\odot$ ), 300 µL ( $\Box$ ) and 1000 µL ( $\Diamond$ ). Viscosity used in the normalization of *R* is that of the pure fluid,  $\eta_f$ . Indeed, at this point, we do not know what is the most relevant viscosity but this one has the advantage of removing temperature effects.

For a given particle size (i.e. in a given subplot), different volumes collapse well under normalization and behave as a power law of time with an **exponent 1/8 at early times**, in a similar manner than pure fluid in figure 5.4(b). Therefore, granular suspensions obey Tanner's law at early times with a radius growth  $R \sim t^{1/8}$ . This first Tanner-like regime is discussed in § 5.4.2. However, drops made of the **largest particles exhibit a change of behavior with a significant slowdown of spreading** in figure 5.5(e, f). This breakdown of Tanner's law is investigated in § 5.5.

#### 5.4.2 Effective viscosity of granular suspensions in the Tanner regime

At first, we focus on the beginning of spreading. In the main graphs in figure 5.5, normalized radii are plotted for granular drops as a function of time. Raw data are displayed in the insets. Black solid lines on each of these graphs indicate where pure fluid experiments lie according to the results presented in figure 5.4(b). Tanner's law thus looks compatible with granular suspensions as the curves are parallel with these lines with a slope 1/8 in log-log representation. However, it appears that the results for the drops made of suspension do not collapse with that of the pure fluid and are shifted below. We define the normalized factor,

$$A^{*} = \frac{A}{\left(\frac{V_{0}^{3}}{\eta_{f}}\right)^{1/8}},$$
(5.4)

related to the curve offset of  $R^*$  in log-log representation with A determined by fitting (5.2) to the data between 0 s and 200 s. The pure-fluid viscosity,  $\eta_f$ , and true drop volume,  $V_0$ , are used for this normalization, similarly to that of radius. This parameter  $A^*$  is plotted in the inset of figure 5.6 for drops of pure fluid (white symbols) and suspensions (colored symbols). For any particle size or drop volume, the value of this parameter in the presence of particles lies below that of the pure fluid,  $A_0^* \simeq 1.94$  (black solid line).

According to Tanner's law (5.1), the normalized factor  $A^*$  only depends on  $k_g$ , g and  $\rho$ . Considering that we are using density-matched suspensions,  $\rho$  is the same as that of the pure fluid. Also, the first two parameters are not affected by the addition of particles. To collapse all the data points, the only possibility is to replace the viscosity used for normalization,  $\eta_f$ , with an effective viscosity. To compare this effective viscosity with that of the bulk, we write the suspension viscosity in Tanner's law,  $\eta_f \times \eta_T (d, V_0)$ , where  $\eta_T$  depends a priori on drop volume and particle diameter. Smaller values of  $A^*$  in the inset in figure 5.6 indicate that the pure fluid viscosity is underestimating viscous dissipation in granular suspension, we should thus have  $\eta_T > 1$ . The effective relative viscosity of the suspension  $\eta_T$  is computed according to

$$A = k_g \left(\frac{\rho g V_0^3}{\eta_f \eta_T}\right)^{1/8} \quad \Longleftrightarrow \quad \eta_T = \left(\frac{k_g}{A}\right)^8 \left(\frac{\rho g V_0^3}{\eta_f}\right) = \left(\frac{A_0^*}{A}\right)^8 \left(\frac{V_0^3}{\eta_f}\right) = \left(\frac{A_0^*}{A^*}\right)^8. \tag{5.5}$$



Figure 5.5: Radius evolution for drops made of suspensions with different volumes, 100 µL, 300 µL and 1000 µL ( $\circ$ ,  $\Box$ ,  $\diamond$  symbols, respectively) and different particle sizes, 20 µm, 40 µm, 80 µm, 140 µm, 250 µm and 550 µm (subplots (a, b, c, d, e, f), respectively). Particles are made of polystyrene and are suspended in density-matched PEG copolymer. Main graphs: normalized radius *R*^{*} versus *t* + *t*₀, see § 5.2.2. Black solid lines: best fit of the data obtained with pure fluid drops, *R*^{*} = 1.94 (*t* + *t*₀)^{1/8}. Pink solid lines: prediction of Tanner's law with suspension bulk viscosity,  $\eta_s$ . Insets: raw measurements of radius versus time.



Figure 5.6: Main graph: relative effective viscosity,  $\eta_T$  in Tanner's law versus particle diameter, d, from (5.5) for drops of granular suspensions with different volumes (100 µL, 300 µL and 1000 µL), and particle sizes (from 20 µm to 550 µm). Red dashed line and pink rectangle: average and standard deviation of  $\eta_T$  over all the experiments. Grey solid line: corresponding bulk viscosity,  $\eta_s$  of the suspensions. Inset: Normalized factor  $A^* = A \left( \eta_f / V_0^3 \right)^{1/8}$  versus particle diameter d. Clear symbols correspond to experiments with pure PEG and the black solid line to the average value  $A_0^* \approx 1.94$ 

In figure 5.6, this effective viscosity of Tanner's law,  $\eta_T$ , is plotted for drops of different volumes and suspensions made with different particle sizes. It is always larger than one (black solid line), meaning that the presence of the particles increases dissipation in the flow. Yet, it is much smaller than the relative viscosity of the bulk  $\eta_s \approx 10$  for these dense monomodal suspensions (grey solid line). In figure 5.5, the prediction of Tanner's law using suspension bulk viscosity is plotted in pink solid lines. Experimental results irrefutably confirm that the effective viscosity is not that of the bulk. Interestingly, we find that  $\eta_T \approx 2.3 \pm 0.4$  (red solid line in the pink rectangle) regardless of drop volume and particle size in figure 5.5.

#### 5.4.3 Polydisperse suspensions

Two series of experiments with polydisperse suspensions have been carried out for drop volumes 100  $\mu$ L, 300  $\mu$ L and 1000  $\mu$ L. Particles are in polystyrene and are suspended in density-matched PEG copolymer. Four diameters are mixed to obtain a total solid volume fraction  $\phi = 40\%$ , with each diameter accounting for 10% of the total volume in each case. The first suspension is made of 10  $\mu$ m, 20  $\mu$ m, 40  $\mu$ m and 80  $\mu$ m particles and the corresponding results are plotted in figure 5.7(a). The second suspension is made of 20  $\mu$ m, 40  $\mu$ m, 80  $\mu$ m and 140  $\mu$ m particles and the corresponding results are plotted in figure 5.7(b).

In the first case, spreading stops above a critical radius for any drop volume, see figure 5.7(a). Such behavior is reminiscent of pure monomodal suspensions of 10- $\mu$ m particles, presented in figure 5.10 in § 5.4.5.1. In contrast, the spreading of the second polydisperse suspension is very similar to previous monomodal cases displayed in figure 5.5(a,b,c,d). The radius growth of this polydisperse suspension seemingly follows Tanner's law, and exhibits a 1/8 slope in figure 5.7(b).

Top views of the late stage of spreading for these polydisperse suspensions are provided in figure 5.8. In addition to the different drop radii, particle organization displays completely different structures. In subplot (a), the suspension made of 10  $\mu$ m, 20  $\mu$ m, 40  $\mu$ m and 80  $\mu$ m particles is split into two

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Figure 5.7: Drop spreading of polystyrene polydisperse suspensions made of (a) 10 µm, 20 µm, 40 µm and 80 µm particles and (b) 20 µm, 40 µm, 80 µm and 140 µm particles. Main graphs: normalized radius  $R^*$  versus  $t + t_0$ , see § 5.2.2. Black solid lines: best fit of the data obtained with pure fluid drops,  $R^* = 1.94 (t + t_0)^{1/8}$ . Insets: raw measurements of radius versus time.

regions, a pure fluid ring near the contact line and a relatively homogeneous suspension in the center of the drop. In subplot (b), a nice size segregation has developped behind the pure fluid region. An enlargement of the different rings is provided in subplot (c). The region identified by "40" should also contain 20- $\mu$ m particles and so on. At the moment, we don't really understand how the small 10- $\mu$ m particle can stop so abruptly the spreading, see § 5.4.5.1. Size segregation likely develops under confinement and is thus prevented in the first situation with a rather thick drop. This effect of the small particles only reveals at long times, typically after 1000 s and hopefully does not affect the previous results obtained with these particles.



Figure 5.8: Late stage of spreading of polymodal suspensions. Top views of a drops made of (a) 10 µm, 20 µm, 40 µm and 80 µm particles (b) 20 µm, 40 µm, 80 µm and 140 µm particles. Scale bar: 2 mm, total picture widths: 16.7 mm (c) Enlargement of the pink rectangle in subplot (b). Regions identified according to: wafer (W), pure fluid (F) and particle sizes in micrometers. Total picture width: 4.4 mm.

In the following, we exclude the polydisperse suspension with 10-µm particles and focus on the second polydisperse suspension. Despite the highly heterogeneous structure observed in figures 5.8(b,c), this suspension made of 20 µm, 40 µm, 80 µm and 140 µm particles spreads like a regular fluid and obeys Tanner's law, see figure 5.7(b). Analysis of spreading returns an effective viscosity  $\eta_T^{poly} = 1.8 \pm 0.3$ , i.e. a slightly smaller value than that of monomodal suspensions,  $\eta_T^{mono} = 2.3 \pm 0.4$ ,

see § 5.4.2. A first and hasty conclusion would therefore state that the decrease in wetting viscosity is larger by 20 % with a polydisperse suspension. However, before jumping to this conclusion, we remind the reader that for a given value of  $\phi$ , the bulk viscosity of a polymodal suspension is smaller than that of the monomodal system with the same fraction of solid. In table 5.1, bulk and effective wetting viscosity of monomodal and polymodal suspensions are gathered. On the last line, the ratio of the bulk and effective wetting viscosity is computed for the two systems and falls very close. The decrease in viscosity during spreading of monomodal and polymodal suspensions is very similar. It would be slightly larger for a monomodal suspension but further experiments are required to consolidate this result.

Suspension	Monomodal	Polymodal
Bulk viscosity $\eta_s$	10	6.7
Effective spreading viscosity $\eta_T$	2.3	1.8
<b>Ratio</b> $\eta_s/\eta_T$	4.3	3.7

Table 5.1: Bulk and effective wetting viscosity of monomodal and polymodal suspensions for  $\phi = 40\%$ .

#### 5.4.4 Discussion on the drop in viscosity

This effective Tanner viscosity  $\eta_T$  is thus relevant to describe the global dynamics of the drop. It differs from the effective wetting viscosity  $\eta_w$  extracted from the Cox-Voinov law in Chapter 4. Indeed,  $\eta_w$  decreases with increasing particle size, d, and reaches a value of one corresponding to the pure fluid for a particle cutoff size  $\approx 100 \,\mu\text{m}$ . Again, this cutoff is explained by the fact that the shape of the interface is not affected by dissipation above this typical height. The difference between  $\eta_w$  and  $\eta_T$  is not surprising as they account for two different energy balances at the local or global scale, i.e. from a balance of capillary and viscous forces or a balance between gravity and viscous forces, respectively.

Tanner's viscosity also happens to be **much smaller than the bulk viscosity of the suspension**. Indeed, for such monomodal granular suspensions, the relative bulk viscosity is  $\eta_s \approx 10$  for  $\phi = 40\%$ , irrespectively of particle size. Several mechanisms could account for this decrease in dissipation in comparison to the bulk case.

A first possibility is that a significant **slip** occurs next to the surface of the substrate, see figure 5.9(a). The creation of a pure-fluid lubrication film near the wall leads to smaller shear stress on the particulate phase. This effect yields an apparent smaller viscosity (Jana et al. 1995). In a rheometer, rough walls circumvent this issue by trapping the first layer of particles in the asperities of the surface. Of course, present experiments with an advancing contact line would be difficult to discuss on such a surface. Unavoidable wall slip could therefore account for a lesser dissipation compared to a bulk suspension.

Another difference may come from the suspension **microstructure** under confinement. In particular, **layering under confinement**, sketched in figure 5.9(b), can result in a significant decrease in the effective viscosity (Ramaswamy et al. 2017; Fornari et al. 2016). In dense suspensions, layering easily spans over 10 particle radii from a wall (Gallier, Lemaire, Lobry, et al. 2016). The size of the ordered region, i.e. the number of layers, increases sharply with solid volume fraction above  $\phi = 40\%$ and with increasing confinement. The high monodispersity of the particles we use is particularly prone to create such regular structures. To test the contribution of microstructure to this decrease in viscosity, experiments with polydisperse suspensions have been carried out. Polydispersity is an efficient manner to prevent layering and its consequence on suspension rheology as evidenced by the experiments of Ramaswamy et al. (2017). Yet, our experiments show that polydispersity hardly affects the dynamics of the radius, see § 5.4.3. This hypothesis is thus not relevant to fully account for the present observations.

Of course, the flow in a spreading drop is very different from a viscometric, pure-shear flow such as that in a rheometer. The shear component across drop thickness is supplemented with an extensional flow, in both the radial and the orthoradial directions, see figure 5.9(c). In a regular Newtonian fluid, the extensional viscosity in these flows is simply three times that of the shear viscosity measured in rotational rheometers for instance (Trouton 1906). The ratio of the extensional and shear viscosity, named after Trouton, can be different in non-Newtonian, complex fluids. For instance, the extensional viscosity, and consequently Trouton's ratio, of polymers increases drastically as polymer chains are stretched (Bach et al. 2003). Numerical simulation suggests that Trouton's ratio in granular suspensions would also increase for frictional particles near jamming, for  $\phi \gtrsim 54\%$ (Cheal and Ness 2018). However, granular suspensions should exhibit the same Trouton ratio, as that of a Newtonian fluid at lower volume fraction. This result is corroborated experimentally by the Newtonian behavior at the beginning of pinch-off with granular suspensions for instance (Bonnoit, Bertrand, et al. 2012) Interestingly, numerical simulation in an extensional



Figure 5.9: Possible mechanisms accounting for the decrease in viscosity during the spreading of a granular drop. (a) Wall slip, (b) layering and microstrucure, (c) non-Newtonian effects, or (d) concentration gradient due to shear-induced particle migration.

flow suggests that the Newtonian behavior would be preserved with granular suspensions made of frictionless particles (Cheal and Ness 2018). For this reason, frictionless particles could be used to test the effect of the extensional component of the flow during drop spreading of granular suspensions. Again, without additional pieces of evidence, the hypothesis of non-Newtonian behavior is not really satisfactory, and the suspensions presently used should behave like a regular Newtonian fluids at  $\phi = 40\%$ .

**Concentration gradients** in the flow could also explain the apparent decrease in viscosity. In addition to the variations induced by confinement, granular suspensions can also become heterogeneous under heterogeneous shear flow. Mappings of the work rate of viscous forces in the drop (not included in the manuscript) reveal that most of the dissipation and therefore **strong shear gradients are encountered near the contact line** in the bent region of drop profile. **Shear-induced particle migration** could then develop and **reduce locally solid concentration** in this region. For instance, in a Couette rheometer, the viscosity of a suspension made of 40-50 µm particles sheared at 24 s⁻¹ in a 2.5-mm gap, is divided by two (Gadala-Maria and Acrivos 1980). A lower concentration near the contact line compared to that initially prescribed could therefore account for the strong decrease in apparent viscosity. This hypothesis can not be dismissed nor confirmed for the moment

with top or side views only. To test this explanation, measurements of local concentration in the flow are required and could be obtained by X-ray tomography. Visualization of particle structure has been attempted and quickly resumed in the last section of this chapter. Unfortunately these observations are not good enough to provide definitive answers to our questions.

In conclusion, several mechanisms probably contribute to this drastic decrease in the spreading viscosity of granular drops, without any clear evidence of the dominant effect at this time. However, for any of the aforementioned mechanisms, particle size plays a role (in velocity slip, layering range, shear-induced flux ...). The selection of this viscosity, irrespectively of particle size is puzzling but robust and could have interesting applications to control the spreading process of viscous fluids.

#### 5.4.5 Additional data

#### 5.4.5.1 10-micron particles



Figure 5.10: Radius evolution of drops made of monomodal 10-µm suspensions with different volumes, 100 µL, 300 µL and 1000 µL ( $\circ$ ,  $\Box$ ,  $\diamond$  symbols, respectively). Particles are made of polystyrene and are suspended in density-matched PEG copolymer. Main graph: normalized radius *R*^{*} versus *t* + *t*₀, see § 5.2.2. Black solid lines: best fit of the data obtained with pure fluid drops, *R*^{*} = 1.94 (*t* + *t*₀)^{1/8}. Inset: raw measurements of radius versus time.

Experiments have also been carried out with 10- $\mu$ m polystyrene particles. The results plotted in figure 5.10 unveil surprising behavior in comparison with other sizes gathered in figure 5.5. First, above a critical radius, spreading stops for any drop volume. It is more abrupt than the slowdown observed with large particles in figure 5.5(e,f). Then, the slope in the log-log representation is smaller than 1/8, as shown by the comparison with the solid black line corresponding to pure fluid experiments.

The discrepancy with Tanner's law and with the other particle sizes can have several origins. The polyvinylpyrolidone (PVP), probably used as a stabilizier with these particles could be responsible for cohesive interactions between the particles, in particular through an aromatic  $\pi$ -system binding (Keiluweit and Kleber 2009). The response of these suspensions could also be a consequence of the small particle size. To this end, experiments with other 10-µm particles in PMMA have been performed to test this hypothesis.

#### 5.4.5.2 PMMA particles



Figure 5.11: (a) Radius evolution of drops made of 10-µm and 20-µm monomodal suspensions,  $V_0 = 100$  µL. Particles are made of PMMA and are suspended in PEG copolymer. Main graph: normalized radius  $R^*$  versus  $t + t_0$ , see § 5.2.2. Black solid lines: best fit of the data obtained with pure fluid drops,  $R^* = 1.94 (t + t_0)^{1/8}$ . Inset: raw measurements of radius versus time. (b) Effective viscosity in Tanner's law as a function of particle diameter. Inset: normalized factor  $A^*$ .

Experiments with 10- $\mu$ m and 20- $\mu$ m PMMA particles are presented in figure 5.11. In contrast with the surprising results obtained with the 10- $\mu$ m polystyrene particles, the two sizes of PMMA particles do not exhibit any slowdown. In addition, data align on straight lines with slopes 1/8 in log-log representation. They thus follow Tanner's law and suggest that the odd results obtained with the small 10- $\mu$ m polystyrene particles is not stemming from a size effect.

Before any further analysis, we remind the reader that PMMA particles in PEG must sink as these suspensions are buoyant with a density difference  $\Delta \rho = 140$  kg.m⁻³ between the solid and the liquid phase. However, sedimentation effects should be presently negligible as the typical drift covered by a single 10-µm or 20-µm particle is 40 µm and 160 µm, respectively. This distance is computed from the Stokes velocity (1.1) for a typical time of  $10^4$  s. In addition, for dense suspensions, this sedimentation speed must be corrected by a factor  $(1 - \phi)^5 \approx 0.08$  at 40 % (Richardson and Zaki 1954), so that a 10-µm and a 20-µm particle would drift of 3 µm and 13 µm, respectively. Therefore, the present density difference is not responsible for strong sedimentation in the droplet.

To compare this results with that obtained with polystyrene particles, we compute once again an effective viscosity of Tanner's law. It is plotted in figure 5.11(b) for PMMA-PEG suspensions. The density used in (5.5) is  $\bar{\rho} = (1 - \phi)\rho^{PEG} + \phi\rho^{PMMA} = 1106 \text{ kg.m}^{-3}$ . With PMMA particles, the effective viscosity is again much smaller than that of the bulk and slightly higher than the viscosity obtained with polystyrene particles, see the pink rectangle and the red solid line which correspond to the results with the polystyrene particles in figure 5.6. More importantly, the effective viscosity poorly depends on particle size. These experiments evidence that granular suspensions of 10-µm particles obey Tanner's law similarly to larger sizes and confirm that the effective viscosity is independent of particle size.

# 5.5 Breakdown of Tanner's law

#### 5.5.1 Observations

The surprinsingly robust Tanner-like behavior of granular suspensions is however failing at some point, more specifically with the largest particle sizes. In this section, we turn to the slowdown of the spreading dynamics, see for instance the 550-µm particles above 200 s in figure 5.5(f).

The deviation from Tanner's law for large particles is easily understood with the top view series of monomodal granular drops displayed in figure 5.12 and 5.13. In particular, top views of spreading droplets containing 250-µm and 550-µm particles **associate the departure from Tanner's law** with the immobilization of the particle-matrix while the fluid continues to drain outward, see figure 5.13 for  $t \ge 200$  s. This freezing is obvious for the 550-µm particles, and is also observed with the 250-µm particles.

Side-view recording of the droplet provides additional elements to predict and rationalize this transition. In figure 5.14(a), profile features of a pure-fluid drop of 300 µL are presented. Time evolution of the radius, R(t), and of the thickness at the drop center,  $h_0$ , are extracted from the synchronized top and side views, respectively. Side-view profiles h(r, t) are plotted with solid lines in figure 5.14 (b), with r the radial distance from the drop center, at the times indicated by the large dots in subplot (a).

In figure 5.14(a), radius data, R(t), are fitted with Tanner's law (red dashed line) and used to compute the central height,  $h_0(t)$  predicted by Hocking (1983) for moderate Bond numbers, Bo = O(1), taking r = 0 in the expression,

$$h(r,t) = \frac{V_0}{\pi R^2 I_2\left(\frac{R}{\ell_c}\right)} \left[ I_0\left(\frac{R}{\ell_c}\right) - I_0\left(\frac{r}{\ell_c}\right) \right].$$
(5.6)

This profile and its derivation have been presented in Chapter 3. In subplot (a), the prediction for  $h_0$  (blue dashed line) is superimposed with the experimental data. Agreement between experiments and the model is excellent. Also, experimental profiles (solid lines) are well captured by (5.6) (dashed lines) in subplot (b). In conclusion, side-views are not necessary since radius data from top views can be used to compute the central thickness,  $h_0$ , with (5.6).

In figure 5.15(a) the radius of a drop of a suspension consisting of 550  $\mu$ m particles is plotted as a function of time. Side-view snapshots numbered from (i) to (iv) illustrate two different regimes in figure 5.15(b). At first, for pictures (i) and (ii), the drop profile is concave and particles move with the fluid. In that regime, the radius growth obeys Tanner's law and the suspension behaves like a continuous fluid with an effective viscosity, see § 5.4.2. Then, while the contact line still progresses from (ii) to (iv), the particles do not move and remain at the center of the drop, the continuous approach no longer holds. Spreading thus enters a new regime with a significant slowdown and departure from Tanner's law, see bending of the curve in subplot (a). In this new regime, fluid drains out of the porous matrix consisting of the large particles. On side views in subplot (b), drop profile takes a convex shape near the edge to connect the contact line with the center of the drop where the particles remain. In these pictures, particle protrusions become more significant and one can clearly identify a monolayer of particles in the picture (iv).



Figure 5.12: Series of top view snapshots for drops made with different particle sizes. From left to right:  $d=20 \ \mu\text{m}$  and  $V_0=114 \ \mu\text{L}$ ,  $d=40 \ \mu\text{m}$  and  $V_0=115 \ \mu\text{L}$ ,  $d=80 \ \mu\text{m}$  and  $V_0=105 \ \mu\text{L}$ .



Figure 5.13: Series of top view snapshots for drops of 100 µL made with different particle sizes. From left to right:  $d=140 \text{ }\mu\text{m}$  and  $V_0=114 \text{ }\mu\text{L}$ ,  $d=250 \text{ }\mu\text{m}$  and  $V_0=124 \text{ }\mu\text{L}$ ,  $d=550 \text{ }\mu\text{m}$  and  $V_0=114 \text{ }\mu\text{L}$ .



Figure 5.14: Experimental spreading of a drop of pure fluid,  $V_0 = 295 \,\mu$ L. (a) Left axis: experimental radius, R, as a function of time and Tanner's law (red dashed line) with the fitted parameters A = 0.0059,  $t_0 = 10.4$  s. Right axis: central thickness,  $h_0$ , as a function of time with the prediction of Hocking (1983) in (5.6) (blue dashed line). (b) Experimental profiles from side views (solid lines) and predicted shapes (dashed lines). The large dots in (a) correspond to the moments in (b). The color gradation indicates time progression.



Figure 5.15: Spreading of a drop of suspension made of 550- $\mu$ m particles,  $V_0 = 133 \mu$ L. (a) Radius as a function of time. (b) Thumbnails (i) to (iv): side-view pictures corresponding to the large dots in (a).



Figure 5.16: Breakdown of Tanner's law for monomodal drops of suspensions. (a) Central drop height computed from radius measurements according to (5.6). Horizontal lines indicate the height *d* for the different particle diameters. (b) Drop radius as a function of time, normalized by  $R_c$  and  $t_c$ , respectively, with  $R_c = At_c^{1/8}$ and  $h_0(R_c) = d$ . Black solid line:  $y = x^{1/8}$ .

#### 5.5.2 Critical confinement

To predict Tanner's law breakdown, we can estimate the time  $t_c$  at which a **particle undergoes** strong confinement,  $h_0(t_c) \approx d$ . The latter means that drop thickness at  $t = t_c$  has reached the typical size of the domain available to the particle. With  $R_c = At_c^{1/8}$  injected in (5.6), this condition can be written

$$d = \frac{V_0}{\pi \left(A t_c^{1/8}\right)^2 I_2\left(\frac{A t_c^{1/8}}{\ell_c}\right)} \left[ I_0\left(\frac{A t_c^{1/8}}{\ell_c}\right) - 1 \right].$$
(5.7)

This equation can be solved numerically to obtain the critical time,  $t_c$ , for each drop. Then, the critical radius  $R_c$ , at time  $t = t_c$  can be compared with experiments to test the validity of the model.

The thickness at the center of the drop,  $h_0(t)$  is plotted as a function of time in figure 5.16(a) for drops made of monomodal suspensions. Again, this quantity is inferred from radius measurement and (5.6). The horizontal lines indicate the heights  $h_0 = d$ , with the colors corresponding to that of the particle diameters. It appears clearly that within a day (i.e.  $10^5$  s), the only drops reaching the height  $h_0 = d$  (horizontal lines) are made of 250 µm or 550 µm particles. In figure 5.16(b), radii are normalized by the critical radius  $R_c$  and plotted as a function of time, normalized by the critical time,  $t_c$ . Spreading behavior deviates from Tanner's law for  $R \approx R_c$  when  $t \approx t_c$  i.e. when  $h_0 = d$  for drops made of 250 µm particles. With smaller particle diameters, the experiments are too short to observe the deviation, i.e.  $h_0 \gg d$ .

Prediction of the deviation from Tanner's law can thus be rationalized with arguments based on the confinement of particles and how it affects their ability to move with the contact line. Note that confinement criterion depends on particle size, d, but it should also depend on particle volume fraction  $\phi$ . Indeed, the volume of fluid available per particle decreases with increasing volume fraction. At higher concentration, confinement by the free interface is thus expected to be seen earlier. This last point has not been studied in detail. Yet, preliminary results, observations and reflections regarding the effect of particle concentration are presented in the next paragraph.



Figure 5.17: Effects of particle volume fraction,  $\phi = 40\%$ , 45% and 50% (from left to right) for drops of 100 µL spreading on a glass slide. (a) top view pictures and (b) side-view pictures after 6 hours of spreading.

## 5.5.3 Higher particle volume fractions

Experiments with 550-µm particles at  $\phi = 40\%$ , 45% and 50% have been carried out to investigate the consequences of a high volume fraction. According to our reasoning, higher particle volume fractions should lead to earlier freezing as the critical thickness of Tanner's regime is expected to increase with  $\phi$ .

In figure 5.17(a), top view pictures confirm this hypothesis. Three drops with increasing volume fractions have been left to spread for several hours on a glass slide. While the suspending fluid still drains out, the particle matrix does not further evolve for any of these drops. As  $\phi$  increases, the width of the region covered by the particles decreases despite the greater number of particles in concentrated drops. Particle freezing thus takes place earlier with increasing  $\phi$  and the particles do not form a monolayer anymore. Side view pictures are also diplayed in figure 5.17(b). At 40%, the initial stage of spreading creates a rather flat and homogeneous mono/bi-layer of particles which ultimately protrudes when the drop is too thin. However, at higher volume fractions, the greater number of particles and the smaller amount of fluid freeze the particle matrix in a pile. To account for the increase in particle number, the heap height increases with concentration  $\phi$ .

This system can thus be considered partially jammed: particles do not flow for  $t > t_c$ . In addition, as fluid drains out of the particle matrix, capillary pressure might build up and strengthen the pile. Such a system can interestingly display jamming features even at volume fractions way too small for the jamming transition in terms of bulk flow.

# 5.6 Visualization of particle flow

As previously mentioned, unveiling the structure of the particulate phase may help to answer questions related to the surprising results found in spreading experiments with granular suspensions. Indeed, a complex and heterogeneous structure might develop due to layering generated near the wall, confinement, and high shear gradients near the contact line. Direct numerical simulation would be a valuable ally to investigate this system but, the implementation of a free-surface flow



Figure 5.18: Experimental apparatus for particle-network imaging in the 2D (rivulet) configuration.

simulation with particles seems to be challenging. Experimentally, X-ray tomography should be able to image the 3D structure but requires a lot of resources. Instead, attempts at imaging particles during spreading with a custom laser-based fluorescence set-up have been carried out. We describe them in this section.

#### 5.6.1 Apparatus and methods

Visualization of the flow in a 3D spreading drop is tricky. Shining a laser sheet through a curved interface would lead to refraction and inhomogeneous lighting in the drop. In the same way, the camera would see a distorted image of the drop inner flow through a curved interface. This distortion is exhibited in figure 5.19(a) for a drop of 60-µm particles at  $\phi = 40\%$ . Therefore, spreading along one direction, i.e. a fluid rivulet, has been examined. Hopefully, this configuration does not alter the conclusions in comparison to the full 3D problem.

The apparatus is presented in figure 5.18 for a rivulet. The rivulet spreads on a transparent glass slide along the *x*-direction. A laser sheet illuminates the drop/rivulet from beneath and shines a vertical slice in a *xz*-plane. Imaging of this fluid slice is done by a monochrome camera (Imaging Source, DMK33UX174, captor size 2.3 MP), mounted with a zero distortion lens (Opto Engineering, reference MC100X) and aligned in the *y*-direction. The typical resolution is 3 µm/pixel. Another glass slide, perpendicular to the bottom one and parallel to the laser sheet creates a flat window for the camera to see through the rivulet, see figure 5.18. The illuminated fluid slice can be observed without distortion through this transparent wall. An example with a rivulet of 300-µm particles at  $\phi = 40\%$  is displayed in figure 5.19(b). The distance between the wall and the laser sheet is typically 5 mm. Also, a red filter is inserted between the camera and the wall to only see the red light emitted by rhodamine fluorescence, see § 2.2.4.2.

The capture of sharp images requires that a few requirements be met. Gentle deposition of a fluid rivulet is done with a spatula starting from the wall, as regularly as possible in the *y*-direction. It is crucial to avoid air bubble entrapment when collecting and releasing the fluid. Indeed, light scattering at bubble interfaces strongly interferes with good imaging. Also, the laser sheet must be as thin as possible and a fine tuning of the camera position must bring the illuminated fluid sheet perfectly into focus. Eventually, a good compromise on light intensity must be found. It must be

5.6



Figure 5.19: Visualization the particles in (a) a drop made of 60-µm particles at  $\phi = 40\%$  and (c) in a rivulet made of 250-µm particles at  $\phi = 40\%$ . In subplot (c), blue and red circles exhibit the size difference between a particle mostly in the light sheet and partially out of the light sheet, respectively. (b,d) Enlargements of the pink rectangles in (a,c), respectively.

high enough to illuminate the flow homogeneously but not too strong to limit the noise coming from out-of-plane scattering and reflections.

#### 5.6.2 Results: particulate structure in the rivulet configuration

As explained in § 2.2.4.2, the rhodamine mixed with the suspending fluid emits red light in all directions when excited with a green laser, while the green laser sheet should not be refracted at the optical interfaces. The camera, orthogonal to the laser sheet and behind a red filter, thus only sees the fluid and the particles appear as black spots.

In a pure-2D flow, a particle would remain forever in its initial *xz*-plane. However, in the drop and in the rivulet configurations, particles eventually disappear because of numerous 3D rearrangements, thus preventing long particle tracking. The observation time of a particle depends on its size. For instance, the 250  $-\mu$ m and 300  $-\mu$ m particles are much larger than the laser sheet thickness and can be followed for a longer time. When they enter or leave the illuminated slice, their apparent radius varies as shown by the red circle in figure 5.19(c). Observations and preliminary results from these visualizations are discussed in the following.

#### 5.6.2.1 Observations and descriptions of the particle flow

At the center of the rivulet, imaging reveals that the particulate structure is almost static. As the thickness decreases, particles close to the free interface flow outward and downward. When these particles get closer to the bottom, confinement is getting stronger and the previous description no longer holds. In this region with typically  $h \leq 5d$ , the first particle layer near the wall seemingly undergoes stretching by the advancing contact line and pressure from the incoming flux of particles. This layer dilates radially and empty spaces are filled with particles coming from the center of the

drop. The particles near the free surface seem to get stuck in the wedge and follow the contact line motion without significant reorganization.

## 5.6.2.2 Wall-slip

Quantitative measurement of the particle speed is still difficult at the moment. An obvious particle slip is observed near the contact line to stretch the first layer of particles. In particular, highly confined particles ( $h \leq 3d$ ) have roughly the speed of the contact line and follow it *en bloc*.

#### 5.6.2.3 Layering and microstrucutre

No clear evidence of microstructure nor major layering is observed in the experiments. In practise, layering near the solid wall is more difficult to observe while layering near the free surface is more easily captured, as shown by the enlargements in figure 5.19(b,d). It is however clear that layering does not span across the whole drop thickness.

#### 5.6.2.4 Concentration gradient

Again, no clear concentration gradient emerges. With large particles, the vicinity of the contact line would even look more packed. Again further analysis would be required.

# 5.7 Conclusions and perpectives

In this chapter, investigation of drop spreading with density-matched dense granular suspensions is reported at a global drop scale. The common description with a regular Newtonian fluid, namely Tanner's law predicts a power-law growth of radius as a function of time with an exponent 1/8. Granular suspensions unambiguously behave similarly, at least when the confinement on the particles is not too strong. However, to obey fully Tanner's law, an effective viscosity must be used. It happens to be roughly twice that of the pure fluid but five times smaller than that of the bulk of the suspension. Akin to bulk viscosity, this effective spreading viscosity does not depend on the particle size. In conclusion, the spreading of a dense granular suspension is very similar to that of a pure continuous fluid but faster than expected compared to the expectation from the bulk properties.

However, a **continuous-medium approach fails under confinement** as the height of the drop becomes comparable to the size of the particles. In this situation, the strong capillary pressure from the interface freezes the particle matrix and the fluid slowly drains out of this porous matrix formed under its own flow. A simple confinement criterion captures well the breakdown of the Tanner-like behavior with granular suspensions. This transition from a Newtonian-like to a discontinuous regime is similar to that reported in other capillary flows of granular suspensions such as pinch-off (Bonnoit, Bertrand, et al. 2012; Château et al. 2018) or dip-coating (Gans et al. 2019; Palma and Henri Lhuissier 2019; Sauret et al. 2019; Jeong et al. 2022) experiments.

The drastic decrease in dissipation compared to that of the bulk is however not fully understood at the moment and offers interesting applications to enhance the spreading rate of viscous fluids.

# 6

# Rayleigh-Taylor instability of thin liquid layers of granular suspensions

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In drop spreading of granular suspensions, confinement by the free interface and its coupling with particle dynamics have revealed interesting effects. Another simple configuration of particle confinement by a free surface is investigated in this chapter to enrich our understanding of capillary flows of granular suspensions. The dynamics of an unstable thin film of granular suspension is studied instead of a drop. The development of the Rayleigh-Taylor instability is here triggered by buoyancy. First, we introduce this instability in the case of a continuous fluid. In the second section, we present the experimental methods and in the third section, the data-analysis process. In the fourth section, we present preliminary results on the instability of thin films of granular suspensions. These results will be further investigated in the near future.

# 6.1 Unstable thin film of continuous liquid: theory & literature

In this chapter we consider interfaces between two regular continuous fluids with an adverse density stratifications, i.e. with the largest density above. This situation is encountered when a liquid layer is above the air for instance. Given that the upper fluid is denser than the lower, the interface is unstable to perturbations by the Rayleigh-Taylor mechanism (Rayleigh 1882; Taylor 1950). This instability is observed in many natural and industrial systems with density gradients, e.g. during the core collapse of massive stars or during the implosion of the targets used in inertial confinement fusion (Sharp 1984). Coating processes can also face homogeneity issues if the surface becomes unstable.

At a fluid-fluid interface, the least surface energy situation is satisfied when the interface is flat, as observed, for example, when a heavy fluid sits beneath a lighter one. In the opposite configuration, and assuming that both fluids extend to infinity, the interface is unstable to perturbations, with gravity promoting the instability and capillarity inhibiting it. In this chapter, we focus on a special case of the Rayleigh-Taylor instability, namely the thin film situation.

#### 6.1.1 Semi-infinite case

The situation of an interface between two semi-infinite layers of inviscid fluids (sketched in figure 6.1) can be treated by linear analysis. In that case, the solution is rather straightforward and a normal-mode perturbation of the surface height,  $\delta h = \exp[i(\mathbf{k} \cdot \mathbf{r} + \omega t)]$ , obeys the dispersion relation,

$$\omega^{2} = \frac{(\rho_{1} - \rho_{2})gk + \gamma k^{3}}{\rho_{1} + \rho_{2}},$$
(6.1)

with  $\mathbf{k} = k_x \mathbf{x} + k_y \mathbf{y}$  the wavenumber such that  $k = ||\mathbf{k}||$ ,  $\gamma$  the surface tension, g the acceleration of gravity, and  $\rho_{1/2}$  the lower/upper fluid density, respectively (Chandrasekhar 2013). The perturbation is unstable if  $\omega^2 < 0$  i.e. when  $\rho_1 < \rho_2$  and  $k^2 \le (\rho_2 - \rho_1) g/\gamma = k_c^2$ . Therefore, the **Rayleigh-Taylor instability amplifies large wavelengths**,  $\lambda \ge \lambda_c = 2\pi/k_c$ . In the case of a air/liquid system,  $\rho_1 + \rho_2 \simeq \rho_2 - \rho_1 \simeq \rho_2$ , and any perturbation such that  $0 < k \le k_c = (\rho_2 g/\gamma)^{1/2}$  is amplified. The growth rate of an amplified wave number then reads,  $\tau^{-1} = (gk - \gamma k^3/\rho_2)^{1/2}$ . It exhibits a maximum which selects a **fastest-growing mode**,  $k^* = [\rho_2 g/(3\gamma)]^{1/2}$ .



Figure 6.1: Rayleigh Taylor instability of a fluid-fluid interface in an infinite system with  $\rho_1 < \rho_2$ .

#### 6.1.2 Thin films

#### 6.1.2.1 Governing equations

The latter relations hold with semi-infinite layers of inviscid fluids and can be generalized to viscous fluids (Harrison 1908; Chandrasekhar 2013). Viscosity will be particularly significant if we now



Figure 6.2: Rayleigh-Taylor instability of a thin liquid film above the air.

consider a *thin* upper layer of liquid of thickness  $h_0$ . This situation with strong effects of the viscosity is further detailed in the following, where  $\rho$  and  $\eta$  are the density and the viscosity of the upper liquid, respectively, and  $\gamma$  is the surface tension of the air/liquid interface. The situation is sketched in figure ??. The initial flat film of thickness  $h_0$ , is assumed to be small compared to the viscous diffusion length scale,

$$\ell_{\eta} = \left(\eta \tau / \rho\right)^{1/2},\tag{6.2}$$

with  $\tau$  a characteristic time scale, e.g. the perturbation growth.

We write  $\delta h(x, y, t)$  the surface displacement compared to the flat situation so that the film thickness is  $h = h_0 + \delta h$ . The vertical direction is directed downwards with the solid surface located at z = 0. In the Stokes regime, Navier-Stokes and continuity equations can be written, respectively,

$$\frac{\partial P}{\partial x} = \eta \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) v_x,$$

$$\frac{\partial P}{\partial y} = \eta \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) v_y,$$

$$\frac{\partial P}{\partial z} - \rho g = \eta \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) v_z,$$
(6.3)

and

$$0 = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}.$$
(6.4)

In the following, we use the gradient and Laplacian operators,  $\nabla = \partial_x \mathbf{x} + \partial_y \mathbf{y}$ , and  $\Delta = \partial_x^2 + \partial_y^2$ , respectively, along the *x* and *y* coordinates. The boundary conditions over the upper solid wall at z = 0 and over the free surface at z = h(x, y, t) read,

$$\upsilon_{x,y}(x,y,0,t) = 0 \quad , \quad \eta \left. \frac{\partial \upsilon_{x,y}}{\partial z} \right|_{z=h} = 0 \quad , \quad P(x,y,h,t) = P^{ext} - \gamma \Delta \delta h, \tag{6.5}$$

the latter coming from the linearization of the interface curvature with the assumption of **small slopes**, i.e.  $\partial_x h \approx \partial_y h \ll 1$ . For any quantity Q, the **lubrication approximation** in the thin film yields  $\partial_x Q \sim \partial_y Q \ll \partial_z Q$ . From the continuity equation, (6.4) and  $L \gg h_0$ , we obtain  $v_z \sim v_{x,y}h_0/L \ll v_{x,y}$  with L the characteristic length scale in the x/y-directions. Under this approximation and the boundary contitions (6.5), integration of the vertical component of the momentum equation (6.3) between z and h(x, y, t) leads to

$$P(x, y, z, t) = P^{ext} - \gamma \Delta \delta h - \rho g \left( h - z \right), \tag{6.6}$$

and the relation (6.6) used in the momentum equation of the  $\alpha$ -component ( $\alpha = x, y$ ) in (6.3) with the boundary conditions (6.5) gives in turn,

$$\upsilon_{\alpha} = -\frac{2hz - z^2}{2\eta} \frac{\partial P}{\partial \alpha} = \frac{2hz + z^2}{2\eta} \frac{\partial}{\partial \alpha} \left(\rho g h + \gamma \Delta \delta h\right). \tag{6.7}$$

Chapter 6 : Rayleigh-Taylor 6.1 Unstable thin film of continuous liquid: theory & literature



Figure 6.3: Dispersion relation (6.12) from the linear analysis of the Rayleigh-Taylor instability of a thin viscous layer of fluid. Perturbation growth rate as a function of (a) wave vector, k, and (b) wavelength,  $\lambda$ . Results for different film thicknesses,  $h_0$  (see legend) and  $\eta = 3$  Pa.s,  $\rho = 1190$  kg.m⁻³ and  $\gamma = 0.032$  N.m⁻¹. Red lines: fastest-growing perturbation. Grey domains: stable, non-amplified perturbations.

The kinematic condition of the free surface also requires,

$$\frac{\partial h}{\partial t} + \left( \left. v_x \right|_{z=h} \frac{\partial h}{\partial x} + \left. v_y \right|_{z=h} \frac{\partial h}{\partial y} \right) = \left. v_z \right|_{z=h} = -\int_0^h \left( \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} \right) \mathrm{d}z, \tag{6.8}$$

which simplifies with Leibniz's rule into,

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x} \left( \int_0^h v_x dz \right) + \frac{\partial}{\partial y} \left( \int_0^h v_y dz \right) = 0.$$
(6.9)

Since  $h = h_0 + \delta h(x, y, t)$ , and with the expression of the velocity fields in (6.7), we obtain from the above relation,

$$\frac{\partial \delta h}{\partial t} + \frac{\partial}{\partial x} \left[ \frac{(h_0 + \delta h)^3}{3\eta} \frac{\partial}{\partial x} \left( \rho g \delta h + \gamma \Delta \delta h \right) \right] + \frac{\partial}{\partial y} \left[ \frac{(h_0 + \delta h)^3}{3\eta} \frac{\partial}{\partial y} \left( \rho g \delta h + \gamma \Delta \delta h \right) \right] = 0.$$
(6.10)

#### 6.1.2.2 Thin films: linear analysis

Dispersion relation: general and linear

Equation (6.10) can be written in terms of a linear and a nonlinear part,

$$\left[\frac{\partial}{\partial t} + \frac{h_0^3}{3\eta}\Delta(\rho g + \gamma\Delta)\right]\delta h + \nabla \cdot \left[\frac{\left(3h_0^2\delta h + 3h_0\delta h^2 + \delta h^3\right)}{3\eta}\nabla(\rho g\delta h + \gamma\Delta\delta h)\right] = 0.$$
(6.11)

The first term in (6.11) leads to the **linear dispersion relation** for of a perturbuation  $\delta h \propto \exp(i\mathbf{k} \cdot \mathbf{r}) \exp(t/\tau)$  and to its **growth rate**, (Babchin et al. 1983),

$$\tau^{-1} = \frac{h_0^3}{3\eta} \left( \rho g k^2 - \gamma k^4 \right). \tag{6.12}$$

The perturbation will be **amplified** provided  $\tau > 0$  i.e.  $k \le k_c = (\rho g / \gamma)^{1/2}$ .

The linear-regime growth rate (6.12),  $\tau^{-1}$  is plotted in figure 6.3 as a function of (a) the perturbation wave number, k, and (b) the perturbation wavelength,  $\lambda$ , for different film thicknesses. Since,  $\tau^{-1} \propto h_0^3$ , film thickness sets the magnitude of the growth rate. In contrast, film thickness does not affect the range of unstable perturbations, i.e.  $k \leq k_c = \ell_c^{-1}$  or  $\lambda \geq \lambda_c = 2\pi\ell_c$ , see subplots (a) and (b), respectively.

#### Dominant mode in the linear regime

The dispersion equation (6.12) has a maximum growth rate, corresponding to the maxima of  $\tau^{-1}$  in figure 6.3. Therefore, the instability selects a fastest-growing mode,

$$k^* = \sqrt{\frac{\rho g}{2\gamma}},\tag{6.13}$$

i.e. a most unstable wavelength,

$$\lambda^* = 2\pi \sqrt{2\ell_c},\tag{6.14}$$

with  $\ell_c = (\gamma/\rho g)^{1/2}$  the fluid capillary length. The characteristic growth time of the dominant mode is

$$\tau^* = \frac{12\eta\gamma}{h_0^3 \rho^2 g^2}.$$
(6.15)

In finite thickness systems, the fastest-growing mode is not the same than in a semi-infinite layer. The corresponding wavelength is shorter but does not depend on the fluid thickness,  $h_0$ . This dominant wavelength provides the length scale in the *x* and *y*-directions and therefore clarifies the "small slope approximation",  $\delta h \ll \lambda^*$  and the viscous regime criterion,  $h_0 \ll \ell_\eta \iff h_0 \ll \left(\frac{12\eta^2 \gamma}{\rho^3 g^2}\right)^{1/5} = 7$  mm presently. Of course, the linear analysis describes a length of the viscous regime criterion is for the viscous regime.

presently. Of course, the linear analysis describes only the onset of the instability and is limited to  $\delta h < h_0 \ll \lambda^*$  and small slopes. Numerical investigation of the evolution of the interface beyond this limit is presented by Yiantsios and Higgins (1989).

#### 6.1.2.3 Lattice geometry

Linear analysis predicts the selection of a fastest-growing wavelength but does not promote any direction due to the symmetry of the system. A superposition of fastest-growing modes is then a solution of the linear problem. The shape of the unstable surface is obtained from the addition of N pairs of modes, each pair composed of 2 normal modes with a wave vector  $\pm \mathbf{k}$  such that  $||\mathbf{k}|| = k^*$ . Some examples of surface patterns for N = 1, 2, 3, are displayed in figure 6.4. They will be named (a) roll , (b) square and (c) hexagonal modes in the following. Note that in figure 6.4(c), i.e. in the hexagonal pattern, the distance between two peaks is not  $\lambda^*$  but  $2\lambda^*/\sqrt{3}$ . The growth rate of any of these modes should be  $1/\tau^*$  since  $||\mathbf{k}|| = k^*$ , according to the linear theory. Yet, experiments indicate a pattern selection which promotes the hexagonal mode (Fermigier, Limat, Wesfreid, Boudinet, Ghidaglia, et al. 1991).

#### 6.1.2.4 Nonlinear regime

This selection in favor of the hexagonal pattern comes from the **nonlinear term** in (6.11), and the full nonlinear equation can be understood as interactions between wave vectors (Fermigier, Limat, Wesfreid, Boudinet, Ghidaglia, et al. 1991; Fermigier, Limat, Wesfreid, Boudinet, and Quilliet 1992). Depending on the configuration, these interactions can **amplify or damp** the initial pattern and lead to the generation of new harmonics. This correction from the nonlinearities particularly



Figure 6.4: Possible patterns from the linear analysis of the Rayleigh-Taylor instability of a thin layer of fluid. (a,c,e) 3D representations and (b,d,f) top views. Each pattern comes from the superposition of N pairs of modes with the same wavelength  $\lambda^*$ . (a,b) N = 1,  $h = h_0 + A \cos\left(\frac{2\pi}{\lambda^*}x\right) \exp\left(\frac{t}{\tau^*}\right)$ , (c,d) N = 2,  $h = h_0 + \frac{A}{2}\left[\cos\left(\frac{2\pi}{\lambda^*}x\right) + \cos\left(\frac{2\pi}{\lambda^*}y\right)\right] \exp\left(\frac{t}{\tau^*}\right)$ , (e,f) N = 3,  $h = h_0 + \frac{A}{3}\left[\cos\left(\frac{2\pi}{\lambda^*}x\right) + \cos\left(\frac{2\pi}{\lambda^*}\left(\frac{x}{2} + \frac{\sqrt{3}y}{2}\right)\right) + \cos\left(\frac{2\pi}{\lambda^*}\left(\frac{x}{2} - \frac{\sqrt{3}y}{2}\right)\right)\right] \exp\left(\frac{t}{\tau^*}\right)$ . In all graphs,  $A \exp(t/\tau^*) = h_0/10$ , where A is the initial perturbation amplitude.



Figure 6.5: Evolution of the perturbation amplitude A(t)/A(0) for the different patterns in figure 6.4. Deviation from a straight line comes from the nonlinearities. Data extracted from (Fermigier, Limat, Wesfreid, Boudinet, and Quilliet 1992).

benefits the **hexagonal mode** which is amplified. In figure 6.5, the amplitude of the different configurations are plotted as a function of time. The hexagonal pattern is amplified in comparison with the two others. The square mode is poorly affected by nonlinearities and its amplitude grows exponentially, in the same way than in the linear regime. On the contrary, the roll mode is highly damped. These results on wavelength and pattern selection are established in the situation of an infinite fluid layer along the x, y-directions. Also in finite systems in the x, y-directions, for example periodic domains, simulation in the nonlinear regime indicates that if the system size is larger than the wavelength of the fastest-growing mode, the interface accommodates in bumps of unequal heights and unequal spacings between the peaks (Yiantsios and Higgins 1989). The wavelength of the instability can thus be modified.

#### 6.1.2.5 Late stage and dripping

As the instability develops, peaks become higher and may eventually release a drop above a critical size.

We consider first the case of extremely thin and/or extremely viscous liquid layers so that it would take forever for a bump to become large enough to generate a drop which detaches from the unstable interface. The stability beyond the linear regime of such an interface configuration is investigated numerically by Yiantsios and Higgins (1989). The authors conclude that the steady-state shape depends on the initial perturbation. The least energy configuration, reached by coalescence of neighboring drops, is prohibited in symmetric cases. On the contrary, two asymmetric drops will approach each other and eventually coalesce.

With a thick layer of fluid, the film will eventually drip when the peak size exceeds a threshold. The stability of isolated pendent drops on a substrate has been investigated theoretically and numerically by disturbing a prescribed drop shape with different volumes. The maximum volume,  $V_0^{\text{max}}$  depends on the capillary length of the fluid and on the equilibrium contact angle  $\theta_e$  with the substrate. The analytical predictions,  $V_0^{\text{max}} \sim 3\pi \ell_c^3$ ,  $5\pi \ell_c^3$  and  $6\pi \ell_c^3$  for  $\theta_e = 50^\circ$ ,  $20^\circ$  and  $5^\circ$ , respectively (Pitts 1974) or  $V_0^{\text{max}} \sim 6\pi \ell_c^3$  for  $\theta_e = 0^\circ$  (Myshkis et al. 1987), are confirmed by numerical solutions (Sumesh and Govindarajan 2010).



Figure 6.6: (a) Unit cell (green) in a hexagonal array of peaks (blue dots). (b) The distance bewteen the centers of two unit cells is  $a = \frac{2\lambda^2}{\sqrt{3}}$ , see figure 6.4(f) since the area of the green hexagon is  $2\sqrt{3}b^2$  with  $b = \frac{a}{2} = \frac{\lambda^2}{\sqrt{3}}$ . From (6.14), the volume of the unit cell in subplot (a) is  $h_0 \left[\sqrt{3}\left(2\pi\sqrt{2}\ell_c/\sqrt{3}\right)^2\right] = 16\pi^2\ell_c^2h_0/\sqrt{3}$ .

All these studies treat the case of isolated pendent drops while our system is a lattice of drops, growing on a thin film of thickness  $h_0$ . The situation is sketched in figure 6.6(a). The available fluid volume per unit cell is  $V_0 = 16\pi^2 h_0 \ell_c^2 / \sqrt{3} \approx 91.2 h_0 \ell_c^2$ . Assuming that only this volume of liquid can be used in a single bump, the dripping criterion  $V_0^{\text{max}} \sim 6\pi \ell_c^3$  inferred from the case  $\theta_e = 0^\circ$  yields

$$h_0 \ge 0.21\ell_c \iff Bo = \frac{h_0^2}{\ell_c^2} \ge 0.04,$$
(6.16)

with *Bo* the Bond number of the problem. In a 2D periodic domain simulation, the growth of a peak on an unstable thin film saturates at  $Bo \approx 0.4$  (Yiantsios and Higgins 1989). However, comparison of experiments with (6.16) from the results of Pitts (1974) or with those of Yiantsios and Higgins (1989) is delicate. In particular, simulation in periodic domains by Yiantsios and Higgins (1989) does not set the size of the base of the drop, unlike the work of Pitts (1974). Their numerical work also does not start from a prescribed shape but instead follows the dynamics of the instability. The growth of the instability slows down tremendously as the liquid layer around the drop becomes thinner, but the drop may not be stable at the (very far) end. The variational methods used by Pitts (1974) to derive the critical volume of a pendant drop examine only the last stage. An asymptotically *unstable* drop can be considered to be *stable* if it takes an eternity to detach from the ceiling. Dripping in real systems is therefore likely to occur at larger volumes than these predictions especially as fluid could be drained from neighbors in a lattice of peaks.

#### 6.1.3 Experiments: literature

#### 6.1.3.1 Semi-infinite case

Although pleasant to study theoretically and numerically, the experimental investigation of the Rayleigh-Taylor instability can be challenging. The main difficulty, namely the preparation of a clean adverse density stratification (i.e. heavy fluid on the top), can be bypassed with several tricks. For instance, reversing the direction of gravity with a vertical acceleration larger than *g* leads to the destabilization of the upper surface of a liquid poured into a vessel (D. Lewis 1950). System size is naturally a big restriction in such devices.

#### 6.1.3.2 Thin layer

The thin film configuration is much easier to realize, by just pouring liquid on a plate and turning over the system. Viscous liquids are more suitable with this method to avoid undesired flow during the plate inversion. The results presented in § 6.1.2.2 and § 6.1.2.4 regarding the dominant wavelength and the hexagonal pattern selection are confirmed by experiments with large thin films of viscous silicone oil (Fermigier, Limat, Wesfreid, Boudinet, Ghidaglia, et al. 1991; Fermigier, Limat,

Wesfreid, Boudinet, and Quilliet 1992; Limat et al. 1992). The instability always nucleates near an edge or a defect (dust, bubble) and then propagates as a front. This observation can be used to force the other patterns introduced in § 6.1.2.3. For instance, a wire across the thin film triggers a roll perturbation, and two perpendicular wires generate locally a square lattice of bumps (Fermigier, Limat, Wesfreid, Boudinet, Ghidaglia, et al. 1991). However, the system eventually relaxes toward the hexagonal pattern.

The regular domes generated by the Rayleigh-Taylor instability can be harnessed to create structured surfaces. For instance, with a thin fluid film covering the inner surface of a rotating cylinder, a polymeric liquid upon curing can freeze the instability, leading to a regular lattice of bumps once unpeeled from the cylinder (Marthelot et al. 2018). By varying the rotation speed and thus the effective gravity, the wavelength of the instability can be tuned to go from 50  $\mu$ m to 1 cm. Pattern periodicity can be greatly enhanced by drawing grooves on the surface and square lattices can be forced with this trick.

#### 6.1.3.3 Dripping and inhibition of the instability

The dripping criterion (6.16) inferred from the critical volume of isolated hanging drops does not work for the lattice of hanging drops formed upon the surface instability (Fermigier, Limat, Wesfreid, Boudinet, and Quilliet 1992). This fact can be explained by the possibility for the drops to merge or by mass transfer from neighboring drops through the film to feed the growing instability. For these reasons, prevention of dripping is complicated. As shown in figure 6.3, any large-wavelength perturbation will grow. The time required to collect enough fluid can just become very large with extremely thin films. Therefore, the Rayleigh-Taylor instability will develop unless the system somehow kills these long-wavelength perturbations or displays additional constraints.

For example, horizontal oscillations of the system (Wolf 1969; Talib and Juel 2007) can be used to stabilize adversed density stratification to study floating under a levitating liquid for instance (Apffel et al. 2020). Alternatively, tangential flow in the liquid film can compete with the growth of the instability. Indeed, shear flow can saturate the instability growth on the underside of a horizontal plane (Babchin et al. 1983) or flow down an inclined plane can hinder instability growth above a critical inclination (Indeikina et al. 1997; Brun et al. 2015). In the latter configuration, the liquid film develops travelling-wave structures that compete with the growth of the instability. This behavior is related to the transition from an absolute instability to a convective instability with growing perturbations swept away by the flow (Scheid et al. 2016). A situation related to this flow-induced stabilization is that of curved surfaces. Indeed, substrate curvature stabilizes the thin film by means of the flow steming from gravity drainage (Trinh et al. 2014; Balestra et al. 2018).

A Marangoni flow can also stabilize or destabilize the interface (Deissler and Oron 1992; Alexeev and Oron 2007; Sterman-Cohen and Oron 2020). Experimentally, in thermocapillary stabilization, the temperature dependency of surface tension can generate a restoring flow when a liquid film destabilizes above a warm gas layer (Burgess et al. 2001). Due to the Marangoni effect, as the liquid sinks in the warm gas layer, it warms up, decreases its surface tension, and flows toward cold thinner regions - with a high surface tension. This flow counteracts the instability growth and stabilization is achieved above a critical temperature difference. Below this threshold, linear analysis predicts well the dominant wavelength, which increases with temperature difference and becomes infinite at the critical temperature difference.

Prevention of the instability has also been reported for a liquid/liquid interface in a vertically confined system (Alqatari et al. 2020). The stabilization is explained by the domination of mass diffusion over buoyancy in highly confined geometries.

In the following, we will investigate the possibility for the particles to stabilize this persistent instability.



Figure 6.7: Rayleigh-Taylor instability of a thin liquid film (a) in a square  $20 \times 20$  cm plastic petri dish and (b) in the configuration used in the following i.e. a hexagonal frame of thickness  $h_0$  (bottom view).

# 6.2 Unstable thin film: methods

#### 6.2.1 Apparatus & methods

#### 6.2.1.1 Film of fluid

Several methods were tested to obtain flat films of controlled thickness. Drawing inspiration from the literature (Fermigier, Limat, Wesfreid, Boudinet, and Quilliet 1992), a first attempt simply consisted in pouring fluid on a glass plate and waiting for a long time for the liquid to spread. The main drawbacks of this method are related to the film thickness, both regarding the measurement of its value and the control of its homogeneity. Indeed, the growth rate of the instability highly depends on the film thickness. In a second attempt, the desired mass of fluid was poured into a vessel (a square 20×20 cm plastic petri dish or a 20 cm wide glass circular petri dish). This method also suffers from major issues: the bottom of the vessel is not perfectly flat and some fluid climbs up the walls of the vessel once turned over, draining liquid out of the film, see figure 6.7(a).

The system used in the end, shown in figure 6.7(b), is made of a glass plate on which a hexagonal frame with side length ~9 cm and thickness  $h_0$  is glued. This frame is cut in a plastic sheet - intended for architectural maquettes - made of extruded copolyester which can come in thicknesses from 500 µm to 2 mm. At the time of writing, the only thickness investigated is  $h_0 = 750$  µm. Other thicknesses will be investigated in the near future. To prepare the liquid film, the plate is placed on a scale, and the desired mass of fluid,  $m_f = \rho_f h_0 A$ , is spread in the frame and left to rest for several hours before an experiment. The area of the hexagon,  $A \approx 220$  cm² is measured with ImageJ. Once turned over, the fluid does not wet the plastic sufficiently to spread on it. As mentioned in § 6.1.3.2, the instability always starts from the edges and propagates to the center. For this reason, a hexagonal frame is preferred to generate directly the most unstable lattice of peaks. This methods has several advantages in comparison with previous attempts among which minimum liquid leakage on the walls and improved surface flatness.

#### 6.2.1.2 Experimental apparatus

The apparatus sketched in figure 6.8, is a 1-meter high structure holding a mirror, the plate, and a LED panel. The acquisition is made with a monochrome Basler camera (reference acA12440 - 35 um, 5 MP) mounted with a distortionless macro lens (reference VS-LLD30). The typical resolution is 130  $\mu$ m/pixel. With a mirror inclined at 45° below the glass plate, the camera can record pictures of the distorted checkerboard from the side. Using a mirror prevents dripping on the optics, but means that the field of view shrinks during an experiment as drops fall on its surface. The distance between the camera and the liquid film is H = 1.1 m. The plate covered by the fluid film is placed above the mirror. A checkerboard, used for Synthetic Schlieren Imaging, see § 6.2.2, is printed on a paper sheet and taped on the top of the glass plate. Each square has a side length 1 mm, i.e. c = 2 mm, where c is the wavelength of the pattern used for Synthetic Schlieren Imaging. A LED panel is placed above the glass plate with lighting strong enough to see through the paper and observe the pattern from below. Louis Grospiron, a graduate student from the École Normale Supérieure de Lyon, has greatly helped to test and design this apparatus.



Figure 6.8: Sketch of the experimental apparatus used to study the Rayleigh-Taylor instability of thin liquid films.

#### 6.2.2 Surface reconstruction

To track the growth of the instability, a range of methods can be used, such as probes, e.g. capacitive wire gauge (Ricard and Falcon 2021), or light absorption by a dye (Fermigier, Limat, Wesfreid, Boudinet, and Quilliet 1992). However, none of these solutions returns a non-local and quantitative mapping of the surface profile. Instead, Synthetic Schlieren Imaging is a **non-invasive** technique enabling the measurement of **surface profile at relatively low costs**. This technique is used primarily in two contexts. First, it is used to reveal patterns in otherwise transparent media by showing 6



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Figure 6.9: Refraction of a light ray going through glass and fluid. The surface displacement of the air/fluid interface,  $\delta h$ , can be computed with Synthetic Schlieren Imaging with the displacement  $\delta r$ .

the variations of the optical index in the flow, for example to reveal internal gravity waves in a stratified fluid (Sutherland et al. 1999) or temperature gradients in convective air flow (Alvarez-Herrera et al. 2009). Second, it can probe the deformation of the interface between two media, since the latter is optically a diopter. Synthetic schlieren imaging has then been used for decades in quantitative studies of interface deformation to investigate surface flows (Le Doudic 2022) or wave interactions (Polly et al. 2021). Note that here the fluid is transparent, so the pattern can be seen through the deformed interface. Profilometry with opaque fluids is feasible with a pattern projected and reflected on the free surface (Tsubaki and Fujita 2005; Cobelli et al. 2009). Again, distortion by a non-flat interface can be used for surface reconstruction.

#### 6.2.2.1 Synthetic Schlieren Imaging for surface topography: elements of theory

We consider the situation sketched in figure 6.9 with a pattern located behind (i.e. above) a glass plate which is covered on its underside by a liquid film. When the air/fluid interface is flat, we define  $h_0$  and  $h_g$ , the thicknesses of the fluid and glass, respectively, and  $n_f$ ,  $n_g$ , their optical indices, respectively. We also define  $n_a$ , the optical index of the air. The typical size of the film on the glass plate is *L*. Here, the camera is located below the pattern/glass/fluid surface. If the camera is assumed far below the pattern, i.e.  $H \gg h_0$ ,  $h_g$ , *L*, a light ray in the air can be considered almost vertical (paraxial approximation). In the non-deformed scenario (flat interface), any light ray hits orthogonally the air/fluid and fluid/glass optical interfaces and is not refracted (green line in figure 6.9). On the contrary, when the air/fluid interface is bent, i.e.  $\delta h \neq 0$ , a light ray is refracted twice, in  $I_{a/f}$  and in  $I_{f/g}$ . Instead of the reference point *M* observed in the flat situation, the point *M'* is now seen (blue line in figure 6.9). The expression of the displacement,  $\delta \mathbf{r} = \overrightarrow{MM'}$ , for arbitrary incidence angles (within the paraxial approximation) is derived by Moisy et al. (2009) in the case of small slopes of the air/fluid interface, i.e.  $\nabla h \ll 1$ , and small interface deformations,  $\delta h \ll h_0$ . In figure 6.9, the approximation of a 2D situation is sketched in vertical incidence.

#### Pattern distortion in vertical incidence

The displacement  $\delta \mathbf{r}$  resulting from the air/fluid interface deformation in figure 6.9, is related to the slope  $\nabla h$  at point  $I_{a/f}$  according to,

$$\nabla h = -\delta \mathbf{r} \left( \frac{1}{\alpha h_p} - \frac{1}{H} \right), \tag{6.17}$$

with

$$\alpha = 1 - \frac{n_a}{n_f}$$
 and  $h_p = h_0 + \frac{n_f}{n_g} h_g.$  (6.18)

Integration of the slope field in (6.17) provides surface reconstruction. Random dot patterns are often used (Moisy et al. 2009). However, 1D periodic patterns (Akatsuka and Nagai 2011; Hatanaka and Saito 2015) and 2D periodic patterns (Wildeman 2018) have proven to return reliable and fast results with optimized Fourier transform algorithms (Vinnichenko et al. 2023). In particular, these algorithms are more robust to large displacement gradients compared to common analysis. In the next paragraph, we describe the case of a checkerboard, the method used in the following.

#### 6.2.2.2 Fast Checkerboard Demodulation

The deformation of a checkerboard pattern can be quickly inverted by the means of Fourier demodulation (Wildeman 2018). The checkerboard is then analogous to a carrier signal with a wave number  $k_0 = 2\pi/c$ , whose phase is modulated because of surface deformation. Demodulation techniques can efficiently extract this phase related to the displacement  $\delta \mathbf{r}$ . A version of the MATLAB script provided with the publication of Wildeman (2018) edited and adapted to our configuration, is used for the analysis.

The signal must obey several criteria to return meaningful results. First, the Nyquist-Shannon rule for a checkerboard pattern indicates that proper sampling of the background pattern requires at least 3.4 pixels per wavelength c (9 pixels in our experiments). Then, the inversion of the phase field raises phase-wrapping issues. More specifically, displacements  $\delta r_0$  and  $\delta r_0 + 2\pi n/k_0$ , with  $n \in \mathbb{N}$  lead to the same phase change of the carrier. Phase wrapping thus imposes an upper limit of the displacement field,

$$|k_0 \delta r| \le \pi \quad \Longleftrightarrow \quad \delta r \le \frac{c}{2},\tag{6.19}$$

which corresponds to the displacement in figure 6.9. In the scripts provided by Wildeman (2018), unwrapping is implemented.

Spacing between carrier peaks in Fourier space also sets an upper limit for the extraction of a physical wave number  $k_s$ . In a square lattice, the distance between peaks in the **x** and **y**-directions for the carrier is  $\sqrt{2}k_0$ , leading to

$$k_s \le \frac{\sqrt{2}k_0}{2}.\tag{6.20}$$

In addition, the main harmonics of the signal must equally satisfy this condition which can be written as

$$k_s k_0 \delta r \le \frac{\sqrt{2k_0}}{2},\tag{6.21}$$

accounting for space variations of the carrier (Wildeman 2018).



Figure 6.10: Criteria for Fast Checkerboard Demodulation on (a) the displacement,  $\delta r$  of the pattern, and on (b) the slope of the liquid surface,  $\nabla h$ , as a function of the signal wavelength,  $\lambda_s$ . Checkerboard wavelength, c = 2 mm. Without phase unwrapping, correct demodulation is possible in the white area only. With phase unwrapping, demodulation also works above the green dashed line.

#### Limitations of Fourier demodulation of a checkerboard pattern

Speaking in terms of signal wavelength,  $\lambda_s = 2\pi/k_s$ , the conditions (6.20) and (6.21) yield,

$$\lambda_s \ge \sqrt{2}c \quad \text{and} \quad \delta r \le \frac{\lambda_s}{2\pi\sqrt{2}}.$$
 (6.22)

Therefore, grid size, *c*, sets the value of the smallest wavelength accesible with the method. The maximum displacement, and consequently the maximum slope, is proportional to  $\lambda_s$ . The last two criteria and the one coming from phase wrapping (6.19), are illustrated in figure 6.10(a).

The different parameters used in the following are gathered in table 6.1. With these values, one can compute the maximum slope related to the displacement field by (6.17). Without the unwrapping algorithm, the maximum slope is thus,

$$\nabla h^{\max} = \frac{c}{2} \left( \frac{1}{\alpha h_p} - \frac{1}{H} \right), \tag{6.23}$$

and lies around 0.9 according to figure 6.10(b). With unwrapping (green region),

$$\nabla h^{\max} = \frac{\lambda_s}{2\pi\sqrt{2}} \left(\frac{1}{\alpha h_p} - \frac{1}{H}\right). \tag{6.24}$$

In our experiments,  $\lambda_s \approx 1.6$  cm. As shown in figure 6.10(b), the maximum slope for this wavelength is  $\nabla h^{\text{max}} \approx 1.59$  and the theoretical maximum surface elevation  $\delta h \sim \lambda_s \nabla h \approx \lambda_s$ . In practise surface reconstruction fails around 2 mm, see § 6.3.4.

Parameter	n _a	n _f	ng	α	$h_0$	$h_g$	h _p	Η	С
Value	1.0	1.45	1.5	0.31	750 µm	3 mm	3.65 mm	1.1 m	2.0 mm

Table 6.1: Parameters for Fast Checkerboard Demodulation in the experiments.

#### 6.2.3 Issues during surface reconstruction

For each frame, surface height is computed with the MATLAB code of Wildeman (2018). Post processing and analyze are done with Python. An example of this first step is provided in figure 6.11. The parameters required to run this algorithm are,

- $\alpha$  and  $h_p$  or the parameters necessary to compute them,
- *H*, the distance between the interface and the camera,
- and the resolution of the checkerboard picture.



Figure 6.11: Surface reconstruction by the MATLAB code of Wildeman (2018). (a) Raw picture i.e. distorted checkerboard. (b) Surface elevation  $\delta h$ . Scale bars: 1 cm.

Several issues can appear at this stage of the analysis. On the top of the raw picture in figure 6.11(a), four drops have dripped on the mirror and locally obstruct the imaging. This dripping is eventually an issue when the mirror is fully covered with fluid but not at the beginning. More annoying phenomena are shown in figure 6.11(b). First, the resolution of the method creates artifacts, see for instance an enlargement in figure 6.12. These structures appear when a peak height reaches typically 2 mm and displays several *inner* peaks that will appear as different single peaks during automated peak detection. Second, some peaks are detected out of the frame, especially near the edges of the picture. A mask of zeros is thereby applied to remove these peaks, see for instance figure 6.13(a). The mask is simply generated with the vertex coordinates of the hexagonal frame with the draw.polygon function from the skimage Python package. Also, a smooth height gradient may develop across the picture, perhaps because of a small displacement of the plate during the experiment. For instance, in figure 6.11(b), a general vertical gradient is observed. Despite great precautions to avoid vibrations, this gradient can appear and bias the measurement of surface height. However, it can be easily corrected and does not prevent peak detections.



Figure 6.12: Artifacts coming from high peaks. Left: example of 3D reconstruction of the peak. Right: example of peak elevation maps with issues.

# 6.3 Data analysis: peak lattice

#### 6.3.1 Detection

Peaks are detected with the peak_local_max function from the skimage.feature Python package. A minimal distance between neighboring peaks can be specified and prevents a peak from being detected more than once because of the artifacts displayed in figure 6.12. However, the position of the center of a peak may be a bit off, especially for the bottom-left peak whose center appears dark. To smooth out these effects and blur the inner peaks of the artifacts, a stack of elevation maps can be summed into a single one as the one presented in figure 6.13(a). Peak detection applied to this smoothed map is displayed in figure 6.13(b).

#### 6.3.2 Distance between peaks

Mean distance between peaks, can be computed with several methods from the list of peak coordinates. For instance, triangulation with the Delaunay function from the scipy.spatial Python package is displayed in figure 6.13(c). Length distribution of the edges is displayed in the histogram in figure 6.13(d). A more straightforward method, using the radial distribution function rdf from the rdfpy Python package, is compared with triangulation in figure 6.13(d). The radial distribution function  $g_r(r)$  returns the number density of neighbors around a peak, in a circular shell of radius r and width  $\delta_r$  (radial increment). The two methods agree on an average distance between neighboring peaks,  $\lambda = (116 \pm 7)$  pixel, i.e.  $\lambda = (15.2 \pm 1.0)$  mm. In figure 6.13(c), edge lengths are shown with colors to highlight the spatial distribution in the lattice. Peak distances seem rather homogeneously distributed.

#### 6.3.3 Hexagonal pattern

Alternatively to the triangulation displayed in figure 6.13(c), the Voronoi diagram of this lattice provides some information about its structure. This kind of diagram is divided into cells, each corresponding to one peak, so that a point in the cell is closer to the peak than to any other. The number of neighbors of a peak is thus given by the number of edges of its cell. This diagram provides several criteria to remove the peaks on the edges of the frame, either from their smaller number of neighbors



Figure 6.13: Lattice of peaks developed in the hexagonal frame with pure fluid. (a) Sum of 80 elevation maps from 10 s to 810 s. (b) Positions of the peaks detected in subplot (a). (c) Triangulation of peak coordinates. An edge color corresponds to its length, increasing from dark to light colors. (d) Left axis: edge length in the triangulation in subplot (c). Right axis: radial distribution function  $g_r$  for different radial increments  $\delta r$  (see legend). Red vertical line: average of the position of the maxima of  $g_r$  for the 6 radial increments.


Figure 6.14: (a) Voronoi diagram. Cell color relates to the number of edges (see legend). (b) Local bondorientational parameter of a hexagonal lattice,  $\varphi_6$ , according to (6.25), indicated by the color of the dots. Red solid lines: edges of the frame.

(typically 4) or from the cell size. In figure 6.14(a), most of the peaks unambiguously have 6 neighbors, in agreement with the expected hexagonal lattice. The local bond-orientational parameter of the *m*-th point of the lattice can also be computed according to,

$$\varphi_6(m) = \frac{1}{N(m)} \sum_{k=1}^{N} (m) e^{i\theta_{m,k}}, \qquad (6.25)$$

with N(m) the number of nearest neighbors of m and  $\theta_{m,k}$  the oriented angle with its k-th neighbor (Qi et al. 2006). If m is in a perfectly hexagonal environment, i.e. 6 neighbors such that  $\theta_{m,k} = \frac{\pi}{3}k$ , then  $\varphi_6(m) = 1$ . Mapping of this order parameter is displayed in figure 6.14(b). It is lower at the center of the frame where the instability has not developed fully and may be frustrated by the different growing fronts coming from the edges. Near the edges of the frame,  $\phi_6$  is closer to 1 and the peak lattice is then more hexagonal.

## 6.3.4 Peak growth

To track the height  $h_m(t)$  of the peak labeled m, one can extract the value of the instantaneous height on the height map at the coordinates  $(\bar{x}_m, \bar{y}_m)$  coming from the averaged peak grid in figure 6.13. However, the peaks move around their mean position, and this method gives poor results. Instead, the coordinates  $(x_m(t), y_m(t))$  of the maximum height around  $(\bar{x}_m, \bar{y}_m)$  within a radius of 30 pixels are computed and define the instantaneous position of the peak m and lead to instantaneous peak height  $h_m(t) = h(x_m(t), y_m(t))$ . Elevation heights are plotted in figure 6.15(a). No height is measured above 2 mm, which is the upper limit of the technique. These raw data are analyzed in order to keep only the first growth for each of the peaks. Figure 6.15(b) shows the corresponding curves. Also, in figure 6.15(b) only the 78 peaks reaching 0.7 mm are plotted (out of 94 peaks).

Two characteristic time scales defined in figure 6.16 can be extracted from these measurements. The first one,  $\tau_1$ , corresponds to the time necessary for the peak to reach its maximum height after the plate is turned over. As we have already noticed, peaks at the edge of the image tend to grow earlier and to have smaller values of  $\tau_1$  in comparison to the peaks in the center of the image. The distribution of  $\tau_1$  is plotted in figure 6.15(c). The minimum value of  $\tau_1$  is 100 s, which provides qualitatively the first dripping event. Small values of  $\tau_1$  correspond to the darker curves in the



Figure 6.15: Growth of the peaks with pure fluid,  $h_0 = 750 \mu m$ . (a) Raw elevation height of the 94 peaks. (b) Peak elevation height during the first growth of the 78 peaks reaching at least 0.7 mm. (c) Distribution of  $\tau_1$ , the time required for a peak to grow after plate flipping, see schematic in figure 6.16. (d) Distribution of  $\tau_2$ , the growth time for a peak between 0.1 mm and final heiht.



Figure 6.16: Definiton of  $\tau_1$  and  $\tau_2$ .

subplot (a,b). Apart from the fact that the smallest values of  $\tau_1$  are systematically located near the edges of the image, no clear conclusion can be drawn about the distribution of  $\tau_1$ .

The second characteristic time  $\tau_2$  is related to the final growth dynamic of the peak. It is calculated by fitting the height of the peak with an exponential function:  $\delta h = A \exp(t/\tau_2)$ . The growth rate of the peak is therefore the inverse of this timescale. In the figure 6.15(a,b), peak height is noisy at the beginning. Therefore, only points such that  $\delta h_m(t) \ge 0.1$  mm are used, and the growth rate is calculated between heights 0.1 mm and 2 mm.

Distribution of the growth time  $\tau_2$  is plotted in figure 6.15(d). Results are centered around 70 s with a standard deviation of 34 s. The growth time expected from the linear analysis,  $\tau^* \approx 25$  s, is of the same order of magnitude but slightly smaller. The small discrepancy with the theory and the scattering of  $\tau_2$  may be due to its strong dependence on the local film thickness, which decreases with time and is influenced by neighboring peaks. Also, the growth of the instability might no longer be in the linear regime with such surface distortions. Still, in addition to wavelength and pattern selection, the linear analysis seems to adequately describe the growth of individual peaks with pure fluid.

# 6.4 Instability of thin films

#### 6.4.1 Pure fluid

All of the previous results come from pure liquid experiments and happen to agree reasonably well with the theory. The mean distance between peaks,  $\lambda = 15.2 \pm 1.0$  mm, is slightly smaller than the prediction from linear analysis,  $\lambda = 16.8$  mm, see table 6.2. Also, the growth of a peak is slightly slower than expected with an average growth time  $\tau_2 \sim 70$  s instead of 25 s, see figure 6.15. The decrease in the thickness of the fluid with time may contribute to an increase in the growth time of the instability. In line with nonlinear analysis, the hexagonal pattern develops over the surface, see figure 6.13. We now turn our attention to the same experiments with the density-matched granular suspensions.

## 6.4.2 Suspensions

Experiments with PMMA particles of 60 µm, 210 µm, 265 µm and 335 µm have been carried out in the density-matched and index-matched mixture of Triton described in § 2.2.4. To obtain such batches of large particles, BS440 PMMA particles have been sieved between mesh sizes 200-228 µm, 250-280 µm, and 315-350 µm, respectively. The smallest 60-µm particles are already highly monodisperse. As explained in § 2.2.4, suspensions are index-matched, i.e. transparent, so that distortion of the checkerboard can be captured through the liquid film as shown in figure 6.11. They are also density-matched ( $\rho = 1190 \text{ kg.m}^{-3}$ ) and surface tension measurements with pending drop experiments yield  $\gamma \approx 32 \pm 2 \text{ mN.m}^{-1}$  with this mixture.

In the following, solid volume fraction is always  $\phi = 30\%$  and film thickness is always  $h_0 = 750 \,\mu\text{m}$ . With the smallest particles, the confinement is thereby mild, with  $h_0 = 12.5 \,d$ . In contrast, the largest particles undergo a strong confinement with  $h_0 \approx 2.3 \,d$ .

#### 6.4.3 Peak lattice: experiments

In figure 6.17, peak lattices are displayed for different fluids. Lines (a), (b), (c), (d), and (e) correspond to pure fluid, 60- $\mu$ m suspension, 210- $\mu$ m suspension, 265- $\mu$ m suspension, and 330- $\mu$ m suspension, respectively. In the first column, peak lattice maps are displayed. The experiment is shorter with the pure fluid and lasts only 440 s before the field of vision becomes obstructed. With suspensions,



Figure 6.17: Peak lattices developed by the Rayleigh-Taylor instability of thin films,  $h_0 = 750 \mu m$ . First column: sum of elevation maps until the end of the experiments and detected peaks (red dots). Second column: triangulation of the peak coordinates. Edge colors are related to their length. Third column: distance between peaks (see figure 6.13). (a) Pure fluid, experiment stopped after 440 s. Suspensions made of (b) 60-µm particles, (c) 210-µm particles, (d) 265-µm particles, and (e) 330-µm particles, experiments stopped after 1800 s.

Fluid	λ
Triton mixture	$15.2 \pm 1.0 \text{ mm}$
$d = 60 \ \mu m$	$16.1 \pm 0.5 \text{ mm}$
$d = 210 \ \mu m$	$15.1 \pm 1.8 \text{ mm}$
$d = 265 \ \mu m$	15.8 ± 1.5 mm
$d = 330 \ \mu m$	$15.9 \pm 0.3 \text{ mm}$
Theory from linear analysis	$16.8 \pm 0.5 \text{ mm}$

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Table 6.2: Mean distance between neighboring peaks from the first maxima of the radial distribution function  $g_r$ .

the instability grows more slowly and imaging can last longer (presently 1800 s). In the first column in figure 6.17, stacks of elevation maps are summed to generate a smoothed map as explained in § 6.3. Average positions of the peaks are then detected and shown with red dots. Triangulation of the peak coordinates are dispayed in the second column with edge colors related to their length. In the third column, edge length distributions are computed by the means of the triangulation or of the radial distribution function  $g_r$ , see § 6.4.3.

In figure 6.17, the patterns developed by the pure fluid in (a) or by the 60-µm suspension in (b) look very similar. At the end of the experiment, the surface of the frame is almost fully covered with peaks in the two cases. The first maxima of the radial distribution functions also coincide. The other local maxima are less pronounced with the suspension but still undoubtedly exist. The mean distance  $\lambda$  bewteen two peaks are gathered in table 6.2. Suspensions of small particle thus destabilize into a pattern similar to that of a continuous fluid and the distance between peaks is in good agreement with the theoretical predictions from linear analysis presented in § 6.1.2.2 or with pure fluid results.

However, these conclusions do not hold with large particles. In figure 6.17(c,d,e), several elements should be noticed. First, a significantly smaller number of peaks are detected, see (a,b). The peak network is less developed and does not span the whole surface of the frame. It may localy develop a hexagonal pattern but to a much lesser degree than those presented in (a,b). The average distance between neighboring peaks is larger and the first peak of the radial distribution function in less pronounced. Its maximum value is nonetheless in good agreement with that of the pure fluid, with that of the suspension made of small particles, and with the prediction from the linear analysis, see table 6.2.

In conclusion, the instability seemingly always selects the same wavelength,  $\lambda \approx 15.6 \pm 0.4$  mm with pure fluid and with granular suspensions made of any particle size. This result could be expected since we do not have any difference in density nor in surface tension between these different fluids. All the systems have thereby the same capillary length and consequently the same linearly most unstable mode according to (6.14).

However, the hexagonal pattern predicted by the nonlinear analysis of the instability hardly develops in confined films of granular suspensions. With continuous fluid and small-particle suspension, the pattern appears over the whole film surface. The propagation of the instability is hindered by large particles. In particular, a new behavior is observed and described in § 6.4.5. In the following, we focus on the dynamics of the instability.

# 6.4.4 Growth of the instability

## 6.4.4.1 General observations

Dynamics of the instability is interesting for several reasons. Firstly, it has been barely addressed in literature even with regular liquids, contrary to wavelength and pattern selection. Secondly, in comparison with pure fluid, the addition of particles should enhance energy dissipation or, equivalently, its effective viscosity. While the perturbation wavelength does not depend on the fluid viscosity, its growth rate does. Signature of the particles should therefore appear in the dynamic of the phenomenon.

In figure 6.18, time series of snapshots for different fluids are displayed. A line corresponds to a fluid, and a column corresponds to the elapsed time since the glass plate is turned over. The selected times are 200 s, 400 s, 600 s and 800 s and particle sizes increase from (b) to (e), with (a) being pure suspending fluid.

Accordingly to previous observations, a perturbation starts from the edge and expands toward the center of the frame. As expected from previous results on peak lattice, the instability grows faster and more regularly on the two top lines in figure 6.18, corresponding to pure fluid and to a suspension made of small particles. With the 210 and 265-µm particles, the instability expands more erraticaly and does not generate a nice hexagonal lattice of peaks. In addition, with the 330-µm particles, the propagation of the front is much slower. To quantify the growth rate of the instability, distribution of the growth-time for the peaks have been extracted from the elevation maps.

## 6.4.4.2 Growth rate

As previously seen with pure fluid in figure 6.15(c,d),  $\tau_2$  seems more relevant than  $\tau_1$  to investigate the growth of the instability. The definitions of  $\tau_1$  and  $\tau_2$  are illustrated in the schematic in figure 6.16. The same analysis was carried out with different suspensions, by varying the particle diameters from 60 to 330 µm. The results are summarized in histograms gathered in figure 6.19. For any particle size, the growth time of the instability,  $\tau_2$ , extends over a much larger range for suspensions than for pure liquid. The small 60-µm particles show a fairly symmetrical distribution similar to the pure fluid. Larger particles tend to have asymmetric distributions of the instability growth time.

For the smallest particles, the average growth time,  $\tau_2 \simeq 346$  s, is 5 times larger than the average value for the pure fluid,  $\tau_2 \simeq 70$  s. At this volume fraction, the ratio of the bulk viscosity of the suspension to that of the pure fluid, i.e. the relative viscosity of the suspension, is also 5. These observations work well with the perturbation growth time expected from the linear analysis,  $\tau \propto \eta$ . In other words, the effective viscosity of the suspension is the bulk viscosity for small non-confined particles. This result could be expected since the 60-µm particles are not strongly confined in the 750-µm film.

On the contrary, with larger confined particles, a significant number of peaks grow more rapidly, i.e. exhibit a relatively small value of  $\tau_2$ . This result is suprising considering the preliminary observations regarding the smaller number of peaks. The instability is not just slower, it fails to develop locally but the few emerging peaks grow rapidly. The effective vicosity of the growth time is then smaller that the suspension bulk viscosity. Once again, we are facing finite size effects when confinement of the particles is too strong to consider the suspension as a continuous fluid. In fact, looking at the movies, a thin film a large particles displays very different instability mechanisms, as explained in the following section.

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Figure 6.18: Series of elevation maps for different fluids at the same times after flipping of the plate (from left to right, 200 s, 400 s, 600 s and 800 s). From top to bottom: Pure suspending fluid, 60- $\mu$ m suspension, 210- $\mu$ m suspension, 265- $\mu$ m suspension and 330- $\mu$ m suspension.



Figure 6.19: Distributions of growth time,  $\tau_2$ , for different fluids between 0.1 mm and 2 mm.

# 6.4.5 Confinement-induced peak mobility

In suspension films made of large particles, the instability first grows near the edges of the frame in a manner similar to films made of pure fluid or suspensions of small particles. A peak grows and eventually releases a drop of suspension. Then, instead of collecting fluid at the same spot, it moves to a region where no peak has grown before. There, it grows again, releases a drop, and moves on. The trajectory of some mobile peaks are shown in figure 6.20. For example, the lowest peak releases 5 drops within 1500 s. This behavior is very different from the observation with pure liquid and suspensions of small particles, where peak positions are stable and where the instability propagates with the generation of new peaks. In the case of large particles, distinct *peaks* in figure 6.13c can be generated by the same traveling peaks.

Previous numerical works have reported the possibility for a pendent drop to move over a flat horizontal liquid film. In periodic numerical simulation, if the width of the system is larger than  $\lambda^*$ , two drops can appear with asymmetric sizes (Yiantsios and Higgins 1989). At some point, they interact, move closer and eventually coalesce to minimize the total surface energy. In this work, the mobility of the drops appears to increase with their size. Coalescence events have also been observed experimentally with any kind of fluid when two drops are too close (Fermigier, Limat, Wesfreid, Boudinet, and Quilliet 1992). 6



Figure 6.20: Temporal tracking of 4 bumps on the surface of a film of suspension made of 330-µm particles.

In the present experiments with films of large particles, the number of coalescence events seems to be larger and isolated moving drops also appear. More recent numerical work on pendent drops on a thin film investigates the possibility of a single bump to move over a uniform surface (Lister et al. 2010). Under a small disturbance, the drop translates and grows, as it leaves a wake as it travels. In addition, if the surface is not flat, the drop will be attracted to thicker areas. In this way, it is a self-propelled system, since the bump is repelled by its own wake. No mention is made of the relationship between the velocity and the volume of the drop.

# 6.4.6 Particle-induced stabilization

# 6.4.6.1 Pendent drops



Figure 6.21

# 6.4.6.2 Thin film

Let's consider just one unit cell, like the one sketched in figure 6.6 and let's assume than the fluid does not feed neighboring peaks. In the hexagonal pattern, the volume of fluid available for one

peak writes,

$$V_{\text{peak}} = \mathcal{A}h_0 = \left(\frac{16\pi^2}{\sqrt{3}}\ell_c^2\right)h_0.$$
(6.26)

In the pure fluid situation, such a volume would drip from the plate if it exceeds the critical dripping volume, see § 6.1.3.3,

$$V_{\rm dripping} \simeq 6\pi \ell_c^3, \tag{6.27}$$

i.e. if the liquid thickness is larger than  $h_0^{\star} = \frac{3\sqrt{3}}{8\pi} \ell_c$ . In practise, in the situation of a pure liquid film, if the volume a unit cell is too small, drainage of the liquid would be possible. With the additional fluid from neighboring cells, dripping could still be observed, provided that the the total fluid volume is larger than  $V_{\text{dripping}}$ .

In the presence of particles, we now assume that the surface is such that local thickness can not gets thinner than a particle diameter. In this situation, a volume  $\mathcal{A}d$  of the fluid in a unit cell is vitually unavailable for dripping and the reasonning aformentioned with pure fluid must be corrected with the substraction of this constrained volume. The dripping criterion now becomes,

$$V_{\text{peak}} - \mathcal{A}d = \mathcal{A}(h_0 - d) \ge V_{\text{dripping}} \quad \Longleftrightarrow \quad d \le h_0 - h_0^{\star} \tag{6.28}$$



Figure 6.22: Stabilization of a thin liquid layer by particles. (a) in normalized units,  $d/h_0^*$  and  $h_0/h_0^*$  with  $h_0^* = 3\sqrt{3}\ell_c/8\pi$  and (b) in dimensional units d and  $h_0$  with  $\ell_c = 1.8$  mm.

This condition is illustrated in the diagrams in figure 6.22. In particular, with  $\ell_c \approx 1.8$  mm, 500 µm and 750 µm-thick layers of suspensions are stabilized by particles larger than 120 µm and 320 µm, respectively.

# 6.5 Concluding remarks

In this chapter, the instability of a thin layer of granular suspension above the air has been investigated experimentally. For a continuous fluid, a hexagonal lattice of peaks develops with a wavelength predicted by linear analysis. Fluid viscosity does not affect the pattern but its growth rate instead. This continuous-fluid description successfully predicts the emerging pattern and the dynamics of its growth for a thin film of small particles,  $h_0 \gtrsim 10d$ . The relevant viscosity is that of the bulk and the instability develops more slowly due to the suspension larger viscosity.

However, the continuous description does not work with larger diameters, when particle undergo a strong confinement,  $h_0 \leq 3d$ . The breakdown of the continuous model probably comes from the difficulty for the fluid film to thin around a peak. If the local thickness reaches a particle diameter, fluid must either drain through a porous matrix and overcome capillary pressure acting on the particles to move them elsewhere. With these suspensions, the hexagonal pattern disappears and the instability is more localized. A smaller number of peaks develops but, interestingly, the growth rate for an individual peak is larger in comparison with suspensions made of smaller particles. This accelerated growth is reminiscent of the accelerated pinch-off in granular suspensions (Bonnoit, Bertrand, et al. 2012). It could also be explained by a smaller particle concentration in the drop. Also, the propagation mechanism of the instability is very different. Some peaks tend to move, which results in several dripping at different spots. This mechanism probably allows the peaks to gather fluid in order to drip, in a smilar manner that pendent drops on a very thin liquid film in the numerical simulation by Lister et al. (2010).

In conclusion, breakdown of the continuous model and new behavior under confinement are once again unveiled in this system confined by a free surface. The local inhibition of the instability with large particles needs further investigation. It paves the way for particle-stabilization of an ustable interface, a real challenge with the Rayleigh-Taylor instability. 7

# Conclusion $\mathcal{O}$ perspectives

Within the framework of complex flows of complex fluids, the capillary flows of dense granular suspensions have been studied in this manuscript. In the dense case, granular suspensions can be tuned to behave like a Newtonian fluid despite the presence of a particle-induced length scale. When designed in this way, their bulk flow is rather predictable using classical hydrodynamic laws. I have shown in this manuscript that this predictability vanishes in the case of free-surface flows with typical sizes on the order of the particle diameter, *d*. This work enriches our knowledge of the confined flow of granular suspensions, which has so far been limited to confinement imposed by a rigid wall. Presently, the confinement is imposed by the free surface, whose dynamics must cope with this highly heterogeneous flow. During the last three years of my Ph.D. studies, I have been investigating these capillary flows of dense granular suspensions, an area that has been little investigated theoretically, numerically, and experimentally. Specifically, I studied **drop spreading** (in Chapters 3, 4 and 5) and **thin film instability** (Chapter 6) of dense granular suspensions.

#### Capillary flows of suspensions: validity and limits of the continuous description

In the literature, **effective-medium mechanical models** are expected to hold for granular suspensions when the size of the system is more than 10 to 20 particle diameters. For example, I showed that in a manner similar to a continuous fluid, a hexagonal lattice of peaks develops over the surface of a film of suspension above air under the **Rayleigh-Taylor instability** when  $h_0 > 10d$ , where  $h_0$  is the thickness of the fluid. The continuous model accurately predicts the wavelength and growth rate of the instability using the **bulk properties of the suspension**. Although the continuous hydrodynamic model seems to work well in some cases, increasing the suspension **inherent size**, i.e. the particle diameter, breaks the continuous description at some point. A transition is observed under strong confinement, typically when  $h_0 \approx 3d$ , probably because of the difficulty for the liquid to become thinner around a peak. In contrast to suspensions of smaller particles, the hexagonal pattern does not develop and the instability is more localized with a smaller number of peaks using suspensions made of large confined particles.

Similar conclusions can be drawn when a drop of suspension spreads and thins over a solid substrate. This capillary flow exhibits a further level of complexity with a moving contact line, which is not easy to handle even for continuous liquids. Nevertheless, granular suspensions exhibit qualitatively Newtonian behavior either at the global macroscopic scale or at local microscopic distances from the advancing contact line. In particular, the drop radius obeys Tanner's law and the dynamic contact angle follows the Cox-Voinov relation. However, unlike the Rayleigh-Taylor instability, the classical wetting laws do not perfectly capture the phenomena. Detailed analysis reveals a **discrepancy between the value of the bulk viscosity and the effective viscosity** obtained from experiments.

Tanner's primary idea of using drop spreading experiments to measure fluid viscosity is compromised by our results! In addition, Tanner's law fails at some point when the drop interface confines the suspension to only a few particle diameters. In such cases, the dynamics of the **two phases** of the suspensions become completely different. A solid particulate matrix then freezes in the center of the drop, and the liquid drains out of this porous medium formed during spreading.

Therefore, the classical continuous description of capillary flows of dense suspensions should work for **small confinement**, i.e. when the system size is much larger than a particle diameter. However, the effective **suspension properties** may be different from those of the bulk and need to be carefully measured.

#### Dense granular suspensions confined by a free surface

In this **capillary-confined regime**, the system can exhibit very different behavior and requires a two-phase description. This transition to a two-phase problem when the size of the system reaches a few diameters has also been reported for other capillary flows. The addition of particles in the confined regime can result in very different consequences depending on the system of interest. For instance, it slows down the spreading at long time and inhibits the growth of the Raleigh-Taylor instability. In dip coating, when the liquid film is thick enough to entrap the particles, an effective viscosity in the continuous Landau-Levich-Derjaguin relation must be used (Jeong et al. 2022). The effective viscosity in some confined flows (dip-coating, Tanner's law, or the Cox-Voinov relation) lies somewhere between the viscosity of the pure fluid and the bulk of the suspension. The effective behavior in these capillary flows is thus midway between pure fluid and bulk suspension. In pinch-off, the confinement of the particles in the neck of the drop leads to accelerated drop detachment compared to pure fluid alone (Bonnoit, Bertrand, et al. 2012; Château et al. 2018). The study of other capillary flows in this extreme confinement regime would help to rationalize and model the underlying mechanics, with the aim of predicting the effect of particles on the flow and the transition from continuous to confined systems. The numerical simulation of confined flows with a free interface would also be valuable to study the coupling of a free surface with the multiphase flow and to reveal the key elements of the dynamics.

#### Microstrucure induced by capillary confinement

In this work, several of these elements have been clearly identified. In particular, the strong confinement of the suspensions leads to an ordering of the particles. This phenomenon has implications on the macroscopic scale as it strongly affects the energy dissipation. For example, it may be partially responsible for the decrease in viscosity in the Tanner and Cox-Voinov relations during drop spreading. This ordering is observed in experiments when the interface height is typically one or two diameters. Top views of the vicinity of an advancing contact line show layering and crystallization of the first particle rows. However, the microstructure in the rest of the drop is difficult to obtain. Playing with multiple particle sizes disrupts ordering and improves our understanding of the complex coupling between microstructure, confinement, and dissipation. For example, in the vicinity of a moving contact line, confinement-induced crystallization may be hindered in bimodal suspensions, resulting in low particle concentration and ultimately low wetting viscosity. A decrease in viscosity could also be explained by **concentration gradients** developed by the flow. For example, shear-induced particle migration could decrease particle concentration in the regions of high shear rate, which are precisely the regions of greatest dissipation in a spreading drop. Tomography could map the 3D microstructure of the particles to measure local concentration or the extent and evolution of layering with increasing confinement.

In summary, order and heterogeneity in particle concentration should arise spontaneously and affect the dynamics of the system under free surface confinement. This particular microstructure has been difficult to study quantitatively.

## Dissipation in capillary flow of dense granular suspensions

The question of **dissipation** is crucial near an advancing contact line, where the shape of the interface is governed by the **balance between capillary and viscous effects**. However, in this region, the fluid thickness vanishes and the confined particles are at a finite distance from the contact line, which increases with particle size. This heterogeneity in the particle concentration near the contact line with a region devoid of particles must result in strong **heterogeneity of local dissipation**. The system then questions how the free surface profile is affected by spatially varying dissipation. Indeed, with non-buoyant dense suspensions, the addition of particles only increases the local dissipation, while capillary and gravitational effects are not affected compared to the pure fluid alone. From the analysis of the equation ruling the drop shape, a scaling law confirmed by experiments has been established for the height  $h^*$  where viscous effects fade out. It can also be interpreted as the height at which the shape of the interface depends only on a gravitational-capillary balance. For drop spreading, this height is approximately 100 µm. To check this prediction, particles can be used as local dissipation probes, exploring only the regions accessible by their size. Additional dissipation is **revealed by the effective wetting viscosity** in the Cox-Voinov relation,  $\eta_w$ , whose value is smaller than that of the bulk and, unlike the latter, depends on the particle size. More specifically, the wetting viscosity decreases with increasing particle diameter and reaches the pure fluid viscosity when the particles are larger than 100 µm. In other words, the free surface does not feel the additional dissipation from particles larger than  $h^*$ , which supports the interpretation of this quantity as a viscous cutoff. At smaller diameters, more particles fill the region  $h < h^*$ , and gradually increase the dissipation reflected in the effective wetting viscosity.

In summary, capillary confinement by a free surface reveals and highlights the coupling between microstructure and dissipation, and provides a new and interesting perspective on these issues. Granular suspensions of frictionless particles would be an exciting extension of this work to study the dissipative contribution of hydrodynamic interactions in these multiphase confined flows. They could also be used to investigate the prediction from numerical simulations of an enhanced ordering (Gallier, Lemaire, Lobry, et al. 2016). In this frictionless limit, possible non-Newtonian behavior in complex flows would also be damped compared to frictional particles (Cheal and Ness 2018). The frictionless PMAA particles recently obtained by Lily Blaiset offer perspectives for this new exciting study (Blaiset et al. 2022).

In summary, my various projects question and answer the validity of regular continuous fluid dynamics models with heterogeneous free surface flow governed by capillary effects. They reveal a high level of complexity where fluid hydrodynamics interacts with confinement, self-assembly and microstructure issues. In pinch-off, dip coating, drop spreading, and thin film instability, a transition from a continuous to a discrete regime is always observed as the particle size increases and undergoes confinement. However, the system behavior in the capillary-confined regime can be very different. Dissipation is also a key issue in my work, especially in a system like a suspension whose viscosity depends on the particle volume fraction.

Many questions remain unanswered and pave the way for future work. Among them, elucidating the origin of the drastic dissipation decrease in Tanner's law would enrich our understanding of granular suspensions in complex geometries. Sliding drops of suspensions on a titled plane could be another interesting system with a strong internal flow, an advancing and a receding contact line, which can be affected very differently by the addition of finite size objects in the flow.

The stabilization of liquid films by particles should also be further investigated in the light of preliminary results on the Rayleigh-Taylor instability with granular suspensions. Particle volume fraction and film thickness are certainly important parameters and more work is needed to determine their contribution to this phenomenon. This thin film stabilization may be related to the observation of the jamming behavior of granular drops at volume fractions far from the jamming transition. Chapter 7 : Conclusion 7.0



Chapter 8 : References 8.0

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